# Synthesis and structural characterization of several salts of 3,5-dinitro-1H-1,2,4-triazole

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# Supporting Information

## Content

# 1 Experimental

**Caution!** The compounds of this work are energetic materials that might explode under certain conditions (e.g. elevated temperatures, impact, friction or electric discharge). Appropriate safety precautions,[1] such as the use of shields or barricades in a fume hood and personal protection equipment (safety glasses, face shields, ear plugs, as well as gloves and suits made from leather and/or Kevlar) should be taken all the time when handling these materials. **Ignoring safety precautions may lead to serious injuries!**

Unless otherwise specified, all chemicals were used as purchased from Alfa Aesar or Sigma-Aldrich without further purification. NMR spectra were recorded on Varian VNMRS-600S spectrometer or Bruker AMX-500 spectrometers. $^{13}C$ NMR spectra were referenced to the deuterated solvent signal and $^{1}H$ spectra were referenced to the residual protic signal. $^{14}N$ spectra were referenced to neat nitromethane and $^{31}P$ spectra were referenced to neat $H_3PO_4$. Raman spectra were recorded at ambient temperature in Pyrex glass melting point capillaries or J.Young NMR tubes on a Bruker Equinox 55 FT-RA spectrometer using a Nd:YAG laser at 1064 nm. Infrared spectra were recorded between 4000 and 400 cm−1 on Midac, M Series or Bruker Optics Alpha FT-IR spectrometers. The samples were either as KBr pellets or AgCl pellets or the neat solid on a ATR module (Bruker). KBr pellets were prepared with an Econo minipress (Barnes Engineering Co.). Differential thermal analysis (DTA) curves were recorded on an OZM Research DTA 552-Ex instrument under a dry nitrogen gas flow with a heating rate of 5 °C using the Meavy 2.2.0 software. Sensitivity measurements were performed on an OZM Research BAM fall hammer BFH-10 and an OZM Research BAM friction apparatus FSKM-10.

The single-crystal X-ray diffraction data were collected on Bruker SMART APEX or APEX DUO diffractometers. The SMART APEX instrument was equipped with an APEX CCD detector and a Cryo Industries low-temperature device. This diffractometer was using graphite monochromatized Mo Kα radiation from a finefocus tube. The APEX DUO diffractometer was equipped with an APEX II CCD detector and an Oxford Cryostream 700 apparatus for low-temperature data collection. The diffractometer was using Mo Kα radiation (Triumph curved-crystal monochromator) from a finefocus tube or Cu Kα radiation (multi-layer optics) from an IμS microsource). The collected frames were integrated with the SAINT algorithm[2] to give the hkl files corrected for Lp/decay. Absorption correction was performed with the SADABS program.[3] The structures were solved by direct methods or intrinsic phasing and refined on $F^2$ by use of the Bruker SHELXTL software package.[4-7] All non-hydrogen atoms were refined anisotropically. Unless noted otherwise, the positions of hydrogen atoms have been located from the difference electron density map. ORTEP drawings were prepared with the ORTEP-III for Windows V2.02 program.[8] Short-contact, hydrogen-bonding and crystal packing drawings of most inorganic salts were prepared with the Mercury 3.1 Development (Build RC5) software.[9] Further crystallographic details can be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; e-mail:

deposit@ccdc.cam.ac.uk) on quoting the deposition no. CCDC 1006182 ([$HNEt_3$][DNT]), 1006181 ([$H_2NEt_2$][DNT] monoclinic) 1013941 ([$H_2NEt_2$][DNT] triclinic), 1006639 ([$CH_6N_3$][DNT]), 1014382 ([$CH_7N_4$][DNT]), 1006408 ([$C_5H_6N$][DNT]), 1009537 ([$PPh_4$][DNT]), 1006184 ([PPN][DNT]), 1031353 ([$NMe_4$][DNT]), and 1006180 ([$NMe_4$][DNT] ·HDNT) from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49) 7247-808-666, e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition numbers CSD 427905 ($LiDNT{\cdot}2H_2O$), 427851 ($NaDNT{\cdot}2H_2O$), 427971 (KDNT), 427853 ($KDNT{\cdot}2H_2O$), 427852 (RbDNT), 427854 (CsDNT), 428080 ($Sr(DNT)_2{\cdot}6H_2O$), 428122 ($Ba(DNT)_2{\cdot}11H_2O$), 427855 ($Ag(NH_3)$DNT), 428079 ($NH_4DNT{\cdot}2H_2O$), 427856 ([$CH_4N_5$][DNT]·$H_2O$).

3,5-dinitro-1H-1,2,4-triazole (HDNT) was prepared according to a modified literature method.[10, 11] All yields are reported with respect to the HDNT starting material. In all cases, the purity of the materials was assessed by $^1H$ and $^{13}C$ NMR spectroscopy.

**Preparation of $LiDNT{\cdot}2H_2O$ (1·$2H_2O$).** A solution of HDNT (0.318 g, 1.5 mmol) in acetone (5 mL) was added to $Li_2CO_3$ (0.370 g, 5.00 mmol). The remaining suspension was stirred for 2 hours and then filtered. The yellow filtrate was taken to dryness by evaporation in air, resulting in the formation of yellow crystals of $LiDNT{\cdot}2H_2O$ formed (yield: 0.230 g, 95 %). DTA: 280 °C decomposition. NMR ($CD_3CN$) $\delta$(ppm): $^{13}C$ (100.54 MHz) 163.8 (s, *C*-$NO_2$); $^{14}N$ (36.14 MHz) -21.6 (s, $\nu_{1/2}$ = 110 Hz, C-*N*$O_2$), -57 (s, $\nu_{1/2}$ > 500 Hz, $DNT^-$ ).

IR (ATR, 20°C) $\tilde{\upsilon}/cm^{-1}$: 3533 (s), 3364 (s), 3250 (m), 2920 (w), 2854 (w), 2774 (w), 2710 (w), 2677 (w), 2480 (w), 2425 (w), 2395 (w), 2217 (w), 2163 (w), 1639 (m), 1542 (s), 1497 (s), 1418 (w), 1395 (s), 1357 (s), 1305 (s), 1115 (m), 1049 (m), 830 (s), 642 (w), 617 (w), 542 (s), 503 (w), 416 (w).

**Preparation of $NaDNT{\cdot}2H_2O$ (2·$2H_2O$).** A solution of HDNT (0.233 g, 1.47 mmol) in acetone (5 mL) was added to a suspension of $Na_2CO_3$ (0.844 g, 7.96 mmol) (Macron) in acetone (30 mL), resulting in effervescence and a color change of the $Na_2CO_3$ from white to yellow. Water (~0.5 mL) was added and the suspension was stirred vigorously for three days. The suspension was then vacuum filtered. The pale yellow filtrate was was taken to dryness by evaporation in air, resulting in the formation of pale yellow crystals. The crystals were dried in an evacuated desiccator for two hours resulting in pale yellow to dark orange microcrystalline $NaDNT{\cdot}2H_2O$ (yield: 0.321 g, 100 %). DTA: 260 °C decomposition. NMR (DMSO-$d_6$) $\delta$(ppm): $^{13}C$ (125.76 MHz) 163.0 (*C*-$NO_2$); $^{14}N$( 36.14 MHz) -20.7 (s, $\nu_{1/2}$ = 200Hz, C-*N*$O_2$), -52(s, $\nu_{1/2}$ = 1000 Hz, $DNT^-$), -145 (s, $\nu_{1/2}$ = 800 Hz, $DNT^-$).

IR (ATR, 20°C) $\tilde{\upsilon}/cm^{-1}$: 3554 (s), 3353 (s), 3260 (m), 3087 (w), 3060 (w), 2923 (w), 2851 (w), 2762 (w), 2699 (w), 2672 (w), 2472 (w), 2147 (w), 1641 (s), 1587 (w), 1537 (s), 1480 (s), 1439 (s), 1394 (m), 1377 (w), 1341 (s), 1307 (s), 1286 (w), 1191 (w), 1164 (w), 1107 (s), 1052 (m),

1037 (w), 1026 (w), 996 (m), 828 (s), 764 (w), 750 (w), 719 (m), 698 (w), 685 (s), 646 (w), 614 (w), 523 (s), 428 (w).

**Preparation of KDNT (3).** HDNT (1.095 g, 6.90 mmol) in acetone (10 mL) was added to a $K_2CO_3$ (6.119 g, 44.30 mmol) suspension in acetone (60 mL), resulting in the immediate orange coloration of the carbonate. The suspension was sonicated and then stirred overnight. The suspension was filtered and the orange solid washed with acetone, and the resulting pale yellow filtrate was taken to dryness by evaporation in air. Colorless needles of KDNT (**3**) crystallized out of the acetone solution. The solid residue was dried in a high vacuum at 50 °C overnight, resulting in colorless to pale yellow KDNT (yield: 1.279 g, 94 %). DTA: 265 °C decomposition. NMR ($CD_3CN$) $\delta$(ppm): $^{13}$C (125.76 MHz) 164.3 (*C*-$NO_2$);$^{14}$N (36.14 MHz) -20.3 (s, $\nu_{1/2}$ = 65Hz, 2N, C-*N*$O_2$), -52 (s, $\nu_{1/2}$ = 500 Hz, $DNT^-$).

Raman (200 mW) $\tilde{\upsilon}$/$cm^{-1}$: 1545 (0.3), 1500 (0.2), 1425 (0.2), 1403 (10.0), 1388 (0.4), 1359 (1.6), 1310 (0.3), 1107 (0.3), 1100 (6.1), 1067 (0.1), 1028 (0.3), 834 (0.8), 769 (0.4), 515 (0.2). IR (ATR) $\tilde{\upsilon}$/$cm^{-1}$: 3604 (m), 3414 (m), 3327 (w), 3233 (w), 2749 (w), 2694 (w), 2663 (w), 2459 (w), 2144 (w), 1672 (w), 1643 (m), 1552 (w), 1536 (s), 1493 (s), 1440 (w), 1415 (w), 1388 (s), 1354 (s), 1341 (w), 1299 (s), 1109 (m), 1100 (w), 1067 (w), 1050 (m), 997 (w), 877 (w), 846 (s), 835 (w), 770 (w), 749 (w), 684 (w), 648 (s), 605 (w), 515 (m), 502 (w), 483 (w), 472 (w), 457 (w), 404 (w).

IR (AgCl pellet) $\tilde{\upsilon}$/$cm^{-1}$: 2757 (w), 2754 (w), 2748 (w), 2691 (w), 2658 (w), 2457 (m), 2399 (w), 2186 (w), 2158 (w), 2139 (w), 1563 (w), 1556 (s), 1540 (w), 1504 (s), 1439 (w), 1414 (m), 1392 (s), 1359 (s), 1343 (w), 1320 (w), 1310 (m), 1301 (s), 1296 (m), 1107 (w), 1100 (s), 1066 (w), 1050 (m), 1044 (m), 1019 (w), 850 (s), 837 (s), 831 (m), 771 (m), 768 (w), 652 (s), 606 (m), 519 (w), 515 (w).

Upon standing in air, the crystals of KDNT picked up moisture and turned yellow-orange.

**Preparation of (3·2$H_2O$).** KDNT (0.100 g, 0.51 mmol) was dissolved in water (5 mL). The yellow-orange solution was allowed to evaporate to dryness in the air, resulting in orange crystals of KDNT·2$H_2O$ (yield: 0.118 g, 100 %).

**Preparation of RbDNT (4).** A solution of HDNT (0.244 g, 1.53 mmol) in acetone (5 mL) was added to a suspension of $Rb_2CO_3$ (1.885 g, 8.16 mmol) in acetone (30 mL) resulting in effervescence and a color change of the $Rb_2CO_3$ to yellow-orange. Water (~0.5 mL) was added and the suspension was stirred vigorously for 24 hours. The suspension was vacuum filtered and the pale yellow filtrate was allowed to evaporate to dryness. The resulting crystals were dried in an evacuated desiccator, yielding a colorless solid of RbDNT (0.369 g, 99 %). DTA : 170 °C melting, 250°C decomposition. NMR (DMSO-$d_6$) $\delta$(ppm): $^{13}$C (100.54 MHz) 162.9 (s, *C*-$NO_2$); $^{14}$N (36.14 MHz) -21.0 (s, $\nu_{1/2}$ = 220 Hz, *N*$O_2$), -50 (s, $\nu_{1/2}$ > 1000 Hz, $DNT^-$), -145 (s, $\nu_{1/2}$ > 1000 Hz, $DNT^-$).

IR (ATR, 20°C) ṽ/cm$^{-1}$: 3396 (w), 2924 (m), 2852 (w), 2748 (w), 2684 (w), 2655 (w), 2449 (w), 2390 (w), 2147 (m), 1712 (w), 1526 (s), 1489 (s), 1444 (w), 1407 (w), 1381 (s), 1352 (s), 1340 (w), 1307 (w), 1293 (s), 1171 (w), 1098 (s), 1079 (w), 1041 (s), 984 (w), 873 (w), 845 (w), 835 (s), 770 (m), 674 (w), 658 (s), 593 (w), 515 (w), 436 (w).

**Synthesis of CsDNT (5).** A solution of HDNT (0.228 g, 1.43 mmol) in acetone (5 mL) was added to a suspension of $Cs_2CO_3$ (2.515 g, 7.72 mmol) in acetone (30 mL) resulting in effervescence and a color change of the $Cs_2CO_3$ to yellow-orange. Water (~0.5 mL) was added and the suspension was stirred vigorously for 24 hours. The suspension was then vacuum filtered and the solvent of the filtrate allowed to evaporate, yielding a pale yellow solid of CsDNT (0.408 g, 98%). DTA : 250 °C decomposition. NMR (DMSO-$d_6$) $\delta$(ppm): $^{13}$C (100.54 MHz) 162.9 (s, *C*-$NO_2$); $^{14}$N (36.14 MHz) -20.5 (s, $\nu_{1/2}$ = 170 Hz, *N*$O_2$), -49 (s, $\nu_{1/2}$ > 1000 Hz, DNT$^-$), -146 (s, $\nu_{1/2}$ > 800 Hz, DNT$^-$).

IR (ATR, 20°C) ṽ/cm$^{-1}$: 2922 (w), 2851 (w), 2744 (w), 2685 (w), 2654 (w), 2449 (w), 2390 (w), 1548 (s), 1537 (w), 1488 (s), 1407 (m), 1384 (s), 1351 (s), 1339 (w), 1304 (w), 1294 (s), 1097 (s), 1042 (m), 1014 (w), 872 (w), 843 (s), 829 (s), 772 (w), 650 (s), 603 (m), 513 (w).

**Preparation of Sr(DNT)$_2$·6H$_2$O (6·6H$_2$O).** A solution of HDNT (0.212 g, 1.34 mmol) in acetone (5 mL) was added to a suspension of $SrCO_3$ (1.018 g, 6.90 mmol) in acetone (30 mL). Water (~0.5 mL) was added, and the suspension was stirred vigorously for 24 hours. The suspension was vacuum filtered. The filtrate was was taken to dryness by evaporation in air resulting in an off-white solid of Sr(DNT)$_2$·6H$_2$O (0.320 g, 46.8%). DTA: 290 °C explosion. NMR (DMSO-$d_6$) $\delta$(ppm): $^{13}$C (100.54 MHz) 162.9 (s, *C*-$NO_2$); $^{14}$N (36.14 MHz) -21.1 (s, $\nu_{1/2}$ = 200 Hz, C-*N*$O_2$), -50 (s, $\nu_{1/2}$ >1000 Hz, DNT$^-$), -147 (s, $\nu_{1/2}$ >700 Hz, DNT$^-$).

IR (ATR, 20°C) ṽ/cm$^{-1}$: 3589 (m), 3393 (s), 2922 (s), 2853 (m), 2483 (w), 2167 (w), 2159 (w), 2020 (w), 1737 (w), 1648 (s), 1556 (s), 1499 (s), 1419 (w), 1394 (s), 1349 (s), 1301 (s), 1125 (m), 1054 (m), 848 (s), 836 (w), 769 (w), 644 (s), 517 (w), 435 (w).

**Preparation of Ba(DNT)$_2$·11H$_2$O (7·11H$_2$O).** A solution of HDNT (0.318 g, 2.00 mmol) in acetone (5 mL) was added to a suspension of $BaCO_3$ (1.200 g, 3.18 mmol) in acetone (10 mL). The suspension was stirred vigorously for one hour and then vacuum filtered. The pale yellow filtrate was taken to dryness by evaporation in air resulting in a pale yellow solid of Ba(DNT)$_2$·11H$_2$O (yield: 0.567 g, 87 %). DTA: 245 °C decomposition. NMR (DMSO-$d_6$) $\delta$(ppm): $^{13}$C (100.54 MHz) 162.9 (s, *C*-$NO_2$); $^{14}$N(36.14 MHz) 21.2 (s, $\nu_{1/2}$ = 220 Hz, *N*$O_2$), -53 (s, $\nu_{1/2}$ >1000 Hz, DNT$^-$), -147 (s, $\nu_{1/2}$ = 800 Hz, DNT$^-$).

IR (ATR, 20°C) ṽ/cm$^{-1}$: 3577 (w), 3415 (w), 2141 (w), 1727 (w), 1626 (w), 1555 (s), 1499 (s), 1384 (m), 1343 (s), 1296 (s), 1135 (w), 1055 (m), 847 (s), 833 (w), 767 (w), 645 (s), 596 (w), 584 (w), 516 (w).

**Preparation of AgDNT (8).** *Caution: AgDNT is an impact and friction sensitive explosive compound!* A solution of $AgNO_3$ (0.357 g, 2.10 mmol) in water (10 mL) was added tp a solution of HDNT (0.318 g, 2.00 mmol) in water (5 mL), resulting in the formation of a white precipitate. The suspension was carefully filtered and the filtration residue washed with water. The solid was dried in a vacuum in darkness, resulting in colorless AgDNT (yield: 0.253 g, 95 %). DTA: 240 °C decomposition.

IR (ATR, 20°C) $\tilde{\upsilon}$/cm$^{-1}$: 3377 (s), 2148 (w), 1644 (w), 1551 (s), 1494 (s), 1401 (m), 1364 (m), 1312 (s), 1130 (w), 1066 (w), 843 (s), 828 (w), 643 (m), 606 (w), 520 (w).

**Preparation of [Ag(NH$_3$)][DNT] (9).** A solution of $AgNO_3$ (0.357 g, 2.10 mmol) in water (10 mL) was added tp a solution of HDNT (0.318 g, 2.00 mmol) in water (5 mL), resulting in the formation of a white precipitate. The suspension was carefully filtered and the filtration residue washed with water. The filtration residue was then dissolved in concentrated aqueous ammonia (5 mL), and the solution was allowed to slowly evaporate in the air under exclusion of light, resulting in crystalline [Ag(NH$_3$)][DNT] (yield: 0.526 g; 93 %). DTA: 155 °C (endotherm, loss of NH$_3$), 245 °C decomposition. NMR (DMSO-$d_6$) $\delta$(ppm): $^1$H (399.80 MHz) 3.34 (s, N$H_3$); $^{13}$C (100.54 MHz) 162.12 (s, *C*-NO$_2$); $^{14}$N (36.14 MHz) -22.9 (s, $\nu_{1/2}$ = 300Hz, *N*O$_2$), -382 (s, $\nu_{1/2}$ = 800 Hz, *N*H$_3$).

IR (ATR, 20°C) $\tilde{\upsilon}$/cm$^{-1}$: 3387 (m), 3297 (m), 2856 (w), 2488 (w), 2144 (w), 1607 (w), 1549 (s), 1492 (s), 1428 (w), 1400 (w), 1382 (m), 1358 (s), 1345 (w), 1304 (s), 1204 (w), 1158 (s), 1129 (m), 1063 (m), 1018 (w), 883 (w), 844 (s), 827 (m), 767 (w), 644 (s), 609 (w), 590 (w), 559 (m), 458 (w), 441 (w), 421 (w).

**Preparation of NH$_4$DNT·2H$_2$O (10·2H$_2$O).** Concentrated aqueous ammonia (2 mL) was added to solution of HDNT (0.204 g, 1.31 mmol) water (5 mL). The solution was allowed to evaporate to dryness in air, resulting in colorless crystals of NH$_4$DNT·2H$_2$O (0.259 g, 93 %). DTA: 140 °C decomposition. NMR (DMSO-$d_6$) $\delta$(ppm): $^1$H (399.80 MHz) 7.13 (s, N$H_4^+$); $^{13}$C (100.54 MHz) 162.9 (*C*-NO$_2$); $^{14}$N (36.14 MHz) -20.9 (s, $\nu_{1/2}$ = 200Hz, *N*O$_2$), -50 (s, $\nu_{1/2}$ = 1000 Hz, DNT$^-$), -147 (s, $\nu_{1/2}$ = 800 Hz, DNT$^-$), -358.5 (s, $\nu_{1/2}$ = 5 Hz, *N*H$_4^+$).

IR (ATR, 20°C) $\tilde{\upsilon}$/cm$^{-1}$: 3591 (m), 3290 (s), 3172 (s), 3051 (s), 2872 (s), 2465 (w), 2140 (w), 1634 (m), 1535 (s), 1494 (s), 1436 (s), 1389 (s), 1352 (s), 1300 (s), 1109 (s), 1049 (m), 1029 (w), 877 (w), 843 (s), 830 (m), 769 (w), 691 (w), 643 (s), 519 (w), 495 (s), 426 (w), 404 (w).

**Preparation of [HNEt$_3$][DNT] (11).** Triethylamine (1.50 g, 14.84 mmol) was added to a solution of HDNT (0.398 g, 2.50 mmol) in water (5 ml). The solvent of the resulting yellow to orange solution was slowly evaporated in air, resulting in an orange crystalline solid of [HNEt$_3$][DNT] (yield 0.593 g, 92 %). DTA: 100 °C melting, 190 °C decomposition. NMR (DMSO-$d_6$) $\delta$(ppm): $^1$H (399.80 MHz) 8.88 (bs, 1H, N$H^+$), 3.10 (q, $^3J$($^1$H$^1$H) = 7 Hz, 6H, NC$H_2$CH$_3$), 1.17 (t, $^3J$($^1$H$^1$H) = 7 Hz, 9H, NCH$_2$C$H_3$); $^{13}$C (100.54 MHz) 162.9 (s, *C*-NO$_2$), 45.8

(s, N*C*H$_2$CH$_3$), 40.2 (s,NCH$_2$*C*H$_3$); $^{14}$N (36.14 MHz) -20.9 (s, $\nu_{1/2}$ = 180Hz, *N*O$_2$), -51 (s, $\nu_{1/2}$ = 1000Hz, DNT$^-$), -147 (s, $\nu_{1/2}$ = 700 Hz, DNT$^-$), -325 (s, $\nu_{1/2}$ = 300Hz, H*N*Et$_3^+$).

IR (ATR, 20°C) $\tilde{\upsilon}$/cm$^{-1}$: 3011 (m), 2780 (w), 2707 (m), 2509 (w), 2456 (w), 1529 (s), 1487 (s), 1473 (w), 1405 (w), 1378 (s), 1346 (s), 1334 (w), 1304 (w), 1292 (s), 1163 (m), 1108 (m), 1073 (w), 1062 (w), 1047 (w), 1030 (s), 1012 (w), 903 (w), 866 (w), 840 (s), 828 (w), 796 (m), 770 (w), 750 (w), 648 (s), 598 (w), 554 (s), 510 (s), 466 (s), 454 (w).

**Preparation of [H$_2$NEt$_2$][DNT] (12).** Diethylamine (1.50 g, 20.54 mmol) was added to a solution of HDNT (0.398 g, 2.50 mmol) in water (5 ml). The solvent of the resulting yellow to orange solution was slowly evaporated in the air, resulting in an orange crystalline solid of monoclinic [HNEt$_3$][DNT] (**12a**) (yield 0.551 g, 95 %).

Crystals of the triclinic polymorph (**12b**) were obtained when a saturated solution of [H$_2$NEt$_2$][DNT] in diethylamine was evaporated in the air.

DTA: 150 °C melting, 190 °C decomposition. NMR (CD$_3$CN) $\delta$(ppm): $^1$H (399.80 MHz) $\delta$(ppm) 6.78 and 6.22 (bs, 2H, N*H*$_2^+$), 3.09 (m, 4H, NC*H*$_2$CH$_3$), 1.26 (m, 6H, NCH$_2$C*H*$_3$); $^{13}$C (100.54 MHz) 163.9 (s, *C*-NO$_2$), 43.7 (s, N*C*H$_2$CH$_3$), 11.6 (s, NCH$_2$*C*H$_3$); $^{14}$N (36.14 MHz) -21.5 (s, $\nu_{1/2}$ = 80 Hz, *N*O$_2$), -330.2(s, $\nu_{1/2}$ = 100 Hz, H$_2$*N*Et$_2^+$).

IR (ATR, 20°C) $\tilde{\upsilon}$/cm$^{-1}$: 3008 (m), 2933 (w), 2863 (w), 2822 (m), 2518 (m), 2420 (w), 2132 (w), 1682 (w), 1623 (m), 1543 (s), 1494 (s), 1476 (m), 1452 (w), 1416 (w), 1381 (s), 1352 (s), 1338 (w), 1297 (s), 1159 (m), 1124 (m), 1048 (w), 970 (w), 915 (w), 862 (w), 841 (s), 828 (m), 800 (m), 770 (w), 750 (w), 646 (s), 604 (w), 538 (w), 511 (m), 491 (w), 432 (w), 412 (w).

**Preparation of guanidinium DNT (13).** A solution of HDNT (0.318 g, 2.00 mmol) in ethanol (5 mL) was added to a suspension of guanidinium carbonate (0.901 g, 5.00 mmol) in ethanol (5 mL). The suspension was stirred for 4 hours and then filtered. The yellow filtrate was taken to dryness by evaporation in air, resulting in colorless to yellow crystals of [CH$_6$N$_3$][DNT] (yield: 0.371 g, 85 %). DTA: 200 °C melting and decomposition. NMR (DMSO-$d_6$) $\delta$(ppm): $^1$H (500.14 MHz) 6.94 (s, C(N*H*$_2$)$_3^+$), $^{13}$C (125.76 MHz) 162.9 (2C, *C*-NO$_2$), 158.0 (*C*(NH$_2$)$_3^+$); $^{14}$N (36.14 MHz) -20.9 (s, $\nu_{1/2}$ = 200 Hz, *N*O$_2$), -50 (s, $\nu_{1/2}$ >1000 Hz, DNT$^-$), -147 (s, $\nu_{1/2}$ = 800Hz, DNT$^-$), -301(s, $\nu_{1/2}$ = 2000Hz, C(*N*H$_2$)$_3^+$).

IR (ATR, 20°C) $\tilde{\upsilon}$/cm$^{-1}$: 3470 (s), 3400 (m), 3357 (m), 3293 (w), 3268 (w), 3190 (m), 2790 (w), 2693 (w), 2464 (w), 2418 (w), 2230 (w), 2148 (w), 1647 (s), 1579 (w), 1526 (s), 1477 (s), 1413 (m), 1387 (s), 1339 (s), 1306 (w), 1294 (s), 1144 (w), 1120 (m), 1048 (m), 1015 (w), 922 (w), 871 (w), 845 (s), 832 (w), 819 (w), 768 (w), 737 (m), 646 (m), 554 (m), 533 (s), 432 (m).

**Preparation of aminoguanidinium DNT (14).** A solution of HDNT (0.513 g, 3.22 mmol) in ethanol (5 mL) was added to a suspension of aminoguanidine bicarbonate (0.438 g, 3.22 mmol) in ethanol (20 mL), resulting in effervescence. The suspension was stirred vigorously for two

days and then vacuum filtered. The pale yellow filtrate was taken to dryness by evaporation of the solvent in air, resulting in a pale yellow solid of $[CH_7N_4][DNT]$ (yield: 0.603 g, 80 %) as an orange-yellow crystalline material. DTA: 200 °C (sharp exotherm) decomposition. NMR (DMSO-$d_6$) $\delta$(ppm): $^1$H (399.80 MHz) 8.54 (s, 1H, N*H*-$NH_2$), 7.24 (bs, 2H, C-N$H_2$) 6.72 (bs, 2H, C-N$H_2$), 4.68 (s, 2H, NH-N$H_2$); $^{13}$C (100.54 MHz) 162.9 (*C*-$NO_2$), 158.8 ($CH_7N_3^+$); $^{14}$N (36.14 MHz) -21.1(s, $\nu_{1/2}$ = 200 Hz, *N*$O_2$), -53 (s, $\nu_{1/2}$ = 1000 Hz, $DNT^-$), -149 (s, $\nu_{1/2}$ = 1000 Hz, $DNT^-$).

IR (ATR, 20°C) $\tilde{\upsilon}$/cm$^{-1}$: 3469 (w), 3418 (s), 3363 (w), 3326 (m), 3293 (w), 3217 (m), 2922 (m), 2852 (w), 2740 (w), 2693 (w), 2647 (w), 2468 (w), 2418 (w), 2147 (w), 1670 (s), 1543 (w), 1529 (s), 1484 (s), 1412 (w), 1386 (s), 1340 (s), 1308 (m), 1294 (m), 1198 (m), 1121 (w), 1078 (m), 1044 (w), 947 (s), 876 (w), 843 (s), 829 (w), 766 (w), 737 (w), 687 (w), 645 (m), 620 (w), 604 (w), 581 (m), 513 (w), 471 (m).

**Preparation of $[C_5H_6N][DNT]\cdot H_2O$ (15·$H_2O$).** Pyridine (1.50 g, 18.97 mmol) was added to a solution of HDNT (0.398 g, 2.50 mmol) in water (5 ml). The resulting yellow to orange solution was taken to dryness by evaporation of the solvent in air, resulting in an orange crystalline solid of $[C_5H_6N][DNT]\cdot H_2O$ (yield: 0.621 g, 97 %). DTA: 120 °C melting, 160 °C decomposition. NMR (DMSO-$d_6$) $\delta$(ppm): $^1$H (399.80 MHz) 8.94 (m, 2H, pyridinium), 8.61 (m, 1H, pyridinium), 8.08 (m, 2H, pyridinium), 6.2 (vbs, 1H, py-*H*). $^{13}$C (100.54 MHz) 162.9 (s, *C*-$NO_2$), 146.2 (s, pyridinium), 142.4 (s, pyridinium), 127.2 (s, pyridinium); $^{14}$N (36.14 MHz) -20.9 (s, $\nu_{1/2}$ = 160 Hz, *N*$O_2$), -51 (s, $\nu_{1/2}$ = 800 Hz, $DNT^-$), -146 (s, $\nu_{1/2}$ = 500 Hz, $DNT^-$), -168.8 (s, $\nu_{1/2}$ = 90 Hz, pyridinium).

IR (ATR, 20°C) $\tilde{\upsilon}$/cm$^{-1}$: 3349 (m), 3141 (w), 3103 (m), 3075 (w), 2160 (m), 2040 (w), 1998 (w), 1724 (m), 1637 (m), 1537 (s), 1486 (s), 1410 (m), 1382 (s), 1348 (s), 1306 (m), 1294 (m), 1257 (m), 1198 (m), 1159 (m), 1120 (m), 1050 (m), 1023 (m), 999 (s), 947 (m), 864 (m), 839 (m), 827 (s), 757 (s), 682 (s), 648 (m), 580 (s).

**Preparation of $[CH_4N_5][DNT]\cdot H_2O$ (16·$H_2O$).** A solution of HDNT (0.232 g, 1.46 mmol) in water (5 mL) was added to a suspension of aminotetrazole (0.124 g, 1.46 mmol) in water (10 mL), which led to the complete consumption of the aminotetrazole. The clear colorless solution was taken to dryness by evaporation of the solvent in air, resulting in colorless crystals of $[CH_4N_5][DNT]\cdot H_2O$ (yield 0.367 g, 96 %). DTA: 160 °C (sharp exotherm) decomposition. NMR (DMSO-$d_6$) $\delta$(ppm): $^1$H (500.14 MHz) 9.00 (bs, 4H, C*H*$_4N_5^+$); $^{13}$C (125.76 MHz) 162.5 (*C*-$NO_2$), 154.2 (s, *C*$H_4N_5^+$); $^{14}$N (36.14 MHz) -22.1 (s, $\nu_{1/2}$ = 250Hz, *N*$O_2$), -58 (s, $\tau_{1/2}\nu_{1/2}$ = 2000Hz, $DNT^-$), -149 (s, $\nu_{1/2}$ = 2000 Hz, $DNT^-$).

IR (ATR, 20°C) $\tilde{\upsilon}$/cm$^{-1}$: 3529 (m), 3316 (w), 3252 (w), 3135 (m), 2972 (w), 2825 (w), 2674 (w), 2160 (w), 1693 (s), 1657 (w), 1558 (w), 1541 (s), 1501 (s), 1398 (m), 1362 (m), 1306 (s), 1136 (m), 1105 (w), 1075 (w), 1037 (m), 986 (m), 896 (w), 844 (s), 826 (m), 770 (w), 736 (w), 673 (w), 643 (s), 609 (w), 516 (m).

**Preparation of [$PPh_4$][DNT] (17).** A solution of HDNT (0.159 g, 1.00 mmol) in water (5 mL) was added to a solution of $PPh_4Cl$ (0.450 g, 1.20 mmol) in water (10 mL), resulting in the precipitation of a white solid. The mixture was filtered and the filtration residue washed with plenty of water. The solid was dried in a vacuum, resulting in an amorphous solid of [$PPh_4$][DNT] (yield: 0.487 g, 98 %). Single crystals suitable for crystal structure determination were grown from an acetone solution. DTA: 180 °C melting, 350 °C decomposition. NMR ($CD_3CN$) $\delta$(ppm): $^{1}H$ (599.81 MHz) 7.7 (m, 16H), 7.9 (m, 4H); $^{13}C$ (150.84 MHz) 164.3 (*C*-$NO_2$), 136.3 (P*Ph*$_4$), 135.6 (P*Ph*$_4$), 131.3 (P*Ph*$_4$), 118.9 (d, $^{1}J(^{13}C^{31}P)$ = 90 Hz, P*Ph*$_4$); $^{14}N$ (36.14 MHz) -19.8(s, $\nu_{1/2}$ = 60 Hz *N*$O_2$), -51 (s, $\nu_{1/2}$ = 500 Hz, $DNT^-$); $^{31}P\{^{1}H\}$an (242.82 MHz) 22.9 (s).

IR (ATR, 20°C) $\tilde{\upsilon}/cm^{-1}$: 3086 (w), 3059 (w), 3026 (w), 1587 (m), 1535 (s), 1479 (s), 1434 (s), 1396 (w), 1377 (s), 1339 (s), 1326 (w), 1299 (w), 1285 (m), 1190 (m), 1164 (m), 1107 (s), 1037 (w), 1026 (w), 996 (m), 938 (w), 862 (w), 836 (s), 827 (w), 764 (m), 750 (s), 720 (s), 699 (m), 686 (s), 651 (w), 615 (m), 525 (s), 470 (w), 441 (w), 428 (w), 409 (w).

**Preparation of [PNP][DNT] (18).** A solution of HDNT (0.875 g; 5.50 mmol) in water (20 mL) was added to solution of PNPCl (3.158 g ; 5.501 mmol) in water (300 mL), resulting in the precipitation of a white solid. The mixture was vacuum filtered, and the filtration residue suspended in water (300 mL) and vacuum filtered again. The obtained solid was dried in a vacuum for 12 hours, resulting in a white amorphous solid of [PNP][DNT] (3.075 g, 80 %). Crystals suitable for X-ray diffraction were grown from an acetone solution. DTA: 150 °C melting, 340 °C decomposition. NMR ($CD_3CN$) $\delta$(ppm): $^{1}H$ (599.81 MHz) 7.5 (m, 12H), 7.6 (m, 12H), 7.7 (m, 6H); $^{13}C$ (150.84 MHz) 164.5 (s, *C*-$NO_2$), 134.6 (P*Ph*$_3$), 133.2 (P*Ph*$_3$), 130.3 (P*Ph*$_3$), 128.8 (P*Ph*$_3$); $^{14}N$ (36.14 MHz) -19.9 (s, $\nu_{1/2}$ = 50 Hz, *N*$O_2$), -51 (s, $\nu_{1/2}$ = 300 Hz, $DNT^-$) $^{31}P\{^{1}H\}$ (242.82 MHz) 20.8.

Raman (20 °C, 200 mW) $\tilde{\upsilon}/cm^{-1}$ 3172 (0.12), 3147 (0.16), 3068 (0.17), 3060 (5.18), 3011 (0.11), 2957 (0.11), 1588 (2.09), 1576 (0.20), 1524 (0.56), 1483 (0.42), 1387 (10.00), 1369 (0.28), 1341 (1.33), 1329 (0.14), 1298 (0.36), 1284 (0.28), 1189 (0.29), 1161 (0.64), 1110 (0.31), 1096 (7.04), 1028 (1.22), 1004 (3.47), 829 (0.84), 767 (0.22), 727 (0.17), 667 (1.33), 616 (0.70), 509 (0.14).

IR (ATR, 20°C) $\tilde{\upsilon}/cm^{-1}$: 3052 (w), 2917 (w), 2038 (w), 1969 (w), 1910 (w), 1828 (w), 1586 (m), 1530 (s), 1479 (s), 1436 (s), 1397 (w), 1374 (m), 1339 (m), 1327 (w), 1296 (w), 1281 (m), 1237 (s), 1180 (m), 1161 (w), 1111 (s), 1075 (w), 1038 (w), 1024 (m), 996 (m), 932 (w), 856 (w), 839 (m), 827 (m), 802 (m), 759 (w), 746 (s), 721 (s), 689 (s), 615 (w), 552 (m), 526 (s), 497 (s), 486 (m), 461 (m), 450 (w), 437 (m).

**Preparation of [TMA][DNT] (19)**. A solution of [TMA][OH]·$5H_2O$ (0.725 g, 4.00 mmol) in water (20 mL) was added to a solution of HDNT (0.636 g, 4.00 mmol) in water (20 mL). The bright yellow solution was taken to dryness on a rotary evaporator. The yellow residue was recrystallized from ethanol, yielding colorless crystals of [TMA][DNT] (0.780 g, 84%). DTA:

225 °C melting, 235 °C decomposition. NMR (acetone-$d_6$) δ(ppm): $^{1}$H (599.81 MHz) 3.51 (12H); $^{13}$C (150.84 MHz) 164.5 (s, *C*-$NO_2$), 56.0 (t, $^{1}J(^{13}C^{14}N)$ = 4 Hz, N*Me*$_4$); $^{14}$N (36.14 MHz) -19.8 (s, $\nu_{1/2}$ = 50 Hz, *N*$O_2$), -51 (s, $\nu_{1/2}$ = 400 Hz, $DNT^-$), -148 (s, $\nu_{1/2}$ = 300 Hz, $DNT^-$).

Raman (20 °C, 200 mW) ṽ/cm$^{-1}$: 3037 (0.8), 2987 (0.4), 2963 (0.2), 2929 (0.4), 1536 (0.5), 1451 (0.2), 1391 (10.0), 1341 (0.6), 1331 (0.6), 1301 (0.3), 1286 (0.5), 1097 (7.1), 1010 (0.4), 952 (0.3), 832 (1.0), 769 (0.1), 759 (1.2), 510 (0.2), 299 (0.3).

IR (ATR, 20°C) ṽ/cm$^{-1}$: 3039 (w), 2961 (vw), 2666 (vw), 2430 (w), 2374 (vw), 1539 (vs), 1518 (m), 1483 (vs), 1451 (w sh), 1418 (vw), 1397 (w), 1376 (s), 1342 (s), 1331 (s), 1298 (m), 1284 (m), 1095 (m), 1038 (w), 951 (s), 841 (vs), 828 (s), 771 (w), 648 (s), 599 (w), 457 (w).

**Vibrational Data for 3,5-dinitro-1*H*-1,2,4-triazole (HDNT)**

IR (ATR, 20°C) ṽ/cm$^{-1}$: 3039 (vw), 2992 (vw), 2934 (vw), 2883 (vw), 2839 (vw), 2802 (vw), 2748 (vw), 2639 (vw), 2557 (vw), 2162 (vw), 1698 (vw), 1563 (vs), 1530 (s sh), 1485 (s), 1430 (w), 1377 (s sh), 1363 (s sh), 1313 (vs), 1281 (m sh), 1174 (m), 1038 (m), 1023 (m sh), 1008 (m sh), 839 (vs), 825 (vs), 764 (vw), 730 (vw), 649 (m), 634 (m sh), 593 (m), 509 (m), 500 (m sh).

# 2 Crystallographic details

## 2.1 Crystal Structure Report for LiDNT·2H$_2$O

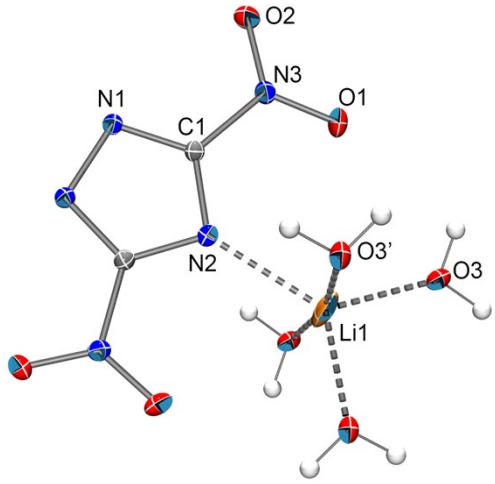


Figure S- 1: The solid-state structure of LiDNT·2H$_2$O. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atom positions were determined from the electron density map and are depicted as spheres of arbitrary radius.

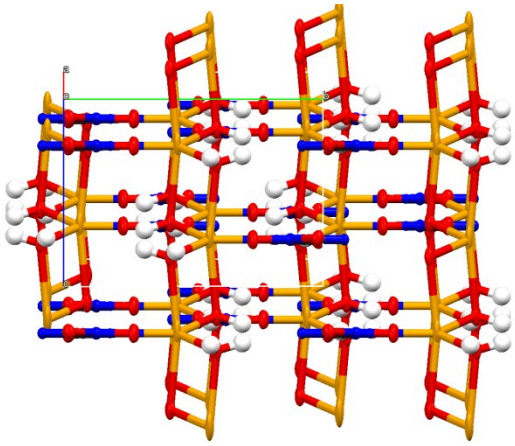

Figure S- 2: Projection of the packing in LiDNT·2H$_2$O along the ***a*** axis.

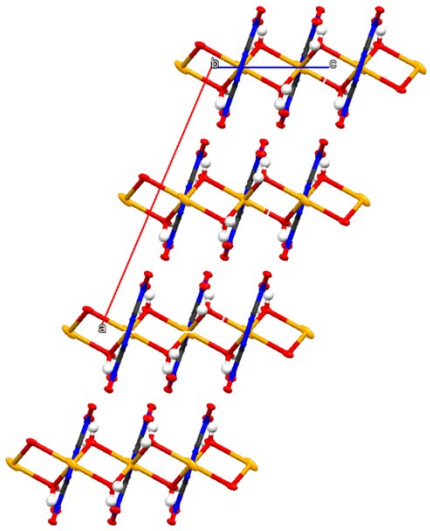

Figure S- 2 : Projection of the packing in LiDNT·2H$_2$O along the ***b*** axis.

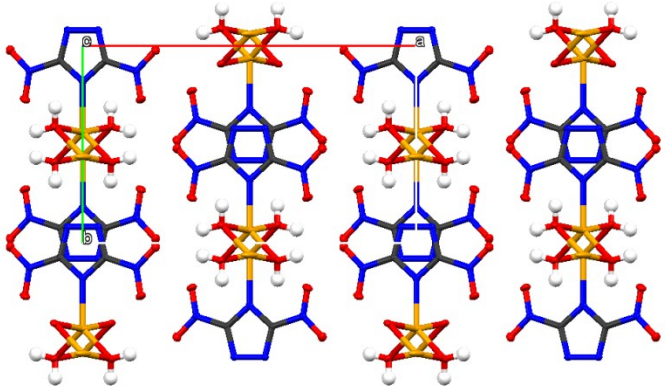


Figure S- 3: Projection of the packing in LiDNT·2$H_2O$ along the **c** axis.

Table S- 1: Sample and crystal data for LiDNT·2$H_2O$.

| | | |
|---|---|---|
| Identification code | LiDNT | |
| Chemical formula | C2H4LiN5O6 | |
| Formula weight | 201.04 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.198 x 0.579 x 0.590 mm | |
| Crystal habit | clear yellow prism | |
| Crystal system | monoclinic | |
| Space group | C 1 2/c 1 | |
| Unit cell dimensions | a = 15.342(2) Å | α = 90° |
| | b = 8.3048(11) Å | β = 113.079(2)° |
| | c = 6.3573(8) Å | γ = 90° |
| Volume | 745.17(17) Å3 | |
| Z | 4 | |
| Density (calculated) | 1.792 g/cm3 | |
| Absorption coefficient | 0.172 mm-1 | |
| F(000) | 408 | |

Table S- 2: Data collection and structure refinement for LiDNT·$2H_2O$.

| | |
|---|---|
| Diffractometer | Bruker APEX DUO |
| Radiation source | fine-focus tube, MoKα |
| Theta range for data collection | 2.85 to 30.53° |
| Index ranges | -21<=h<=21, -11<=k<=11, -9<=l<=9 |
| Reflections collected | 8446 |
| Independent reflections | 1124 [R(int) = 0.0269] |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.9670 and 0.9050 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXTL XT 2013/6 (Sheldrick, 2013) |
| Refinement method | Full-matrix least-squares on F2 |
| Refinement program | SHELXTL XLMP 2014/1 (Bruker AXS, 2013) |
| Function minimized | Σ w(Fo2 - Fc2)2 |
| Data / restraints / parameters | 1124 / 0 / 71 |
| Goodness-of-fit on F2 | 1.077 |
| Final R indices | 991 data; I>2σ(I) R1 = 0.0311, wR2 = 0.0850 |
| | all data R1 = 0.0359, wR2 = 0.0894 |
| Weighting scheme | w=1/[σ2(Fo2)+(0.0488P)2+0.4470P] where P=(Fo2+2Fc2)/3 |
| Largest diff. peak and hole | 0.365 and -0.291 eÅ-3 |
| R.M.S. deviation from mean | 0.072 eÅ-3 |

Table S- 3: Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for LiDNT·$2H_2O$

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| C1 | 0.56778(6) | 0.42525(10) | 0.76357(14) | 0.01048(19) |
| Li1 | 0.5 | 0.0625(3) | 0.75 | 0.0425(9) |
| N1 | 0.54592(5) | 0.58127(9) | 0.75943(12) | 0.01112(18) |
| N2 | 0.5 | 0.31978(13) | 0.75 | 0.0111(2) |
| N3 | 0.66007(5) | 0.37365(10) | 0.77706(13) | 0.01309(18) |
| O1 | 0.67360(5) | 0.22857(9) | 0.77381(14) | 0.0238(2) |
| O2 | 0.71789(5) | 0.47932(9) | 0.78882(13) | 0.01921(19) |
| O3 | 0.58355(6) | 0.91065(10) | 0.66968(16) | 0.0243(2) |

Table S- 4: Bond lengths (Å) for LiDNT·$2H_2O$.

| | | | |
|---|---|---|---|
| C1-N1 | 1.3360(11) | C1-N2 | 1.3362(11) |
| C1-N3 | 1.4494(11) | C1-C1 | 2.0183(17) |
| Li1-O3 | 2.002(2) | Li1-O3 | 2.002(2) |
| Li1-N2 | 2.136(3) | Li1-O3 | 2.4758(10) |
| Li1-O3 | 2.4758(10) | Li1-Li1 | 3.3441(18) |
| Li1-Li1 | 3.3441(18) | N1-N1 | 1.3665(15) |
| N2-C1 | 1.3362(11) | N3-O1 | 1.2241(11) |
| N3-O2 | 1.2291(11) | O3-Li1 | 2.4758(10) |
| O3-H1 | 0.857(17) | O3-H2 | 0.828(17) |

Table S- 5: Bond angles (°) for LiDNT·$2H_2O$.

| | | | |
|---|---|---|---|
| N1-C1-N2 | 116.84(8) | N1-C1-N3 | 121.31(8) |
| N2-C1-N3 | 121.83(8) | N1-C1-C1 | 75.88(5) |
| N2-C1-C1 | 40.96(5) | N3-C1-C1 | 162.76(5) |
| O3-Li1-O3 | 101.89(14) | O3-Li1-N2 | 129.06(7) |
| O3-Li1-N2 | 129.06(7) | O3-Li1-O3 | 83.95(5) |
| O3-Li1-O3 | 102.63(6) | N2-Li1-O3 | 84.84(7) |
| O3-Li1-O3 | 102.63(6) | O3-Li1-O3 | 83.95(5) |
| N2-Li1-O3 | 84.84(7) | O3-Li1-O3 | 169.68(14) |
| O3-Li1-Li1 | 106.57(12) | O3-Li1-Li1 | 47.41(5) |
| N2-Li1-Li1 | 108.10(9) | O3-Li1-Li1 | 149.24(7) |
| O3-Li1-Li1 | 36.54(2) | O3-Li1-Li1 | 47.41(5) |
| O3-Li1-Li1 | 106.57(12) | N2-Li1-Li1 | 108.10(9) |
| O3-Li1-Li1 | 36.54(2) | O3-Li1-Li1 | 149.24(7) |
| Li1-Li1-Li1 | 143.80(19) | C1-N1-N1 | 104.12(5) |
| C1-N2-C1 | 98.09(10) | C1-N2-Li1 | 130.96(5) |
| C1-N2-Li1 | 130.96(5) | O1-N3-O2 | 125.50(8) |
| O1-N3-C1 | 117.27(8) | O2-N3-C1 | 117.23(8) |
| Li1-O3-Li1 | 96.05(5) | Li1-O3-H1 | 116.4(11) |
| Li1-O3-H1 | 110.3(11) | Li1-O3-H2 | 119.4(11) |
| Li1-O3-H2 | 109.6(11) | H1-O3-H2 | 104.7(16) |

Table S- 6: Anisotropic atomic displacement parameters (Å$^2$) for LiDNT·2$H_2O$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0113(4) | 0.0105(4) | 0.0100(4) | -0.0001(3) | 0.0045(3) | 0.0006(3) |
| Li1 | 0.056(2) | 0.0085(12) | 0.090(3) | 0 | 0.058(2) | 0 |
| N1 | 0.0113(4) | 0.0105(4) | 0.0120(3) | -0.0001(3) | 0.0050(3) | 0.0001(3) |
| N2 | 0.0129(5) | 0.0101(5) | 0.0106(5) | 0 | 0.0049(4) | 0 |
| N3 | 0.0128(4) | 0.0125(4) | 0.0143(4) | 0.0003(3) | 0.0057(3) | 0.0014(3) |
| O1 | 0.0206(4) | 0.0125(4) | 0.0381(5) | -0.0022(3) | 0.0113(3) | 0.0042(3) |
| O2 | 0.0146(3) | 0.0174(4) | 0.0281(4) | 0.0024(3) | 0.0110(3) | -0.0012(3) |
| O3 | 0.0191(4) | 0.0119(4) | 0.0457(5) | -0.0007(3) | 0.0169(3) | -0.0033(3) |

Table S- 7: Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å$^2$) for LiDNT·2$H_2O$**.**

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H1 | 0.5832(11) | -0.188(2) | 0.710(3) | 0.029 |
| H2 | 0.6403(12) | -0.067(2) | 0.708(3) | 0.029 |

## 2.2 Crystal Structure Report for NaDNT·2$H_2O$

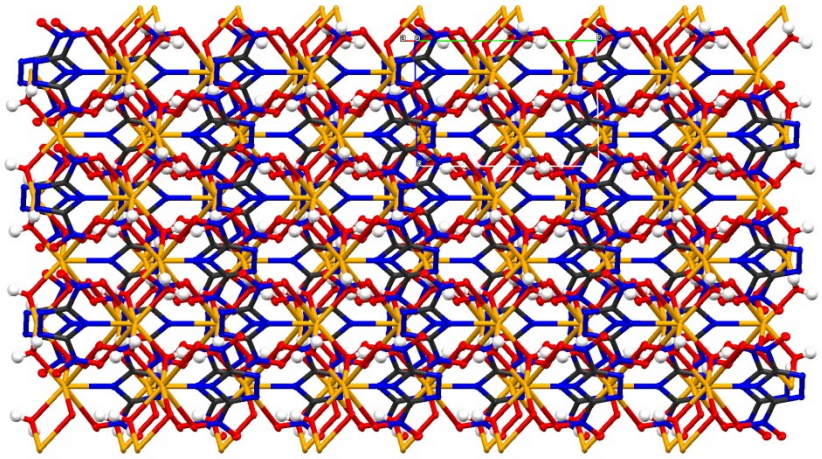

Figure S- 4: Projection of the packing in NaDNT·2$H_2O$ down the a axis.

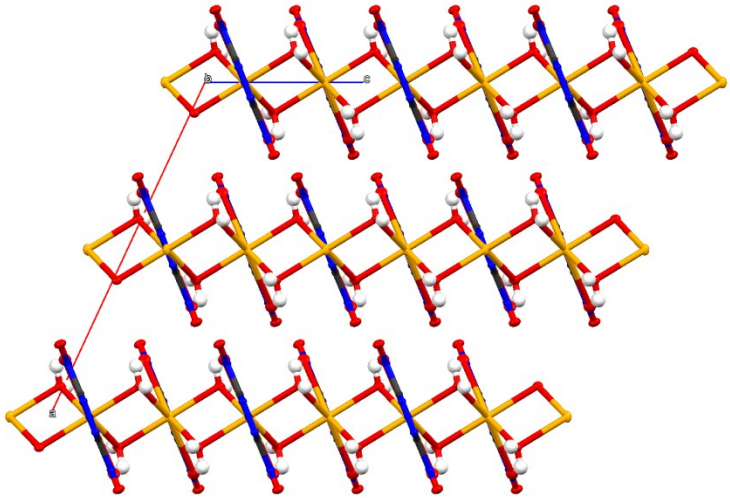

Figure S- 5: Projection of the packing in NaDNT·2$H_2O$ down the b axis.

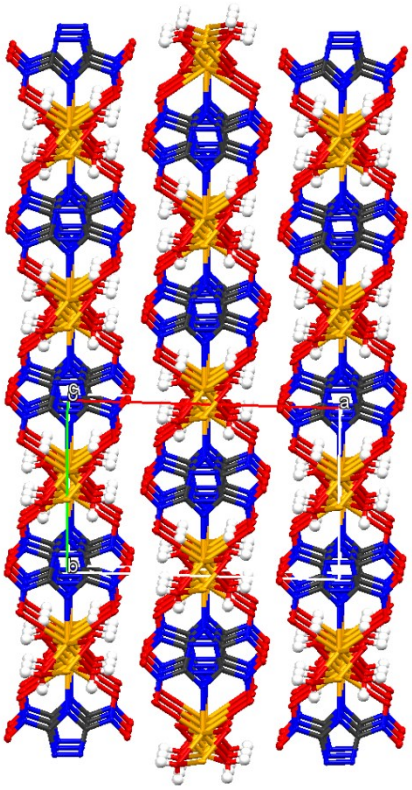

Figure S- 6: Projection of the packing in NaDNT·2$H_2O$ down the c axis.

Table S- 8: Sample and crystal data for NaDNT·2$H_2O$.

| | | |
|---|---|---|
| Identification code | NaDNT_2H2O | |
| Chemical formula | $C_4H_8N_{10}Na_2O_{12}$ | |
| Formula weight | 434.18 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.174 x 0.373 x 0.511 mm | |
| Crystal habit | clear colourless prism | |
| Crystal system | monoclinic | |
| Space group | C 1 2/c 1 | |
| Unit cell dimensions | a = 15.3444(7) Å | α = 90° |
| | b = 8.7270(4) Å | β = 114.9340(6)° |
| | c = 6.6379(3) Å | γ = 90° |
| Volume | 806.04(6) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.789 $g/cm^3$ | |
| Absorption coefficient | 0.216 $mm^{-1}$ | |
| F(000) | 440 | |

Table S- 9: Data collection and structure refinement for NaDNT·2$H_2O$.

| | |
|---|---|
| Diffractometer | Bruker APEX DUO |
| Radiation source | fine-focus tube, MoKα |
| Theta range for data collection | 2.75 to 30.45° |
| Index ranges | -21<=h<=21, -12<=k<=12, -9<=l<=9 |
| Reflections collected | 9609 |
| Independent reflections | 1231 [R(int) = 0.0207] |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.9630 and 0.8980 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXTL XS 2013/1 (Sheldrick, 2013) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXTL XLMP 2014/1 (Bruker AXS, 2013) |
| Function minimized | $\Sigma\, w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 1231 / 0 / 72 |
| Goodness-of-fit on $F^2$ | 1.095 |
| $\Delta/\sigma_{max}$ | 0.001 |
| Final R indices | 1159 data; I>2σ(I) R1 = 0.0237, wR2 = 0.0662 |
| | all data R1 = 0.0254, wR2 = 0.0673 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0342P)^2+0.4360P]$ where $P=(F_o^2+2F_c^2)/3$ |
| Extinction coefficient | 0.0089(13) |
| Largest diff. peak and hole | 0.411 and -0.255 eÅ$^{-3}$ |
| R.M.S. deviation from mean | 0.046 eÅ$^{-3}$ |

Table S- 10: Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for NaDNT·2$H_2O$.U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| C1 | 0.43262(5) | 0.44351(8) | 0.62868(12) | 0.01140(15) |
| N1 | 0.45432(4) | 0.59200(7) | 0.66789(10) | 0.01180(14) |
| N2 | 0.5 | 0.34382(10) | 0.75 | 0.01218(18) |
| N3 | 0.34129(5) | 0.39166(8) | 0.45896(11) | 0.01477(15) |
| Na1 | 0.5 | 0.07107(5) | 0.75 | 0.01607(13) |
| O1 | 0.32948(5) | 0.25310(7) | 0.42985(11) | 0.02269(16) |
| O2 | 0.28254(4) | 0.49061(8) | 0.35416(11) | 0.02148(16) |
| O3 | 0.59192(4) | 0.89595(7) | 0.02433(10) | 0.01538(14) |

Table S- 11: Bond lengths (Å) for NaDNT·2$H_2O$.

| | | | |
|---|---|---|---|
| C1-N2 | 1.3313(9) | C1-N1 | 1.3360(9) |
| C1-N3 | 1.4515(10) | C1-C1 | 2.0155(14) |
| N1-N1 | 1.3657(13) | N2-C1 | 1.3313(9) |
| N2-Na1 | 2.3803(10) | N3-O1 | 1.2259(9) |
| N3-O2 | 1.2303(9) | Na1-O3 | 2.3400(7) |
| Na1-O3 | 2.3400(7) | Na1-O3 | 2.4693(6) |

| | | | |
|---|---|---|---|
| Na1-O3 | 2.4693(6) | Na1-Na1 | 3.5432(3) |
| Na1-Na1 | 3.5432(3) | O3-Na1 | 2.4693(6) |
| O3-H1 | 0.793(13) | O3-H2 | 0.853(13) |

Table S- 12: Bond angles (°) for NaDNT·2$H_2O$.

| | | | |
|---|---|---|---|
| N2-C1-N1 | 116.73(7) | N2-C1-N3 | 121.02(7) |
| N1-C1-N3 | 122.24(7) | N2-C1-C1 | 40.80(4) |
| N1-C1-C1 | 75.93(4) | N3-C1-C1 | 161.79(4) |
| C1-N1-N1 | 104.07(4) | C1-N2-C1 | 98.39(9) |
| C1-N2-Na1 | 130.80(4) | C1-N2-Na1 | 130.80(4) |
| O1-N3-O2 | 125.37(7) | O1-N3-C1 | 117.39(7) |
| O2-N3-C1 | 117.23(7) | O3-Na1-O3 | 98.44(3) |
| O3-Na1-N2 | 130.778(17) | O3-Na1-N2 | 130.778(17) |
| O3-Na1-O3 | 103.72(2) | O3-Na1-O3 | 85.13(2) |
| N2-Na1-O3 | 83.305(17) | O3-Na1-O3 | 85.13(2) |
| O3-Na1-O3 | 103.72(2) | N2-Na1-O3 | 83.305(17) |
| O3-Na1-O3 | 166.61(3) | O3-Na1-Na1 | 105.20(2) |
| O3-Na1-Na1 | 43.980(16) | N2-Na1-Na1 | 110.493(14) |
| O3-Na1-Na1 | 41.150(14) | O3-Na1-Na1 | 146.576(17) |
| O3-Na1-Na1 | 43.980(16) | O3-Na1-Na1 | 105.20(2) |
| N2-Na1-Na1 | 110.493(14) | O3-Na1-Na1 | 146.576(17) |
| O3-Na1-Na1 | 41.150(14) | Na1-Na1-Na1 | 139.01(3) |
| Na1-O3-Na1 | 94.87(2) | Na1-O3-H1 | 115.2(9) |
| Na1-O3-H1 | 110.8(9) | Na1-O3-H2 | 120.5(8) |
| Na1-O3-H2 | 109.2(8) | H1-O3-H2 | 105.6(12) |

Table S- 13: Anisotropic atomic displacement parameters ($Å^2$) for $NaDNT \cdot 2H_2O$.

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0123(3) | 0.0112(3) | 0.0115(3) | -0.0007(2) | 0.0058(3) | -0.0012(2) |
| N1 | 0.0122(3) | 0.0107(3) | 0.0126(3) | 0.0001(2) | 0.0053(2) | -0.0002(2) |
| N2 | 0.0144(4) | 0.0101(4) | 0.0139(4) | 0 | 0.0077(3) | 0 |
| N3 | 0.0142(3) | 0.0167(3) | 0.0143(3) | -0.0024(2) | 0.0069(2) | -0.0036(2) |
| Na1 | 0.0246(3) | 0.0095(2) | 0.0162(2) | 0 | 0.01070(19) | 0 |
| O1 | 0.0244(3) | 0.0165(3) | 0.0268(3) | -0.0070(2) | 0.0104(3) | -0.0086(2) |
| O2 | 0.0154(3) | 0.0236(3) | 0.0197(3) | 0.0013(2) | 0.0018(2) | 0.0004(2) |
| O3 | 0.0145(3) | 0.0117(3) | 0.0180(3) | -0.0015(2) | 0.0050(2) | -0.00141(19) |

Table S- 14: Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for $NaDNT \cdot 2H_2O$.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H1 | 0.5893(9) | -0.1901(15) | 0.984(2) | 0.018 |
| H2 | 0.6513(9) | -0.0869(14) | 1.105(2) | 0.018 |

## 2.3 Crystal Structure Report for KDNT

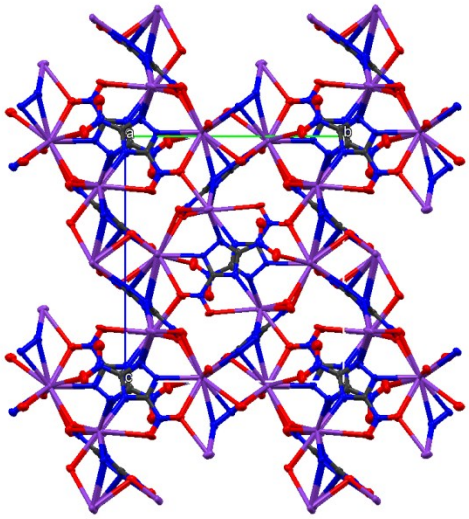

Figure S- 7: Projection of the packing in KDNT down the a axis.

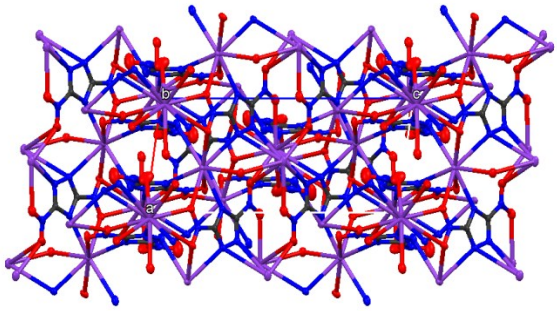

Figure S- 8: Projection of the packing in KDNT down the b axis.

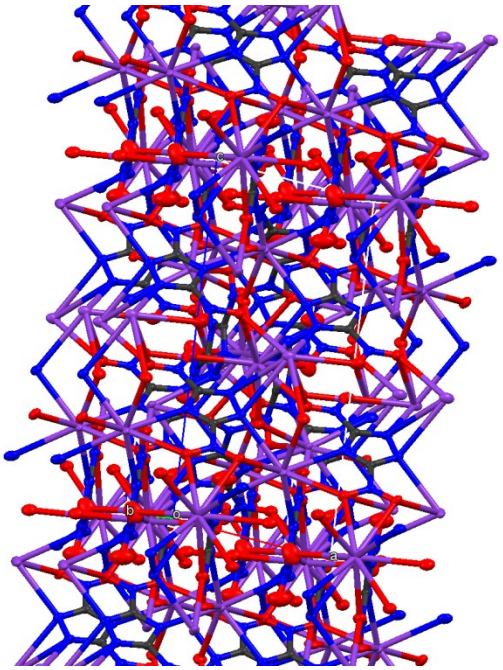

Figure S- 9 : Projection of the packing in KDNT down the c axis.

Table S- 15: Sample and crystal data for KDNT.

| | | |
|---|---|---|
| Identification code | XGC4_144_imported | |
| Chemical formula | $C_2KN_5O_4$ | |
| Formula weight | 197.17 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.076 x 0.234 x 0.353 mm | |
| Crystal habit | colorless blade | |
| Crystal system | monoclinic | |
| Space group | P 1 21/n 1 | |
| Unit cell dimensions | a = 6.741(2) Å | α = 90° |
| | b = 12.997(4) Å | β = 97.697(5)° |
| | c = 14.749(5) Å | γ = 90° |
| Volume | 1280.6(7) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 2.045 $g/cm^3$ | |
| Absorption coefficient | 0.813 $mm^{-1}$ | |
| F(000) | 784 | |

Table S- 16: Data collection and structure refinement for KDNT.

| | |
|---|---|
| Diffractometer | Bruker APEX DUO |

| | |
|---|---|
| Radiation source | fine-focus tube, MoKα |
| Theta range for data collection | 2.10 to 30.35° |
| Index ranges | -9<=h<=9, -18<=k<=18, -20<=l<=17 |
| Reflections collected | 14946 |
| Independent reflections | 3713 [R(int) = 0.0395] |
| Coverage of independent reflections | 96.3% |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.9510 and 0.7990 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXTL XS 2013/1 (Bruker AXS) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXL-2013 (Sheldrick, 2013) |
| Function minimized | $\Sigma\, w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 3713 / 0 / 217 |
| Goodness-of-fit on $F^2$ | 1.277 |
| Final R indices | 3121 data; I>2σ(I) R1 = 0.0764, wR2 = 0.1578 |
| | all data R1 = 0.0900, wR2 = 0.1620 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+7.1292P]$ where $P=(F_o^2+2F_c^2)/3$ |
| Absolute structure parameter | 0.0(0) |
| Largest diff. peak and hole | 1.247 and -0.759 eÅ$^{-3}$ |
| R.M.S. deviation from mean | 0.120 eÅ$^{-3}$ |

Table S- 17: Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for KDNT.

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| C1 | 0.4481(6) | 0.4771(3) | 0.1382(3) | 0.0205(8) |
| C2 | 0.3623(6) | 0.3658(3) | 0.2178(3) | 0.0184(7) |
| N1 | 0.3694(5) | 0.2839(3) | 0.2844(2) | 0.0199(7) |
| N2 | 0.1901(5) | 0.4029(3) | 0.1757(2) | 0.0214(7) |
| N3 | 0.2497(6) | 0.4793(3) | 0.1216(2) | 0.0218(7) |
| N4 | 0.5708(6) | 0.5465(3) | 0.0927(2) | 0.0257(8) |
| N5 | 0.5297(5) | 0.4079(3) | 0.1979(2) | 0.0207(7) |
| O1 | 0.5344(5) | 0.2584(3) | 0.3232(2) | 0.0268(7) |
| O2 | 0.2123(5) | 0.2445(2) | 0.2993(2) | 0.0257(7) |
| O3 | 0.4875(6) | 0.6157(3) | 0.0474(2) | 0.0332(8) |
| O4 | 0.7524(5) | 0.5294(3) | 0.1015(2) | 0.0330(8) |
| C3 | 0.7157(6) | 0.5984(3) | 0.4349(3) | 0.0169(7) |
| C4 | 0.7598(6) | 0.4840(3) | 0.5259(3) | 0.0225(8) |
| N6 | 0.6938(5) | 0.6574(3) | 0.3511(2) | 0.0226(7) |
| N7 | 0.6991(6) | 0.6436(3) | 0.5139(2) | 0.0264(8) |
| N8 | 0.7310(7) | 0.5654(3) | 0.5756(3) | 0.0298(9) |
| N9 | 0.7969(6) | 0.3829(3) | 0.5656(3) | 0.0333(9) |
| N10 | 0.7533(5) | 0.4984(3) | 0.4370(3) | 0.0239(7) |
| O5 | 0.8019(8) | 0.3088(3) | 0.5161(4) | 0.0597(13) |

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| O6 | 0.8210(9) | 0.3782(4) | 0.6457(3) | 0.0651(14) |
| O7 | 0.6544(5) | 0.7486(3) | 0.3561(2) | 0.0285(7) |
| O8 | 0.7142(6) | 0.6122(3) | 0.2806(2) | 0.0406(9) |
| K1 | 0.89451(14) | 0.38058(9) | 0.29755(6) | 0.0280(2) |
| K2 | 0.55209(17) | 0.85028(7) | 0.51763(6) | 0.0271(2) |

Table S- 18: Bond lengths (Å) for KDNT.

| | | | |
|---|---|---|---|
| C1-N5 | 1.325(5) | C1-N3 | 1.327(5) |
| C1-N4 | 1.448(5) | C2-N5 | 1.322(5) |
| C2-N2 | 1.332(5) | C2-N1 | 1.444(5) |
| C2-K1 | 3.515(4) | N1-O2 | 1.222(5) |
| N1-O1 | 1.227(5) | N1-K2 | 3.381(4) |
| N1-K1 | 3.468(4) | N2-N3 | 1.368(5) |
| N2-K1 | 2.871(4) | N2-K2 | 3.164(4) |
| N3-K2 | 2.913(4) | N3-K2 | 3.170(4) |
| N4-O3 | 1.212(5) | N4-O4 | 1.234(5) |
| N5-K1 | 2.714(4) | O1-K2 | 2.865(3) |
| O1-K1 | 2.967(4) | O2-K1 | 2.775(3) |
| O2-K2 | 3.191(3) | O3-K2 | 2.942(4) |
| O4-K2 | 2.955(4) | O4-K2 | 3.296(4) |
| C3-N7 | 1.322(5) | C3-N10 | 1.325(5) |
| C3-N6 | 1.445(5) | C4-N8 | 1.316(6) |
| C4-N10 | 1.320(6) | C4-N9 | 1.447(6) |
| N6-O8 | 1.217(5) | N6-O7 | 1.220(5) |
| N7-N8 | 1.362(5) | N7-K2 | 2.866(4) |
| N8-K1 | 3.017(5) | N9-O6 | 1.173(6) |
| N9-O5 | 1.211(6) | N10-K1 | 2.829(4) |
| O5-K2 | 3.147(5) | O7-K1 | 2.826(3) |
| O7-K2 | 2.887(4) | O8-K1 | 3.244(4) |
| K1-O2 | 2.775(3) | K1-O7 | 2.826(3) |
| K1-N2 | 2.871(4) | K1-N8 | 3.017(5) |
| K1-N1 | 3.468(4) | K1-C2 | 3.515(4) |
| K1-K2 | 4.7265(19) | K2-O1 | 2.866(3) |
| K2-N3 | 2.913(4) | K2-O3 | 2.942(4) |
| K2-O4 | 2.954(4) | K2-O5 | 3.147(5) |
| K2-N2 | 3.164(4) | K2-N3 | 3.170(4) |
| K2-O2 | 3.191(3) | K2-O4 | 3.296(4) |
| K2-N1 | 3.381(4) | | |

Table S- 19: Bond angles (°) for KDNT.

| | | | |
|---|---|---|---|
| N5-C1-N3 | 117.1(4) | N5-C1-N4 | 121.2(4) |
| N3-C1-N4 | 121.6(4) | N5-C2-N2 | 117.6(4) |
| N5-C2-N1 | 120.3(4) | N2-C2-N1 | 122.1(4) |
| N5-C2-K1 | 151.9(3) | N2-C2-K1 | 51.1(2) |

| | | | |
|---|---|---|---|
| N1-C2-K1 | 76.2(2) | O2-N1-O1 | 123.8(4) |
| O2-N1-C2 | 118.7(3) | O1-N1-C2 | 117.5(3) |
| O2-N1-K2 | 70.6(2) | O1-N1-K2 | 55.3(2) |
| C2-N1-K2 | 162.6(3) | O2-N1-K1 | 46.6(2) |
| O1-N1-K1 | 149.1(3) | C2-N1-K1 | 79.9(2) |
| K2-N1-K1 | 100.23(9) | C2-N2-N3 | 103.2(3) |
| C2-N2-K1 | 107.8(2) | N3-N2-K1 | 136.2(3) |
| C2-N2-K2 | 130.9(3) | N3-N2-K2 | 77.7(2) |
| K1-N2-K2 | 102.98(11) | C1-N3-N2 | 104.1(3) |
| C1-N3-K2 | 119.5(3) | N2-N3-K2 | 135.2(3) |
| C1-N3-K2 | 130.7(3) | N2-N3-K2 | 77.3(2) |
| K2-N3-K2 | 81.53(10) | O3-N4-O4 | 124.9(4) |
| O3-N4-C1 | 117.8(4) | O4-N4-C1 | 117.3(4) |
| C2-N5-C1 | 97.9(3) | C2-N5-K1 | 124.3(3) |
| C1-N5-K1 | 135.5(3) | N1-O1-K2 | 104.1(2) |
| N1-O1-K1 | 120.1(3) | K2-O1-K1 | 128.91(12) |
| N1-O2-K1 | 114.7(3) | N1-O2-K2 | 88.2(2) |
| K1-O2-K2 | 123.37(11) | N4-O3-K2 | 125.0(3) |
| N4-O4-K2 | 125.8(3) | N4-O4-K2 | 122.2(3) |
| K2-O4-K2 | 78.81(9) | N7-C3-N10 | 117.1(4) |
| N7-C3-N6 | 120.5(4) | N10-C3-N6 | 122.5(4) |
| N8-C4-N10 | 116.9(4) | N8-C4-N9 | 122.3(4) |
| N10-C4-N9 | 120.8(4) | O8-N6-O7 | 124.8(4) |
| O8-N6-C3 | 117.7(4) | O7-N6-C3 | 117.5(3) |
| C3-N7-N8 | 103.5(3) | C3-N7-K2 | 120.2(3) |
| N8-N7-K2 | 135.3(3) | C4-N8-N7 | 104.4(4) |
| C4-N8-K1 | 111.0(3) | N7-N8-K1 | 106.6(3) |
| O6-N9-O5 | 123.7(5) | O6-N9-C4 | 116.6(5) |
| O5-N9-C4 | 119.7(5) | C4-N10-C3 | 98.1(4) |
| C4-N10-K1 | 132.6(3) | C3-N10-K1 | 126.7(3) |
| N9-O5-K2 | 122.4(4) | N6-O7-K1 | 123.0(3) |
| N6-O7-K2 | 124.9(3) | K1-O7-K2 | 111.64(12) |
| N6-O8-K1 | 117.8(3) | N5-K1-O2 | 136.94(11) |
| N5-K1-O7 | 69.21(11) | O2-K1-O7 | 68.15(10) |
| N5-K1-N10 | 87.38(11) | O2-K1-N10 | 132.27(11) |
| O7-K1-N10 | 153.75(11) | N5-K1-N2 | 107.58(11) |
| O2-K1-N2 | 58.04(10) | O7-K1-N2 | 64.88(10) |
| N10-K1-N2 | 136.86(11) | N5-K1-O1 | 56.06(10) |
| O2-K1-O1 | 107.55(10) | O7-K1-O1 | 76.59(10) |
| N10-K1-O1 | 80.57(10) | N2-K1-O1 | 141.46(10) |
| N5-K1-N8 | 158.09(12) | O2-K1-N8 | 64.00(11) |
| O7-K1-N8 | 129.53(11) | N10-K1-N8 | 76.02(11) |
| N2-K1-N8 | 76.79(11) | O1-K1-N8 | 132.55(10) |
| N5-K1-O8 | 62.22(11) | O2-K1-O8 | 150.80(10) |
| O7-K1-O8 | 119.96(10) | N10-K1-O8 | 52.73(10) |
| N2-K1-O8 | 98.19(10) | O1-K1-O8 | 101.65(10) |
| N8-K1-O8 | 96.07(11) | N5-K1-N1 | 142.49(10) |
| O2-K1-N1 | 18.68(9) | O7-K1-N1 | 75.22(9) |
| N10-K1-N1 | 129.76(10) | N2-K1-N1 | 43.82(9) |

| | | | |
|---|---|---|---|
| O1-K1-N1 | 126.19(9) | N8-K1-N1 | 54.32(10) |
| O8-K1-N1 | 132.14(10) | N5-K1-C2 | 127.90(10) |
| O2-K1-C2 | 40.74(9) | O7-K1-C2 | 73.27(10) |
| N10-K1-C2 | 132.61(11) | N2-K1-C2 | 21.14(10) |
| O1-K1-C2 | 143.07(10) | N8-K1-C2 | 60.42(10) |
| O8-K1-C2 | 111.63(10) | N1-K1-C2 | 23.86(8) |
| N5-K1-K2 | 70.19(8) | O2-K1-K2 | 78.21(7) |
| O7-K1-K2 | 34.60(7) | N10-K1-K2 | 146.86(9) |
| N2-K1-K2 | 40.72(8) | O1-K1-K2 | 104.62(7) |
| N8-K1-K2 | 117.49(8) | O8-K1-K2 | 94.52(6) |
| N1-K1-K2 | 73.89(6) | C2-K1-K2 | 58.44(7) |
| O1-K2-N7 | 70.28(10) | O1-K2-O7 | 123.20(10) |
| N7-K2-O7 | 55.52(10) | O1-K2-N3 | 94.17(10) |
| N7-K2-N3 | 125.99(12) | O7-K2-N3 | 129.73(11) |
| O1-K2-O3 | 105.07(10) | N7-K2-O3 | 78.64(11) |
| O7-K2-O3 | 81.28(10) | N3-K2-O3 | 55.27(10) |
| O1-K2-O4 | 72.09(10) | N7-K2-O4 | 139.63(11) |
| O7-K2-O4 | 147.15(10) | N3-K2-O4 | 70.57(11) |
| O3-K2-O4 | 125.61(11) | O1-K2-O5 | 64.67(12) |
| N7-K2-O5 | 68.77(12) | O7-K2-O5 | 80.14(12) |
| N3-K2-O5 | 150.09(12) | O3-K2-O5 | 147.41(11) |
| O4-K2-O5 | 82.39(12) | O1-K2-N2 | 135.02(10) |
| N7-K2-N2 | 108.86(10) | O7-K2-N2 | 60.46(9) |
| N3-K2-N2 | 117.02(10) | O3-K2-N2 | 119.09(10) |
| O4-K2-N2 | 87.91(10) | O5-K2-N2 | 73.19(11) |
| O1-K2-N3 | 127.43(10) | N7-K2-N3 | 132.61(11) |
| O7-K2-N3 | 84.91(9) | N3-K2-N3 | 98.47(10) |
| O3-K2-N3 | 123.94(10) | O4-K2-N3 | 64.87(9) |
| O5-K2-N3 | 80.67(11) | N2-K2-N3 | 24.94(9) |
| O1-K2-O2 | 41.36(9) | N7-K2-O2 | 61.32(10) |
| O7-K2-O2 | 112.00(9) | N3-K2-O2 | 73.00(10) |
| O3-K2-O2 | 63.77(9) | O4-K2-O2 | 98.10(9) |
| O5-K2-O2 | 99.26(11) | N2-K2-O2 | 169.74(9) |
| N3-K2-O2 | 162.91(9) | O1-K2-O4 | 157.61(10) |
| N7-K2-O4 | 119.18(10) | O7-K2-O4 | 74.13(9) |
| N3-K2-O4 | 63.65(10) | O3-K2-O4 | 60.75(9) |
| O4-K2-O4 | 101.19(9) | O5-K2-O4 | 136.79(12) |
| N2-K2-O4 | 64.03(9) | N3-K2-O4 | 63.20(9) |
| O2-K2-O4 | 122.31(9) | O1-K2-N1 | 20.60(9) |
| N7-K2-N1 | 61.22(9) | O7-K2-N1 | 116.69(9) |
| N3-K2-N1 | 86.00(10) | O3-K2-N1 | 84.88(9) |
| O4-K2-N1 | 87.04(9) | O5-K2-N1 | 79.93(11) |
| N2-K2-N1 | 153.07(10) | N3-K2-N1 | 147.65(10) |
| O2-K2-N1 | 21.18(8) | O4-K2-N1 | 142.85(9) |

Table S- 20: Anisotropic atomic displacement parameters ($Å^2$) for KDNT.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C1 | 0.023(2) | 0.024(2) | 0.0154(17) | -0.0005(15) | 0.0064(15) | -0.0020(16) |
| C2 | 0.0240(19) | 0.0185(18) | 0.0137(16) | 0.0002(14) | 0.0060(14) | 0.0002(15) |
| N1 | 0.0235(17) | 0.0194(16) | 0.0179(16) | 0.0004(13) | 0.0065(13) | 0.0011(13) |
| N2 | 0.0236(17) | 0.0202(17) | 0.0217(16) | 0.0024(13) | 0.0079(14) | -0.0001(14) |
| N3 | 0.0259(18) | 0.0218(17) | 0.0190(16) | 0.0025(13) | 0.0073(14) | -0.0018(14) |
| N4 | 0.033(2) | 0.0288(19) | 0.0170(16) | -0.0036(14) | 0.0078(15) | -0.0095(16) |
| N5 | 0.0201(16) | 0.0247(17) | 0.0177(15) | -0.0014(13) | 0.0046(13) | -0.0033(14) |
| O1 | 0.0254(16) | 0.0308(17) | 0.0246(15) | 0.0053(13) | 0.0049(12) | 0.0062(13) |
| O2 | 0.0260(15) | 0.0243(15) | 0.0292(16) | 0.0033(13) | 0.0125(13) | -0.0006(13) |
| O3 | 0.047(2) | 0.0262(16) | 0.0278(16) | 0.0032(14) | 0.0109(15) | -0.0026(16) |
| O4 | 0.0320(18) | 0.044(2) | 0.0241(16) | -0.0035(14) | 0.0063(14) | -0.0119(16) |
| C3 | 0.0150(17) | 0.0171(17) | 0.0190(17) | -0.0005(14) | 0.0035(14) | -0.0018(14) |
| C4 | 0.0127(17) | 0.0194(19) | 0.036(2) | 0.0054(17) | 0.0071(16) | 0.0008(15) |
| N6 | 0.0234(18) | 0.0263(18) | 0.0181(16) | -0.0001(14) | 0.0031(13) | -0.0028(15) |
| N7 | 0.045(2) | 0.0174(17) | 0.0181(16) | 0.0025(13) | 0.0083(15) | 0.0043(16) |
| N8 | 0.045(2) | 0.0230(18) | 0.0231(18) | 0.0058(15) | 0.0117(17) | 0.0043(17) |
| N9 | 0.0237(19) | 0.032(2) | 0.044(2) | 0.0116(19) | 0.0065(17) | 0.0050(17) |
| N10 | 0.0200(17) | 0.0194(17) | 0.0326(19) | -0.0024(15) | 0.0039(15) | 0.0021(14) |
| O5 | 0.070(3) | 0.029(2) | 0.075(3) | -0.006(2) | -0.012(3) | 0.016(2) |
| O6 | 0.109(4) | 0.042(2) | 0.047(3) | 0.008(2) | 0.020(3) | 0.015(3) |
| O7 | 0.0359(18) | 0.0260(16) | 0.0237(15) | 0.0065(13) | 0.0043(13) | 0.0023(14) |
| O8 | 0.058(2) | 0.046(2) | 0.0200(16) | -0.0098(15) | 0.0125(16) | -0.0052(19) |
| K1 | 0.0201(4) | 0.0442(6) | 0.0201(4) | -0.0106(4) | 0.0045(3) | 0.0029(4) |
| K2 | 0.0437(6) | 0.0158(4) | 0.0217(4) | -0.0002(3) | 0.0045(4) | 0.0061(4) |

## 2.4 Crystal Structure Report for KDNT·2$H_2O$

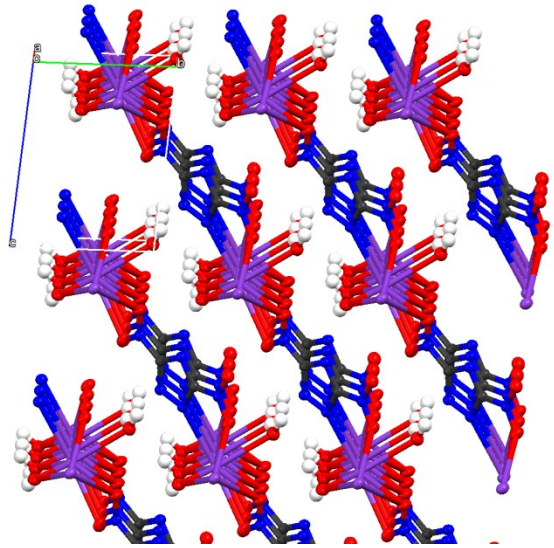

Figure S- 10 : Projection of the packing in KDNT·2$H_2O$ approximately down the a axis.

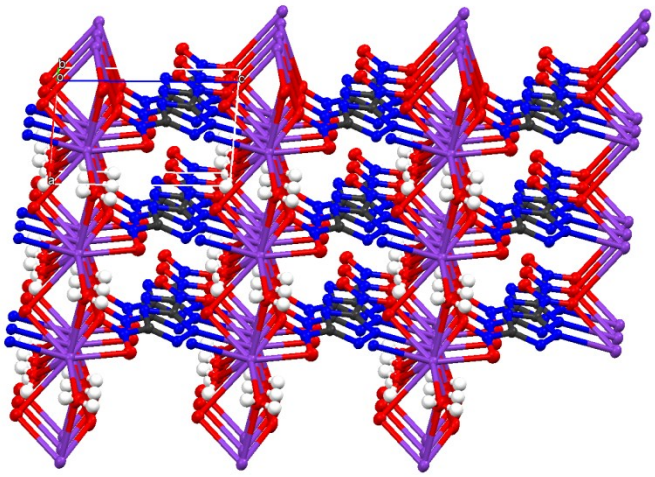

Figure S- 11: Projection of the packing in KDNT·2$H_2O$ approximately down the b axis.

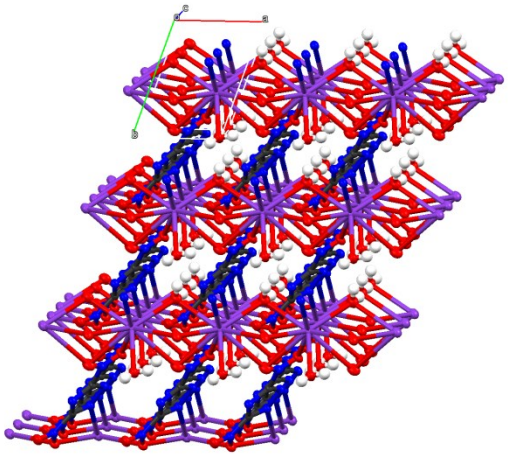

Figure S- 12: Projection of the packing in KDNT·$2H_2O$ approximately down the c axis.

Table S- 21**:** Sample and crystal data for KDNT·$2H_2O$.

| | | |
|---|---|---|
| Identification code | KDNT2H2O_2 | |
| Chemical formula | $C_2H_4KN_5O_6$ | |
| Formula weight | 233.20 | |
| Temperature | 130(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.110 x 0.150 x 0.360 mm | |
| Crystal habit | clear orange prism | |
| Crystal system | triclinic | |
| Space group | P 1 | |
| Unit cell dimensions | a = 4.5220(15) Å | α = 96.093(4)° |
| | b = 6.355(2) Å | β = 92.533(4)° |
| | c = 7.770(3) Å | γ = 108.569(4)° |
| Volume | 209.75(12) $Å^3$ | |
| Z | 1 | |
| Density (calculated) | 1.846 $g/cm^3$ | |
| Absorption coefficient | 0.652 $mm^{-1}$ | |
| F(000) | 118 | |

Table S- 22: Data collection and structure refinement for KDNT·2$H_2O$.

| | |
|---|---|
| Diffractometer | Bruker SMART APEX |
| Radiation source | fine-focus tube, MoKα |
| Theta range for data collection | 2.65 to 27.48° |
| Index ranges | -5<=h<=5, -8<=k<=7, -9<=l<=9 |
| Reflections collected | 2303 |
| Independent reflections | 1445 [R(int) = 0.0228] |
| Coverage of independent reflections | 95.9% |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.9320 and 0.7990 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXTL XT 2013/6 (Sheldrick, 2013) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXTL XLMP 2014/1 (Bruker AXS, 2013) |
| Function minimized | $\Sigma\, w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 1445 / 3 / 127 |
| Goodness-of-fit on $F^2$ | 1.138 |
| $\Delta/\sigma_{max}$ | 0.011 |
| Final R indices | 1416 data; I>2σ(I) R1 = 0.0255, wR2 = 0.0714 |
| | all data R1 = 0.0263, wR2 = 0.0725 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0385P)^2+0.0115P]$ where $P=(F_o^2+2F_c^2)/3$ |
| Absolute structure parameter | 0.1(0) |
| Largest diff. peak and hole | 0.219 and -0.233 eÅ$^{-3}$ |
| R.M.S. deviation from mean | 0.057 eÅ$^{-3}$ |

Table S- 23: Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for KDNT·2$H_2O$.U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| C1 | 0.5258(7) | 0.1469(5) | 0.6173(4) | 0.0230(6) |
| C2 | 0.4075(7) | 0.3987(5) | 0.7418(4) | 0.0224(6) |
| K1 | 0.75879(7) | 0.62090(6) | 0.19420(6) | 0.03001(19) |
| N1 | 0.5705(6) | 0.3413(5) | 0.8631(3) | 0.0253(5) |
| N2 | 0.6514(7) | 0.1710(4) | 0.7801(3) | 0.0253(6) |
| N3 | 0.3686(7) | 0.2854(5) | 0.5840(3) | 0.0247(5) |
| N4 | 0.5607(7) | 0.9799(5) | 0.4855(3) | 0.0277(6) |
| N5 | 0.2739(7) | 0.5753(5) | 0.7795(4) | 0.0261(6) |
| O1 | 0.4193(7) | 0.9549(5) | 0.3415(3) | 0.0397(6) |
| O2 | 0.7292(6) | 0.8719(4) | 0.5244(3) | 0.0351(6) |
| O3 | 0.1286(6) | 0.6225(4) | 0.6622(3) | 0.0334(6) |
| O4 | 0.3145(6) | 0.6685(4) | 0.9311(3) | 0.0352(6) |
| O5 | 0.9768(6) | 0.9883(4) | 0.0163(3) | 0.0320(5) |
| O6 | 0.1379(7) | 0.3789(4) | 0.2572(3) | 0.0358(6) |

Table S- 24: Bond lengths (Å) for KDNT·2$H_2O$.

| | | | |
|---|---|---|---|
| C1-N3 | 1.333(4) | C1-N2 | 1.337(4) |
| C1-N4 | 1.445(4) | C2-N1 | 1.321(4) |
| C2-N3 | 1.329(4) | C2-N5 | 1.445(4) |
| K1-O6 | 2.703(3) | K1-O5 | 2.771(2) |
| K1-O6 | 2.832(3) | K1-N1 | 2.894(3) |
| K1-O2 | 2.906(3) | K1-O4 | 2.909(3) |
| K1-O1 | 3.143(3) | K1-O1 | 3.144(3) |
| K1-O4 | 3.269(3) | K1-N4 | 3.393(3) |
| K1-K1 | 4.5220(15) | K1-K1 | 4.5220(15) |
| K1-H2 | 3.0281 | N1-N2 | 1.359(4) |
| N1-K1 | 2.894(3) | N4-O2 | 1.225(4) |
| N4-O1 | 1.233(4) | N5-O3 | 1.218(4) |
| N5-O4 | 1.239(4) | O1-K1 | 3.143(3) |
| O4-K1 | 2.909(3) | O4-K1 | 3.269(3) |
| O5-H1 | 0.795 | O5-H2 | 0.809 |
| O6-K1 | 2.832(3) | O6-H3 | 0.808 |
| O6-H4 | 0.8062 | | |

Table S- 25: Bond angles (°) for KDNT·2$H_2O$.

| | | | |
|---|---|---|---|
| N3-C1-N2 | 116.2(3) | N3-C1-N4 | 122.3(3) |
| N2-C1-N4 | 121.4(3) | N1-C2-N3 | 117.2(3) |
| N1-C2-N5 | 121.5(3) | N3-C2-N5 | 121.3(3) |
| O6-K1-O5 | 119.02(8) | O6-K1-O6 | 109.55(9) |
| O5-K1-O6 | 129.63(7) | O6-K1-N1 | 86.69(8) |
| O5-K1-N1 | 88.59(8) | O6-K1-N1 | 81.36(8) |
| O6-K1-O2 | 106.41(7) | O5-K1-O2 | 96.26(8) |
| O6-K1-O2 | 81.64(8) | N1-K1-O2 | 161.28(8) |
| O6-K1-O4 | 142.15(7) | O5-K1-O4 | 64.51(7) |
| O6-K1-O4 | 69.36(7) | N1-K1-O4 | 55.48(8) |
| O2-K1-O4 | 110.65(7) | O6-K1-O1 | 71.86(8) |
| O5-K1-O1 | 65.65(7) | O6-K1-O1 | 148.34(7) |
| N1-K1-O1 | 129.74(8) | O2-K1-O1 | 68.21(7) |
| O4-K1-O1 | 129.64(8) | O6-K1-O1 | 148.19(7) |
| O5-K1-O1 | 75.23(8) | O6-K1-O1 | 70.28(8) |
| N1-K1-O1 | 123.62(8) | O2-K1-O1 | 41.84(7) |
| O4-K1-O1 | 68.99(7) | O1-K1-O1 | 91.98(7) |
| O6-K1-O4 | 65.53(7) | O5-K1-O4 | 57.71(7) |
| O6-K1-O4 | 146.03(7) | N1-K1-O4 | 65.04(7) |
| O2-K1-O4 | 132.33(7) | O4-K1-O4 | 93.93(7) |
| O1-K1-O4 | 64.71(7) | O1-K1-O4 | 132.53(7) |
| O6-K1-N4 | 127.01(8) | O5-K1-N4 | 84.59(7) |
| O6-K1-N4 | 76.36(7) | N1-K1-N4 | 144.25(8) |
| O2-K1-N4 | 20.61(7) | O4-K1-N4 | 90.29(7) |
| O1-K1-N4 | 78.36(7) | O1-K1-N4 | 21.31(7) |
| O4-K1-N4 | 134.95(6) | O6-K1-K1 | 143.84(6) |
| O5-K1-K1 | 96.28(5) | O6-K1-K1 | 34.29(6) |
| N1-K1-K1 | 86.59(6) | O2-K1-K1 | 74.93(6) |

| | | | |
|---|---|---|---|
| O4-K1-K1 | 46.15(5) | O1-K1-K1 | 135.98(5) |
| O1-K1-K1 | 44.00(5) | O4-K1-K1 | 140.08(5) |
| N4-K1-K1 | 59.50(5) | O6-K1-K1 | 36.16(6) |
| O5-K1-K1 | 83.72(5) | O6-K1-K1 | 145.71(6) |
| N1-K1-K1 | 93.41(6) | O2-K1-K1 | 105.07(5) |
| O4-K1-K1 | 133.85(5) | O1-K1-K1 | 44.02(5) |
| O1-K1-K1 | 135.99(5) | O4-K1-K1 | 39.92(5) |
| N4-K1-K1 | 120.50(5) | K1-K1-K1 | 180.0 |
| O6-K1-H2 | 104.3 | O5-K1-H2 | 15.2 |
| O6-K1-H2 | 141.9 | N1-K1-H2 | 83.6 |
| O2-K1-H2 | 105.3 | O4-K1-H2 | 73.2 |
| O1-K1-H2 | 60.1 | O1-K1-H2 | 89.9 |
| O4-K1-H2 | 42.7 | N4-K1-H2 | 97.0 |
| K1-K1-H2 | 110.2 | K1-K1-H2 | 69.8 |
| C2-N1-N2 | 104.3(3) | C2-N1-K1 | 119.6(2) |
| N2-N1-K1 | 135.1(2) | C1-N2-N1 | 104.2(3) |
| C2-N3-C1 | 98.1(3) | O2-N4-O1 | 124.2(3) |
| O2-N4-C1 | 117.7(3) | O1-N4-C1 | 118.1(3) |
| O2-N4-K1 | 56.63(17) | O1-N4-K1 | 67.89(18) |
| C1-N4-K1 | 171.5(2) | O3-N5-O4 | 124.2(3) |
| O3-N5-C2 | 118.6(3) | O4-N5-C2 | 117.2(3) |
| N4-O1-K1 | 130.0(2) | N4-O1-K1 | 90.8(2) |
| K1-O1-K1 | 91.98(7) | N4-O2-K1 | 102.76(19) |
| N5-O4-K1 | 124.2(2) | N5-O4-K1 | 124.3(2) |
| K1-O4-K1 | 93.93(7) | K1-O5-H1 | 132.8 |
| K1-O5-H2 | 100.8 | H1-O5-H2 | 101.4 |
| K1-O6-K1 | 109.55(9) | K1-O6-H3 | 114.5 |
| K1-O6-H3 | 102.9 | K1-O6-H4 | 128.8 |
| K1-O6-H4 | 96.1 | H3-O6-H4 | 101.1 |

Table S- 26: Anisotropic atomic displacement parameters (Å$^2$) for KDNT·2H$_2$O.The anisotropic atomic displacement factor exponent takes the form:
$-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0244(15) | 0.0234(14) | 0.0217(13) | 0.0011(11) | -0.0008(11) | 0.0094(12) |
| C2 | 0.0206(14) | 0.0228(14) | 0.0244(14) | 0.0034(11) | 0.0000(11) | 0.0079(11) |
| K1 | 0.0351(4) | 0.0306(4) | 0.0260(3) | -0.0016(2) | -0.0024(3) | 0.0152(3) |
| N1 | 0.0260(14) | 0.0278(14) | 0.0240(12) | 0.0029(10) | -0.0005(10) | 0.0119(11) |
| N2 | 0.0280(14) | 0.0264(14) | 0.0231(12) | 0.0018(10) | -0.0011(10) | 0.0118(11) |
| N3 | 0.0270(13) | 0.0263(13) | 0.0221(11) | 0.0024(10) | 0.0007(10) | 0.0109(10) |
| N4 | 0.0293(15) | 0.0261(14) | 0.0268(14) | 0.0003(11) | 0.0020(11) | 0.0090(11) |
| N5 | 0.0251(14) | 0.0251(13) | 0.0291(13) | 0.0032(10) | -0.0009(11) | 0.0102(11) |
| O1 | 0.0552(17) | 0.0406(14) | 0.0248(11) | -0.0043(10) | -0.0067(11) | 0.0216(13) |
| O2 | 0.0389(15) | 0.0332(13) | 0.0390(13) | -0.0016(10) | -0.0002(11) | 0.0223(11) |
| O3 | 0.0344(14) | 0.0340(13) | 0.0357(13) | 0.0074(10) | -0.0029(10) | 0.0162(11) |
| O4 | 0.0373(14) | 0.0368(13) | 0.0328(12) | -0.0074(10) | -0.0035(10) | 0.0185(11) |
| O5 | 0.0317(13) | 0.0332(13) | 0.0349(12) | 0.0070(10) | 0.0000(10) | 0.0155(11) |
| O6 | 0.0479(16) | 0.0360(13) | 0.0257(11) | 0.0043(10) | -0.0066(10) | 0.0178(12) |

Table S- 27: Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å$^2$) for KDNT·2H$_2$O.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H1 | 0.9038 | 0.0286 | -0.0639 | 0.038 |
| H2 | 1.1282 | -0.0338 | -0.0235 | 0.038 |
| H3 | 1.1008 | -0.7362 | 0.1924 | 0.043 |
| H4 | 1.1827 | -0.6592 | 0.3478 | 0.043 |

## 2.5 Crystal Structure Report for RbDNT

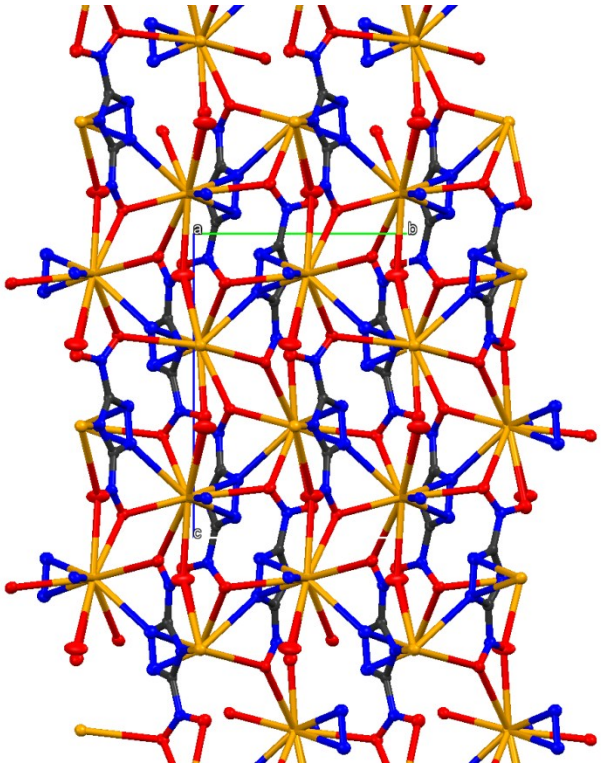


Figure S- 13: Projection of the packing of RbDNT down the a axis.

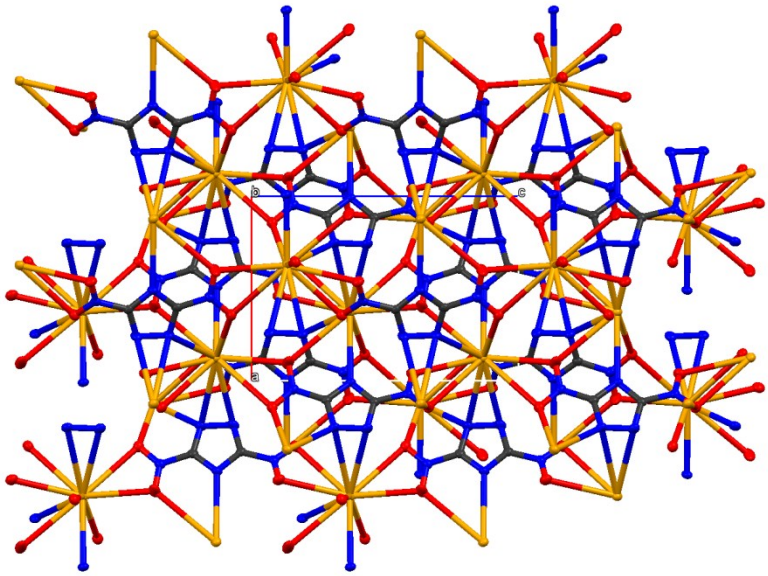

Figure S- 14: Projection of the packing of RbDNT down the b axis.

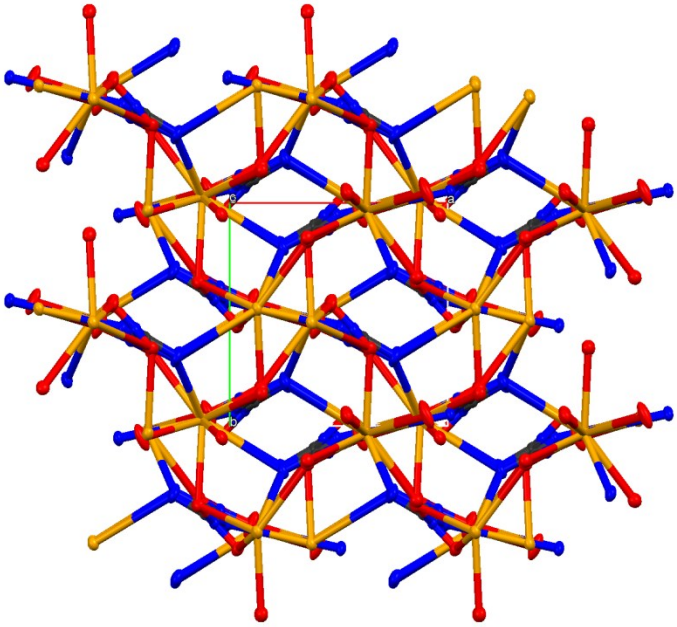

Figure S- 15: Projection of the packing of RbDNT down the c axis.

Table S- 28: Sample and crystal data for RbDNT.

| | | |
|---|---|---|
| Identification code | RbDNT | |
| Chemical formula | $C_2N_5O_4Rb$ | |
| Formula weight | 243.54 | |
| Temperature | 140(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.040 x 0.200 x 0.220 mm | |
| Crystal habit | clear yellow plate | |
| Crystal system | orthorhombic | |
| Space group | P 21 21 21 | |
| Unit cell dimensions | a = 7.6561(12) Å | α = 90° |
| | b = 7.8172(12) Å | β = 90° |
| | c = 11.0946(17) Å | γ = 90° |
| Volume | 664.00(18) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 2.436 $g/cm^3$ | |
| Absorption coefficient | 7.440 $mm^{-1}$ | |
| F(000) | 464 | |

Table S- 29: Data collection and structure refinement for RbDNT.

| | |
|---|---|
| Diffractometer | Bruker SMART APEX |

| | |
|---|---|
| Radiation source | fine-focus tube, MoKα |
| Theta range for data collection | 3.19 to 28.72° |
| Index ranges | -9<=h<=10, -10<=k<=10, -14<=l<=9 |
| Reflections collected | 4210 |
| Independent reflections | 1583 [R(int) = 0.0400] |
| Coverage of independent reflections | 94.2% |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.7550 and 0.2910 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXTL XT 2013/6 (Sheldrick, 2013) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXTL XLMP 2014/1 (Bruker AXS, 2013) |
| Function minimized | $\Sigma\, w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 1583 / 0 / 109 |
| Goodness-of-fit on $F^2$ | 0.998 |
| $\Delta/\sigma_{max}$ | 0.001 |
| Final R indices | 1421 data; I>2σ(I) R1 = 0.0335, wR2 = 0.0703 |
| | all data R1 = 0.0399, wR2 = 0.0729 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0277P)^2]$ where $P=(F_o^2+2F_c^2)/3$ |
| Absolute structure parameter | 0.0(0) |
| Largest diff. peak and hole | 0.858 and -0.796 eÅ$^{-3}$ |
| R.M.S. deviation from mean | 0.123 eÅ$^{-3}$ |

Table S- 30: Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for RbDNT.U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| C1 | 0.6039(7) | 0.6239(7) | 0.7206(5) | 0.0191(12) |
| C2 | 0.6133(7) | 0.6031(7) | 0.5403(5) | 0.0181(11) |
| N1 | 0.7600(6) | 0.6879(7) | 0.5689(5) | 0.0255(12) |
| N2 | 0.7538(6) | 0.7007(7) | 0.6904(5) | 0.0239(11) |
| N3 | 0.5098(5) | 0.5578(6) | 0.6299(4) | 0.0199(10) |
| N4 | 0.5480(6) | 0.6150(6) | 0.8436(4) | 0.0215(11) |
| N5 | 0.5708(5) | 0.5651(6) | 0.4173(5) | 0.0196(11) |
| O1 | 0.4023(6) | 0.5518(7) | 0.8631(4) | 0.0466(14) |
| O2 | 0.6435(5) | 0.6683(5) | 0.9236(4) | 0.0234(9) |
| O3 | 0.4630(5) | 0.4509(5) | 0.3977(4) | 0.0268(10) |
| O4 | 0.6442(5) | 0.6468(5) | 0.3364(3) | 0.0240(9) |
| Rb1 | 0.37462(6) | 0.52819(7) | 0.13279(5) | 0.02106(16) |

Table S- 31: Bond lengths (Å) for RbDNT.

| | | | |
|---|---|---|---|
| C1-N2 | 1.338(7) | C1-N3 | 1.341(7) |
| C1-N4 | 1.431(7) | C1-C2 | 2.009(8) |
| C2-N3 | 1.319(7) | C2-N1 | 1.343(7) |
| C2-N5 | 1.433(7) | N1-N2 | 1.353(7) |

| | | | |
|---|---|---|---|
| N1-Rb1 | 3.344(5) | N1-Rb1 | 3.626(6) |
| N2-Rb1 | 3.032(5) | N2-Rb1 | 3.421(5) |
| N3-Rb1 | 3.019(4) | N4-O2 | 1.224(6) |
| N4-O1 | 1.239(6) | N4-Rb1 | 3.538(5) |
| N5-O3 | 1.235(6) | N5-O4 | 1.237(6) |
| N5-Rb1 | 3.508(5) | O1-Rb1 | 3.005(4) |
| O1-Rb1 | 3.379(4) | O2-Rb1 | 3.025(4) |
| O2-Rb1 | 3.290(4) | O3-Rb1 | 3.076(4) |
| O3-Rb1 | 3.547(4) | O4-Rb1 | 3.005(4) |
| O4-Rb1 | 3.197(4) | Rb1-O4 | 3.005(4) |
| Rb1-N3 | 3.019(4) | Rb1-O2 | 3.025(4) |
| Rb1-N2 | 3.032(5) | Rb1-O3 | 3.076(4) |
| Rb1-O4 | 3.197(4) | Rb1-N1 | 3.344(5) |
| Rb1-O1 | 3.379(4) | Rb1-N2 | 3.421(5) |
| Rb1-N5 | 3.508(5) | | |

Table S- 32: Bond angles (°) for RbDNT.

| | | | |
|---|---|---|---|
| N2-C1-N3 | 116.4(5) | N2-C1-N4 | 121.1(5) |
| N3-C1-N4 | 122.4(5) | N2-C1-C2 | 75.9(4) |
| N3-C1-C2 | 40.6(3) | N4-C1-C2 | 163.0(5) |
| N3-C2-N1 | 117.2(5) | N3-C2-N5 | 121.7(5) |
| N1-C2-N5 | 121.2(5) | N3-C2-C1 | 41.4(3) |
| N1-C2-C1 | 75.8(4) | N5-C2-C1 | 163.0(5) |
| C2-N1-N2 | 104.1(5) | C2-N1-Rb1 | 120.1(4) |
| N2-N1-Rb1 | 81.7(4) | C2-N1-Rb1 | 88.8(3) |
| N2-N1-Rb1 | 123.4(4) | Rb1-N1-Rb1 | 137.67(15) |
| C1-N2-N1 | 104.3(5) | C1-N2-Rb1 | 114.4(4) |
| N1-N2-Rb1 | 133.3(4) | C1-N2-Rb1 | 121.7(4) |
| N1-N2-Rb1 | 75.3(3) | Rb1-N2-Rb1 | 103.46(13) |
| C2-N3-C1 | 98.0(4) | C2-N3-Rb1 | 130.8(4) |
| C1-N3-Rb1 | 126.9(4) | O2-N4-O1 | 123.2(5) |
| O2-N4-C1 | 119.8(4) | O1-N4-C1 | 117.1(5) |
| O2-N4-Rb1 | 68.4(3) | O1-N4-Rb1 | 55.0(3) |
| C1-N4-Rb1 | 170.3(4) | O3-N5-O4 | 123.3(5) |
| O3-N5-C2 | 118.0(5) | O4-N5-C2 | 118.7(4) |
| O3-N5-Rb1 | 59.7(3) | O4-N5-Rb1 | 65.4(3) |
| C2-N5-Rb1 | 166.1(3) | N4-O1-Rb1 | 105.2(3) |
| N4-O1-Rb1 | 120.4(3) | Rb1-O1-Rb1 | 134.23(13) |
| N4-O2-Rb1 | 117.8(3) | N4-O2-Rb1 | 91.4(3) |
| Rb1-O2-Rb1 | 140.63(13) | N5-O3-Rb1 | 100.0(3) |
| N5-O3-Rb1 | 117.1(3) | Rb1-O3-Rb1 | 99.72(11) |
| N5-O4-Rb1 | 114.1(3) | N5-O4-Rb1 | 94.0(3) |
| Rb1-O4-Rb1 | 109.71(12) | O4-Rb1-O1 | 100.23(12) |
| O4-Rb1-N3 | 74.55(11) | O1-Rb1-N3 | 94.11(12) |
| O4-Rb1-O2 | 140.70(12) | O1-Rb1-O2 | 77.71(13) |
| N3-Rb1-O2 | 66.56(11) | O4-Rb1-N2 | 127.25(13) |
| O1-Rb1-N2 | 128.51(15) | N3-Rb1-N2 | 82.26(13) |

| | | | |
|---|---|---|---|
| O2-Rb1-N2 | 53.65(12) | O4-Rb1-O3 | 72.95(10) |
| O1-Rb1-O3 | 161.43(12) | N3-Rb1-O3 | 100.42(12) |
| O2-Rb1-O3 | 118.71(11) | N2-Rb1-O3 | 65.55(12) |
| O4-Rb1-O4 | 103.78(8) | O1-Rb1-O4 | 129.81(11) |
| N3-Rb1-O4 | 134.55(12) | O2-Rb1-O4 | 107.24(11) |
| N2-Rb1-O4 | 62.43(11) | O3-Rb1-O4 | 40.52(10) |
| O4-Rb1-O2 | 116.14(10) | O1-Rb1-O2 | 39.93(11) |
| N3-Rb1-O2 | 132.58(12) | O2-Rb1-O2 | 87.65(5) |
| N2-Rb1-O2 | 114.49(12) | O3-Rb1-O2 | 127.00(10) |
| O4-Rb1-O2 | 89.88(10) | O4-Rb1-N1 | 64.08(11) |
| O1-Rb1-N1 | 76.17(13) | N3-Rb1-N1 | 134.49(12) |
| O2-Rb1-N1 | 147.31(12) | N2-Rb1-N1 | 138.19(13) |
| O3-Rb1-N1 | 85.38(12) | O4-Rb1-N1 | 75.89(11) |
| O2-Rb1-N1 | 59.68(11) | O4-Rb1-O1 | 72.56(12) |
| O1-Rb1-O1 | 143.96(6) | N3-Rb1-O1 | 49.86(11) |
| O2-Rb1-O1 | 86.25(12) | N2-Rb1-O1 | 56.54(14) |
| O3-Rb1-O1 | 51.60(9) | O4-Rb1-O1 | 85.66(10) |
| O2-Rb1-O1 | 171.03(12) | N1-Rb1-O1 | 126.28(13) |
| O4-Rb1-N2 | 59.96(11) | O1-Rb1-N2 | 99.18(13) |
| N3-Rb1-N2 | 134.12(12) | O2-Rb1-N2 | 159.27(11) |
| N2-Rb1-N2 | 119.89(7) | O3-Rb1-N2 | 62.35(11) |
| O4-Rb1-N2 | 58.86(11) | O2-Rb1-N2 | 77.62(11) |
| N1-Rb1-N2 | 23.03(13) | O1-Rb1-N2 | 106.48(12) |
| O4-Rb1-N5 | 89.97(10) | O1-Rb1-N5 | 149.40(11) |
| N3-Rb1-N5 | 116.45(12) | O2-Rb1-N5 | 111.85(11) |
| N2-Rb1-N5 | 59.40(12) | O3-Rb1-N5 | 20.29(10) |
| O4-Rb1-N5 | 20.59(9) | O2-Rb1-N5 | 109.84(10) |
| N1-Rb1-N5 | 82.77(11) | O1-Rb1-N5 | 66.62(10) |
| N2-Rb1-N5 | 61.23(11) | | |

Table S- 33: Anisotropic atomic displacement parameters (Å$^2$) for RbDNT.The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C1 | 0.015(3) | 0.019(3) | 0.024(3) | 0.001(2) | 0.000(2) | 0.003(2) |
| C2 | 0.016(2) | 0.017(3) | 0.021(3) | 0.000(2) | -0.003(2) | 0.002(3) |
| N1 | 0.020(3) | 0.030(3) | 0.027(3) | -0.002(3) | 0.004(2) | -0.008(2) |
| N2 | 0.017(2) | 0.029(3) | 0.026(3) | 0.000(2) | 0.002(2) | -0.005(2) |
| N3 | 0.0142(19) | 0.023(3) | 0.023(3) | -0.003(2) | 0.002(2) | -0.0018(16) |
| N4 | 0.020(2) | 0.021(3) | 0.023(3) | 0.002(2) | 0.003(2) | 0.0007(19) |
| N5 | 0.015(2) | 0.021(3) | 0.022(3) | -0.001(2) | 0.0027(19) | 0.0032(17) |
| O1 | 0.031(2) | 0.082(4) | 0.027(3) | -0.003(3) | 0.006(2) | -0.031(2) |
| O2 | 0.025(2) | 0.023(2) | 0.022(2) | -0.0028(17) | -0.0012(19) | 0.001(2) |
| O3 | 0.0215(19) | 0.029(2) | 0.030(3) | -0.002(2) | -0.0036(17) | -0.0050(17) |
| O4 | 0.024(2) | 0.026(2) | 0.022(2) | 0.0029(17) | 0.0036(19) | 0.0003(19) |
| Rb1 | 0.0177(2) | 0.0244(3) | 0.0212(3) | -0.0015(2) | 0.0012(2) | 0.0025(2) |

## 2.6 Crystal Structure Report for CsDNT

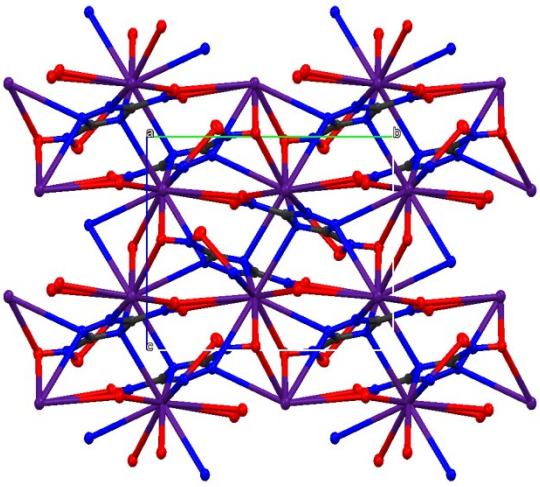

Figure S- 16 : Projection of the packing in **CsDNT** down the a axis.

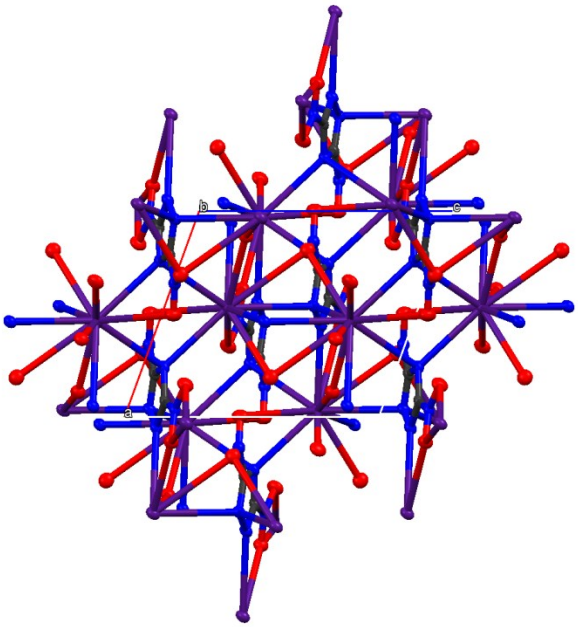

Figure S- 17: Projection of the packing in **CsDNT** down the b axis.

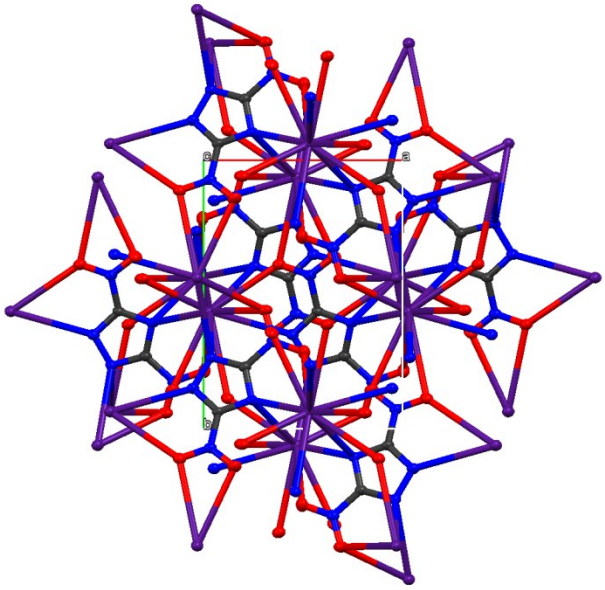

Figure S- 18 : Projection of the packing in **CsDNT** down the c axis.

Table S- 34: Sample and crystal data for **CsDNT**.

| | | |
|---|---|---|
| Identification code | CsDNT_2 | |
| Chemical formula | $C_2CsN_5O_4$ | |
| Formula weight | 290.98 | |
| Temperature | 133(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.040 x 0.190 x 0.290 mm | |
| Crystal habit | clear pale orange plate | |
| Crystal system | monoclinic | |
| Space group | P 1 21/n 1 | |
| Unit cell dimensions | a = 7.974(3) Å | α = 90° |
| | b = 10.088(3) Å | β = 109.941(4)° |
| | c = 9.267(3) Å | γ = 90° |
| Volume | 700.8(4) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 2.758 $g/cm^3$ | |
| Absorption coefficient | 5.269 $mm^{-1}$ | |
| F(000) | 536 | |

Table S- 35: Data collection and structure refinement for **CsDNT**.

| | |
|---|---|
| Diffractometer | Bruker SMART APEX |
| Radiation source | fine-focus tube, MoKα |
| Theta range for data collection | 2.92 to 28.63° |
| Index ranges | -9<=h<=10, -13<=k<=10, -12<=l<=12 |
| Reflections collected | 3944 |
| Independent reflections | 1589 [R(int) = 0.1014] |
| Coverage of independent reflections | 88.2% |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.8170 and 0.3100 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXTL XT 2013/6 (Sheldrick, 2013) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXTL XLMP 2014/1 (Bruker AXS, 2013) |
| Function minimized | $\Sigma w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 1589 / 0 / 109 |
| Goodness-of-fit on $F^2$ | 1.040 |
| Final R indices | 1433 data; I>2σ(I) R1 = 0.0332, wR2 = 0.0848 |
| | all data R1 = 0.0357, wR2 = 0.0869 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0434P)^2]$ where $P=(F_o^2+2F_c^2)/3$ |
| Largest diff. peak and hole | 1.170 and -1.327 $eÅ^{-3}$ |
| R.M.S. deviation from mean | 0.222 $eÅ^{-3}$ |

Table S- 36: Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for **CsDNT**.U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| C1 | 0.4253(6) | 0.4374(3) | 0.6360(4) | 0.0187(8) |
| C2 | 0.2914(5) | 0.2697(3) | 0.5558(4) | 0.0202(7) |
| Cs1 | 0.96841(3) | 0.43708(2) | 0.74916(3) | 0.02347(13) |
| N1 | 0.4624(4) | 0.2360(3) | 0.5860(4) | 0.0219(6) |
| N2 | 0.5531(4) | 0.3504(3) | 0.6399(3) | 0.0223(6) |
| N3 | 0.2577(4) | 0.3941(3) | 0.5834(3) | 0.0195(6) |
| N4 | 0.4664(5) | 0.5723(3) | 0.6867(4) | 0.0204(7) |
| N5 | 0.1491(4) | 0.1750(3) | 0.4930(3) | 0.0235(6) |
| O1 | 0.3432(4) | 0.6427(3) | 0.6934(3) | 0.0303(6) |
| O2 | 0.6214(4) | 0.6120(3) | 0.7186(3) | 0.0266(6) |
| O3 | 0.9950(4) | 0.2154(3) | 0.4538(3) | 0.0327(7) |
| O4 | 0.1917(5) | 0.0583(2) | 0.4816(4) | 0.0297(7) |

Table S- 37: Bond lengths (Å) for **CsDNT**.

| | | | |
|---|---|---|---|
| C1-N3 | 1.331(5) | C1-N2 | 1.336(5) |
| C1-N4 | 1.440(4) | C2-N3 | 1.326(4) |
| C2-N1 | 1.339(4) | C2-N5 | 1.445(5) |
| Cs1-N3 | 3.207(3) | Cs1-O2 | 3.212(3) |
| Cs1-O4 | 3.233(3) | Cs1-N2 | 3.236(3) |
| Cs1-O1 | 3.288(3) | Cs1-N1 | 3.340(3) |
| Cs1-O2 | 3.391(3) | Cs1-N3 | 3.444(3) |
| Cs1-O4 | 3.571(4) | Cs1-N1 | 3.591(3) |
| Cs1-O3 | 3.597(3) | Cs1-N4 | 3.736(3) |
| N1-N2 | 1.364(4) | N1-Cs1 | 3.340(3) |
| N1-Cs1 | 3.591(3) | N2-Cs1 | 3.236(3) |
| N3-Cs1 | 3.444(3) | N4-O1 | 1.230(4) |
| N4-O2 | 1.236(5) | N4-Cs1 | 3.736(3) |
| N5-O3 | 1.226(4) | N5-O4 | 1.240(4) |
| O1-Cs1 | 3.288(3) | O2-Cs1 | 3.212(3) |
| O2-Cs1 | 3.391(3) | O4-Cs1 | 3.233(3) |
| O4-Cs1 | 3.571(4) | | |

Table S- 38: Bond angles (°) for **CsDNT**.

| | | | |
|---|---|---|---|
| N3-C1-N2 | 117.1(3) | N3-C1-N4 | 121.2(3) |
| N2-C1-N4 | 121.7(4) | N3-C2-N1 | 117.3(3) |
| N3-C2-N5 | 121.4(3) | N1-C2-N5 | 121.3(3) |
| N3-Cs1-O2 | 140.42(7) | N3-Cs1-O4 | 82.55(9) |
| O2-Cs1-O4 | 109.29(8) | N3-Cs1-N2 | 129.80(8) |
| O2-Cs1-N2 | 50.35(7) | O4-Cs1-N2 | 147.43(9) |
| N3-Cs1-O1 | 65.92(7) | O2-Cs1-O1 | 147.42(7) |
| O4-Cs1-O1 | 90.02(7) | N2-Cs1-O1 | 99.72(7) |
| N3-Cs1-N1 | 107.92(8) | O2-Cs1-N1 | 63.08(7) |
| O4-Cs1-N1 | 48.80(7) | N2-Cs1-N1 | 112.26(7) |
| O1-Cs1-N1 | 138.26(8) | N3-Cs1-O2 | 96.85(7) |
| O2-Cs1-O2 | 109.74(4) | O4-Cs1-O2 | 116.38(6) |
| N2-Cs1-O2 | 62.74(7) | O1-Cs1-O2 | 37.90(6) |
| N1-Cs1-O2 | 147.08(7) | N3-Cs1-N3 | 83.16(8) |
| O2-Cs1-N3 | 58.45(7) | O4-Cs1-N3 | 123.28(7) |
| N2-Cs1-N3 | 71.71(7) | O1-Cs1-N3 | 131.49(7) |
| N1-Cs1-N3 | 85.25(7) | O2-Cs1-N3 | 119.70(7) |
| N3-Cs1-O4 | 169.73(7) | O2-Cs1-O4 | 49.85(7) |
| O4-Cs1-O4 | 93.29(9) | N2-Cs1-O4 | 54.21(8) |
| O1-Cs1-O4 | 104.84(6) | N1-Cs1-O4 | 75.64(7) |
| O2-Cs1-O4 | 76.52(6) | N3-Cs1-O4 | 106.90(8) |
| N3-Cs1-N1 | 125.14(8) | O2-Cs1-N1 | 94.44(7) |
| O4-Cs1-N1 | 76.66(8) | N2-Cs1-N1 | 79.92(7) |
| O1-Cs1-N1 | 63.95(7) | N1-Cs1-N1 | 95.18(7) |
| O2-Cs1-N1 | 52.22(7) | N3-Cs1-N1 | 149.34(7) |
| O4-Cs1-N1 | 44.59(7) | N3-Cs1-O3 | 46.58(7) |
| O2-Cs1-O3 | 123.17(7) | O4-Cs1-O3 | 124.83(8) |
| N2-Cs1-O3 | 85.04(7) | O1-Cs1-O3 | 54.51(7) |
| N1-Cs1-O3 | 150.02(7) | O2-Cs1-O3 | 62.28(7) |
| N3-Cs1-O3 | 77.02(7) | O4-Cs1-O3 | 132.53(6) |
| N1-Cs1-O3 | 112.39(7) | N3-Cs1-N4 | 81.89(8) |
| O2-Cs1-N4 | 128.63(8) | O4-Cs1-N4 | 102.43(7) |
| N2-Cs1-N4 | 81.70(8) | O1-Cs1-N4 | 18.82(7) |
| N1-Cs1-N4 | 145.51(7) | O2-Cs1-N4 | 19.19(8) |
| N3-Cs1-N4 | 129.17(7) | O4-Cs1-N4 | 89.89(6) |
| N1-Cs1-N4 | 54.92(7) | O3-Cs1-N4 | 57.81(7) |
| C2-N1-N2 | 103.7(3) | C2-N1-Cs1 | 108.8(2) |
| N2-N1-Cs1 | 127.8(2) | C2-N1-Cs1 | 104.9(2) |
| N2-N1-Cs1 | 124.6(2) | Cs1-N1-Cs1 | 84.82(7) |
| C1-N2-N1 | 104.0(3) | C1-N2-Cs1 | 121.4(2) |
| N1-N2-Cs1 | 134.6(2) | C2-N3-C1 | 97.9(3) |
| C2-N3-Cs1 | 116.5(2) | C1-N3-Cs1 | 125.2(2) |
| C2-N3-Cs1 | 112.0(2) | C1-N3-Cs1 | 108.6(2) |
| Cs1-N3-Cs1 | 96.84(8) | O1-N4-O2 | 123.4(3) |
| O1-N4-C1 | 117.7(3) | O2-N4-C1 | 118.8(3) |
| O1-N4-Cs1 | 59.56(17) | O2-N4-Cs1 | 64.44(17) |
| C1-N4-Cs1 | 170.5(2) | O3-N5-O4 | 124.5(3) |

| | | | |
|---|---|---|---|
| O3-N5-C2 | 118.0(3) | O4-N5-C2 | 117.5(3) |
| N4-O1-Cs1 | 101.6(2) | N4-O2-Cs1 | 127.2(2) |
| N4-O2-Cs1 | 96.4(2) | Cs1-O2-Cs1 | 136.46(9) |
| N5-O3-Cs1 | 107.1(2) | N5-O4-Cs1 | 118.4(2) |
| N5-O4-Cs1 | 106.4(2) | Cs1-O4-Cs1 | 86.71(9) |

Table S- 39: Anisotropic atomic displacement parameters ($Å^2$) for **CsDNT**.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0249(19) | 0.0143(17) | 0.0215(18) | 0.0003(12) | 0.0137(16) | 0.0020(12) |
| C2 | 0.0253(17) | 0.0167(15) | 0.0222(16) | 0.0007(14) | 0.0127(14) | 0.0013(14) |
| Cs1 | 0.02321(18) | 0.01906(18) | 0.03195(19) | -0.00085(8) | 0.01432(12) | 0.00045(7) |
| N1 | 0.0231(14) | 0.0172(14) | 0.0279(14) | -0.0001(13) | 0.0121(13) | 0.0013(12) |
| N2 | 0.0243(15) | 0.0190(13) | 0.0269(14) | -0.0020(13) | 0.0130(13) | 0.0001(12) |
| N3 | 0.0240(15) | 0.0150(13) | 0.0224(14) | 0.0009(12) | 0.0115(12) | 0.0011(12) |
| N4 | 0.0263(17) | 0.0169(15) | 0.0213(17) | -0.0001(11) | 0.0125(15) | 0.0006(11) |
| N5 | 0.0266(16) | 0.0209(15) | 0.0236(14) | -0.0005(13) | 0.0095(13) | -0.0018(12) |
| O1 | 0.0303(14) | 0.0221(13) | 0.0425(15) | -0.0059(13) | 0.0177(13) | 0.0045(11) |
| O2 | 0.0271(14) | 0.0202(13) | 0.0339(14) | 0.0002(12) | 0.0121(11) | -0.0025(11) |
| O3 | 0.0230(14) | 0.0311(15) | 0.0416(16) | -0.0074(13) | 0.0082(12) | -0.0008(12) |
| O4 | 0.0355(17) | 0.0187(14) | 0.0339(16) | -0.0014(10) | 0.0104(15) | 0.0006(10) |

## 2.7 Crystal Structure Report for $Sr(DNT)_2 \cdot 6H_2O$

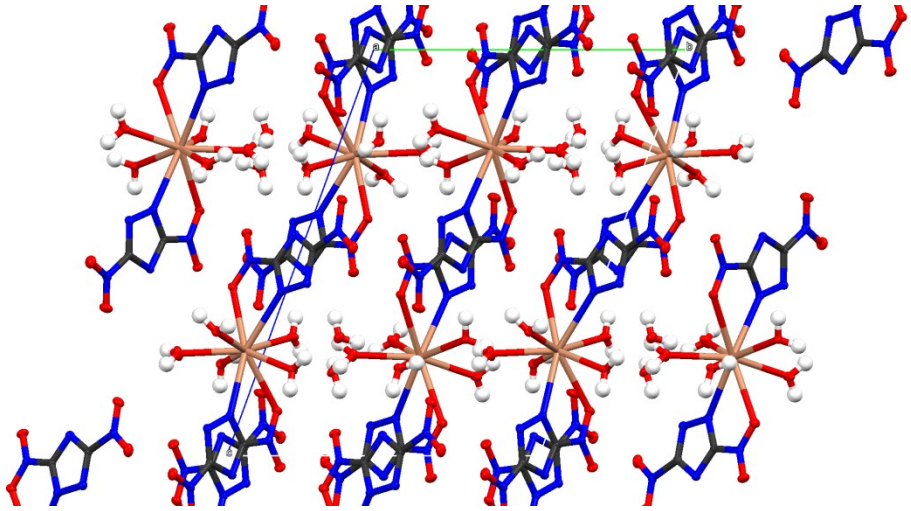

Figure S- 19: Projection of the packing of $Sr(DNT)_2 \cdot 6H2O$ down the a axis.

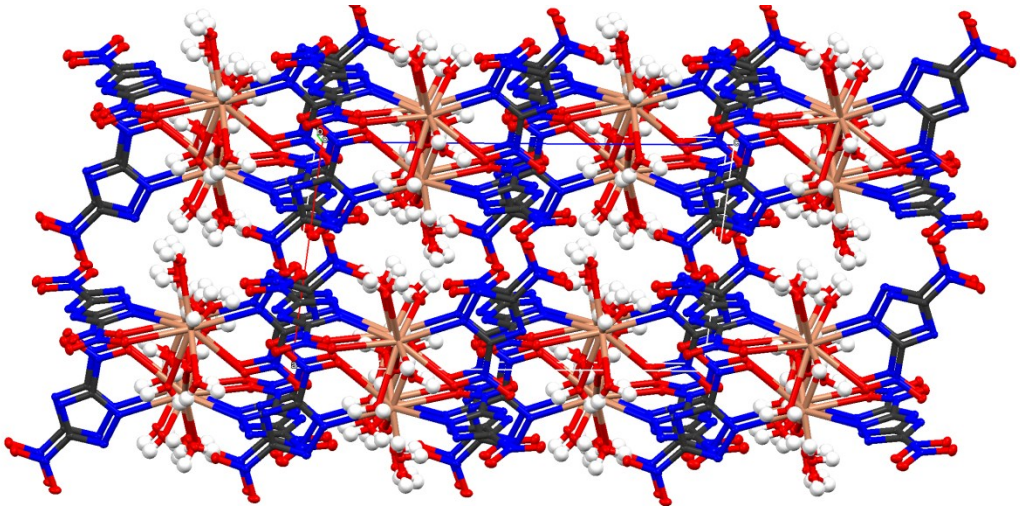

Figure S- 20: Projection of the packing of $Sr(DNT)_2 \cdot 6H2O$ approximately down the b axis.

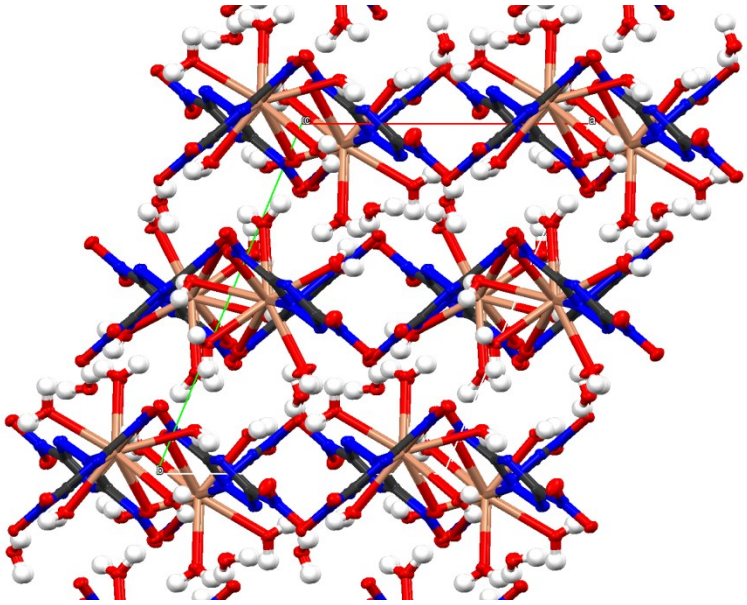

Figure S- 21: Projection of the packing of **Sr(DNT)2·6H2O** down the c axis.

Table S- 40: Sample and crystal data for **Sr(DNT)2·6H2O**.

| | | |
|---|---|---|
| Identification code | SrDNT | |
| Chemical formula | $C_4H_{12}N_{10}O_{14}Sr$ | |
| Formula weight | 511.86 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.200 x 0.310 x 0.410 mm | |
| Crystal habit | clear yellow-orange prism | |
| Crystal system | triclinic | |
| Space group | P -1 | |
| Unit cell dimensions | a = 9.2895(3) Å | α = 108.2150(10)° |
| | b = 12.8551(4) Å | β = 90.8870(10)° |
| | c = 16.5552(7) Å | γ = 111° |
| Volume | 1736.03(11) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.958 $g/cm^3$ | |
| Absorption coefficient | 3.204 $mm^{-1}$ | |
| F(000) | 1024 | |

Table S- 41: Data collection and structure refinement for **Sr(DNT)2·6H2O**.

| | |
|---|---|
| Diffractometer | Bruker APEX DUO |
| Radiation source | fine-focus tube, MoKα |
| Theta range for data collection | 1.83 to 30.62° |
| Index ranges | -13<=h<=13, -18<=k<=18, -23<=l<=23 |
| Reflections collected | 42154 |
| Independent reflections | 10328 [R(int) = 0.0331] |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.5670 and 0.3530 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXTL XS 2013/1 (Sheldrick, 2013) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXTL XLMP 2014/1 (Bruker AXS, 2013) |
| Function minimized | $\Sigma\, w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 10328 / 0 / 619 |
| Goodness-of-fit on $F^2$ | 1.032 |
| $\Delta/\sigma_{max}$ | 0.001 |
| Final R indices | 8672 data; I>2σ(I) R1 = 0.0240, wR2 = 0.0491 |
| | all data R1 = 0.0351, wR2 = 0.0520 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0239P)^2+0.2726P]$ where $P=(F_o^2+2F_c^2)/3$ |
| Largest diff. peak and hole | 0.331 and -0.430 eÅ$^{-3}$ |
| R.M.S. deviation from mean | 0.079 eÅ$^{-3}$ |

Table S- 42: Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for **Sr(DNT)2·6H2O**.U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| C1 | 0.28742(16) | 0.96148(12) | 0.50698(9) | 0.0124(3) |
| C2 | 0.19556(16) | 0.06666(12) | 0.47739(9) | 0.0113(3) |
| C3 | 0.34392(17) | 0.04502(12) | 0.98202(9) | 0.0125(3) |
| C4 | 0.15622(16) | 0.96025(12) | 0.02854(9) | 0.0116(3) |
| C5 | 0.67363(16) | 0.45509(12) | 0.50591(9) | 0.0123(3) |
| C6 | 0.86602(16) | 0.54876(12) | 0.46736(9) | 0.0109(3) |
| C7 | 0.69557(17) | 0.55253(13) | 0.98939(9) | 0.0134(3) |
| C8 | 0.79199(16) | 0.44800(12) | 0.01756(9) | 0.0121(3) |
| N1 | 0.23892(14) | 0.01506(10) | 0.40446(8) | 0.0125(2) |
| N2 | 0.30156(14) | 0.94384(11) | 0.42462(8) | 0.0131(2) |
| N3 | 0.22085(14) | 0.03733(10) | 0.54542(7) | 0.0118(2) |
| N4 | 0.34929(14) | 0.90381(10) | 0.55337(8) | 0.0130(2) |
| N5 | 0.12493(14) | 0.15152(10) | 0.48142(8) | 0.0125(2) |
| N6 | 0.25763(14) | 0.03588(10) | 0.09834(8) | 0.0133(2) |
| N7 | 0.38570(14) | 0.09296(11) | 0.06670(8) | 0.0142(2) |
| N8 | 0.20134(14) | 0.96114(10) | 0.95270(8) | 0.0124(2) |
| N9 | 0.45033(14) | 0.08124(11) | 0.92371(8) | 0.0149(2) |
| N10 | 0.00343(14) | 0.88310(11) | 0.03722(8) | 0.0131(2) |
| N11 | 0.77002(14) | 0.47932(11) | 0.39466(8) | 0.0132(2) |

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| N12 | 0.63871(14) | 0.41627(11) | 0.42081(8) | 0.0137(2) |
| N13 | 0.81486(14) | 0.53849(10) | 0.54036(7) | 0.0115(2) |
| N14 | 0.56207(14) | 0.40906(11) | 0.55862(8) | 0.0146(2) |
| N15 | 0.02161(14) | 0.62832(10) | 0.46614(8) | 0.0121(2) |
| N16 | 0.75549(14) | 0.50274(11) | 0.09176(8) | 0.0135(2) |
| N17 | 0.68955(15) | 0.57301(11) | 0.07278(8) | 0.0152(2) |
| N18 | 0.75880(14) | 0.47485(11) | 0.94944(8) | 0.0129(2) |
| N19 | 0.63474(14) | 0.61217(11) | 0.94431(8) | 0.0150(2) |
| N20 | 0.86851(14) | 0.36664(11) | 0.01384(8) | 0.0138(2) |
| O1 | 0.40974(12) | 0.83705(9) | 0.51289(7) | 0.0176(2) |
| O2 | 0.33953(13) | 0.92763(10) | 0.63072(7) | 0.0187(2) |
| O3 | 0.11355(12) | 0.17638(9) | 0.41553(6) | 0.0160(2) |
| O4 | 0.08090(13) | 0.19364(9) | 0.54853(7) | 0.0170(2) |
| O5 | 0.58438(12) | 0.15158(9) | 0.95500(7) | 0.0188(2) |
| O6 | 0.40222(13) | 0.03825(11) | 0.84651(7) | 0.0253(3) |
| O7 | 0.97400(12) | 0.89160(9) | 0.11104(7) | 0.0160(2) |
| O8 | 0.91328(12) | 0.81630(9) | 0.97161(7) | 0.0172(2) |
| O9 | 0.43035(12) | 0.34082(10) | 0.52271(7) | 0.0207(2) |
| O10 | 0.60606(13) | 0.44273(11) | 0.63614(7) | 0.0227(2) |
| O11 | 0.06115(12) | 0.62899(9) | 0.39539(6) | 0.0147(2) |
| O12 | 0.10484(12) | 0.68849(9) | 0.53531(6) | 0.0156(2) |
| O13 | 0.57488(13) | 0.67888(9) | 0.98636(7) | 0.0205(2) |
| O14 | 0.64682(13) | 0.59144(10) | 0.86796(7) | 0.0206(2) |
| O15 | 0.89219(13) | 0.34903(9) | 0.08110(7) | 0.0178(2) |
| O16 | 0.90613(13) | 0.32084(9) | 0.94530(7) | 0.0181(2) |
| O17 | 0.27215(16) | 0.27382(11) | 0.25204(9) | 0.0244(3) |
| O18 | 0.47108(13) | 0.17794(10) | 0.30667(7) | 0.0168(2) |
| O19 | 0.26115(13) | 0.88937(10) | 0.21139(8) | 0.0174(2) |
| O20 | 0.91095(14) | 0.92716(11) | 0.29252(8) | 0.0192(2) |
| O21 | 0.93339(14) | 0.12401(10) | 0.22651(8) | 0.0178(2) |
| O22 | 0.98866(14) | 0.71255(10) | 0.24853(8) | 0.0209(2) |
| O23 | 0.15510(13) | 0.55040(10) | 0.21547(7) | 0.0172(2) |
| O24 | 0.01381(14) | 0.37089(10) | 0.28663(7) | 0.0178(2) |
| O25 | 0.63724(16) | 0.29371(11) | 0.19526(9) | 0.0299(3) |
| O26 | 0.67692(15) | 0.59784(12) | 0.28098(9) | 0.0248(3) |
| O27 | 0.63755(15) | 0.75583(11) | 0.20757(8) | 0.0221(3) |
| O28 | 0.38415(14) | 0.77718(11) | 0.29102(8) | 0.0198(2) |
| Sr1 | 0.17257(2) | 0.06259(2) | 0.25909(2) | 0.01000(3) |
| Sr2 | 0.86295(2) | 0.49550(2) | 0.24229(2) | 0.01128(3) |

Table S- 43: Bond lengths (Å) for **Sr(DNT)2·6H2O**.

| | | | |
|---|---|---|---|
| C1-N2 | 1.3272(18) | C1-N3 | 1.3391(18) |
| C1-N4 | 1.4548(18) | C2-N1 | 1.3287(18) |
| C2-N3 | 1.3367(17) | C2-N5 | 1.4464(18) |
| C3-N7 | 1.3298(18) | C3-N8 | 1.3361(18) |
| C3-N9 | 1.4517(18) | C4-N8 | 1.3319(17) |

| | | | |
|---|---|---|---|
| C4-N6 | 1.3333(18) | C4-N10 | 1.4521(18) |
| C5-N12 | 1.3304(18) | C5-N13 | 1.3363(18) |
| C5-N14 | 1.4485(18) | C6-N11 | 1.3294(18) |
| C6-N13 | 1.3328(17) | C6-N15 | 1.4469(18) |
| C7-N17 | 1.3282(18) | C7-N18 | 1.3408(18) |
| C7-N19 | 1.4554(18) | C8-N16 | 1.3274(18) |
| C8-N18 | 1.3396(18) | C8-N20 | 1.4475(18) |
| N1-N2 | 1.3615(16) | N1-Sr1 | 2.7725(12) |
| N4-O1 | 1.2236(15) | N4-O2 | 1.2329(15) |
| N5-O4 | 1.2211(15) | N5-O3 | 1.2417(15) |
| N6-N7 | 1.3653(16) | N6-Sr1 | 2.7409(12) |
| N9-O6 | 1.2260(16) | N9-O5 | 1.2326(16) |
| N10-O8 | 1.2221(15) | N10-O7 | 1.2364(15) |
| N11-N12 | 1.3645(16) | N11-Sr2 | 2.7237(12) |
| N14-O9 | 1.2268(16) | N14-O10 | 1.2295(16) |
| N15-O12 | 1.2243(15) | N15-O11 | 1.2345(15) |
| N16-N17 | 1.3626(17) | N16-Sr2 | 2.7112(12) |
| N19-O14 | 1.2232(16) | N19-O13 | 1.2282(16) |
| N20-O16 | 1.2239(15) | N20-O15 | 1.2350(15) |
| O3-Sr1 | 2.7195(10) | O7-Sr1 | 2.7995(11) |
| O11-Sr2 | 2.7637(10) | O15-Sr2 | 2.8261(11) |
| O17-Sr1 | 2.5788(12) | O17-H1 | 0.78(3) |
| O17-H2 | 0.79(3) | O18-Sr1 | 2.6027(11) |
| O18-H3 | 0.88(3) | O18-H4 | 0.80(2) |
| O19-Sr1 | 2.5473(11) | O19-H5 | 0.87(2) |
| O19-H6 | 0.81(2) | O20-Sr1 | 2.6201(11) |
| O20-H7 | 0.85(2) | O20-H8 | 0.78(2) |
| O21-Sr1 | 2.7080(11) | O21-H9 | 0.79(2) |
| O21-H10 | 0.86(2) | O22-Sr2 | 2.5784(11) |
| O22-H11 | 0.89(3) | O22-H12 | 0.87(3) |
| O23-Sr2 | 2.6316(11) | O23-H13 | 0.81(2) |
| O23-H14 | 0.90(3) | O24-Sr2 | 2.7157(11) |
| O24-H15 | 0.86(2) | O24-H16 | 0.82(2) |
| O25-Sr2 | 2.5560(12) | O25-H17 | 0.83(2) |
| O25-H18 | 0.78(2) | O26-Sr2 | 2.5018(12) |
| O26-H19 | 0.76(2) | O26-H20 | 0.87(3) |
| O27-H21 | 0.79(2) | O27-H22 | 0.81(3) |
| O28-H23 | 0.78(2) | O28-H24 | 0.80(2) |
| Sr2-H13 | 2.86(2) | | |

Table S- 44: Bond angles (°) for **Sr(DNT)2·6H2O**.

| | | | |
|---|---|---|---|
| N2-C1-N3 | 117.46(13) | N2-C1-N4 | 120.27(13) |
| N3-C1-N4 | 122.21(12) | N1-C2-N3 | 117.37(13) |
| N1-C2-N5 | 120.25(12) | N3-C2-N5 | 122.38(12) |
| N7-C3-N8 | 117.50(13) | N7-C3-N9 | 121.15(13) |
| N8-C3-N9 | 121.35(12) | N8-C4-N6 | 116.99(12) |
| N8-C4-N10 | 122.90(12) | N6-C4-N10 | 120.10(12) |

| | | | |
|---|---|---|---|
| N12-C5-N13 | 117.22(13) | N12-C5-N14 | 121.05(13) |
| N13-C5-N14 | 121.73(12) | N11-C6-N13 | 117.24(13) |
| N11-C6-N15 | 120.81(12) | N13-C6-N15 | 121.90(12) |
| N17-C7-N18 | 117.12(13) | N17-C7-N19 | 120.68(13) |
| N18-C7-N19 | 122.20(13) | N16-C8-N18 | 116.85(13) |
| N16-C8-N20 | 119.86(12) | N18-C8-N20 | 123.26(12) |
| C2-N1-N2 | 104.10(11) | C2-N1-Sr1 | 118.42(9) |
| N2-N1-Sr1 | 137.37(9) | C1-N2-N1 | 103.96(11) |
| C2-N3-C1 | 97.10(11) | O1-N4-O2 | 125.01(12) |
| O1-N4-C1 | 117.40(12) | O2-N4-C1 | 117.58(12) |
| O4-N5-O3 | 124.56(12) | O4-N5-C2 | 118.43(12) |
| O3-N5-C2 | 117.01(11) | C4-N6-N7 | 104.29(11) |
| C4-N6-Sr1 | 120.70(9) | N7-N6-Sr1 | 134.66(9) |
| C3-N7-N6 | 103.61(11) | C4-N8-C3 | 97.60(11) |
| O6-N9-O5 | 124.18(13) | O6-N9-C3 | 118.02(12) |
| O5-N9-C3 | 117.78(12) | O8-N10-O7 | 125.02(12) |
| O8-N10-C4 | 117.97(12) | O7-N10-C4 | 117.00(12) |
| C6-N11-N12 | 104.11(11) | C6-N11-Sr2 | 119.40(9) |
| N12-N11-Sr2 | 136.45(9) | C5-N12-N11 | 103.86(11) |
| C6-N13-C5 | 97.55(11) | O9-N14-O10 | 125.00(13) |
| O9-N14-C5 | 117.53(12) | O10-N14-C5 | 117.46(12) |
| O12-N15-O11 | 124.99(12) | O12-N15-C6 | 117.47(12) |
| O11-N15-C6 | 117.53(11) | C8-N16-N17 | 104.50(11) |
| C8-N16-Sr2 | 121.43(9) | N17-N16-Sr2 | 132.70(9) |
| C7-N17-N16 | 103.98(12) | C8-N18-C7 | 97.54(12) |
| O14-N19-O13 | 125.55(13) | O14-N19-C7 | 117.49(12) |
| O13-N19-C7 | 116.96(12) | O16-N20-O15 | 124.51(13) |
| O16-N20-C8 | 118.47(12) | O15-N20-C8 | 117.01(12) |
| N5-O3-Sr1 | 125.21(8) | N10-O7-Sr1 | 123.81(8) |
| N15-O11-Sr2 | 123.20(8) | N20-O15-Sr2 | 121.91(9) |
| Sr1-O17-H1 | 123.(2) | Sr1-O17-H2 | 125.8(18) |
| H1-O17-H2 | 107.(3) | Sr1-O18-H3 | 120.2(16) |
| Sr1-O18-H4 | 119.1(18) | H3-O18-H4 | 105.(2) |
| Sr1-O19-H5 | 130.0(15) | Sr1-O19-H6 | 116.0(15) |
| H5-O19-H6 | 107.(2) | Sr1-O20-H7 | 125.6(13) |
| Sr1-O20-H8 | 122.8(18) | H7-O20-H8 | 107.(2) |
| Sr1-O21-H9 | 106.1(17) | Sr1-O21-H10 | 116.0(15) |
| H9-O21-H10 | 104.(2) | Sr2-O22-H11 | 125.9(16) |
| Sr2-O22-H12 | 126.4(16) | H11-O22-H12 | 107.(2) |
| Sr2-O23-H13 | 98.1(17) | Sr2-O23-H14 | 117.8(15) |
| H13-O23-H14 | 109.(2) | Sr2-O24-H15 | 118.1(14) |
| Sr2-O24-H16 | 120.3(14) | H15-O24-H16 | 107.2(19) |
| Sr2-O25-H17 | 124.7(17) | Sr2-O25-H18 | 131.5(17) |
| H17-O25-H18 | 104.(2) | Sr2-O26-H19 | 129.3(19) |
| Sr2-O26-H20 | 125.8(17) | H19-O26-H20 | 104.(2) |
| H21-O27-H22 | 113.(2) | H23-O28-H24 | 107.(2) |
| O19-Sr1-O17 | 135.11(4) | O19-Sr1-O18 | 80.75(4) |
| O17-Sr1-O18 | 66.28(4) | O19-Sr1-O20 | 90.54(4) |
| O17-Sr1-O20 | 133.53(4) | O18-Sr1-O20 | 146.64(4) |

| | | | |
|---|---|---|---|
| O19-Sr1-O21 | 140.99(4) | O17-Sr1-O21 | 68.71(4) |
| O18-Sr1-O21 | 134.21(4) | O20-Sr1-O21 | 68.51(4) |
| O19-Sr1-O3 | 130.46(3) | O17-Sr1-O3 | 81.57(4) |
| O18-Sr1-O3 | 91.09(3) | O20-Sr1-O3 | 70.27(4) |
| O21-Sr1-O3 | 74.38(3) | O19-Sr1-N6 | 70.31(4) |
| O17-Sr1-N6 | 75.73(4) | O18-Sr1-N6 | 82.51(4) |
| O20-Sr1-N6 | 124.79(4) | O21-Sr1-N6 | 94.42(4) |
| O3-Sr1-N6 | 157.11(3) | O19-Sr1-N1 | 72.38(4) |
| O17-Sr1-N1 | 122.71(4) | O18-Sr1-N1 | 74.72(3) |
| O20-Sr1-N1 | 71.95(4) | O21-Sr1-N1 | 126.04(4) |
| O3-Sr1-N1 | 58.42(3) | N6-Sr1-N1 | 138.75(4) |
| O19-Sr1-O7 | 71.60(3) | O17-Sr1-O7 | 113.18(4) |
| O18-Sr1-O7 | 137.20(3) | O20-Sr1-O7 | 66.98(3) |
| O21-Sr1-O7 | 69.98(3) | O3-Sr1-O7 | 131.71(3) |
| N6-Sr1-O7 | 57.91(3) | N1-Sr1-O7 | 123.94(3) |
| O26-Sr2-O25 | 90.58(5) | O26-Sr2-O22 | 69.28(4) |
| O25-Sr2-O22 | 151.93(4) | O26-Sr2-O23 | 137.87(4) |
| O25-Sr2-O23 | 129.77(4) | O22-Sr2-O23 | 68.72(4) |
| O26-Sr2-N16 | 75.24(4) | O25-Sr2-N16 | 82.99(4) |
| O22-Sr2-N16 | 73.29(4) | O23-Sr2-N16 | 95.75(4) |
| O26-Sr2-O24 | 146.75(4) | O25-Sr2-O24 | 81.80(4) |
| O22-Sr2-O24 | 125.73(4) | O23-Sr2-O24 | 63.93(4) |
| N16-Sr2-O24 | 134.92(4) | O26-Sr2-N11 | 71.24(4) |
| O25-Sr2-N11 | 77.59(4) | O22-Sr2-N11 | 111.89(4) |
| O23-Sr2-N11 | 122.85(4) | N16-Sr2-N11 | 140.76(4) |
| O24-Sr2-N11 | 75.51(4) | O26-Sr2-O11 | 93.67(4) |
| O25-Sr2-O11 | 131.90(4) | O22-Sr2-O11 | 70.87(3) |
| O23-Sr2-O11 | 69.56(3) | N16-Sr2-O11 | 144.12(3) |
| O24-Sr2-O11 | 69.04(3) | N11-Sr2-O11 | 58.91(3) |
| O26-Sr2-O15 | 130.00(4) | O25-Sr2-O15 | 69.51(4) |
| O22-Sr2-O15 | 108.08(4) | O23-Sr2-O15 | 67.96(3) |
| N16-Sr2-O15 | 57.62(3) | O24-Sr2-O15 | 77.31(3) |
| N11-Sr2-O15 | 139.69(3) | O11-Sr2-O15 | 134.09(3) |
| O26-Sr2-H13 | 151.6(5) | O25-Sr2-H13 | 117.9(5) |
| O22-Sr2-H13 | 83.9(5) | O23-Sr2-H13 | 16.2(5) |
| N16-Sr2-H13 | 106.5(5) | O24-Sr2-H13 | 47.8(5) |
| N11-Sr2-H13 | 112.7(5) | O11-Sr2-H13 | 68.0(5) |
| O15-Sr2-H13 | 66.4(5) | | |

Table S- 45: Anisotropic atomic displacement parameters ($Å^2$) for Sr(DNT)2·6H2O.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0120(7) | 0.0125(6) | 0.0129(7) | 0.0051(5) | 0.0010(5) | 0.0044(5) |
| C2 | 0.0098(6) | 0.0099(6) | 0.0129(7) | 0.0034(5) | 0.0008(5) | 0.0027(5) |
| C3 | 0.0136(7) | 0.0126(6) | 0.0129(7) | 0.0055(5) | 0.0027(5) | 0.0058(6) |

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C4 | 0.0111(7) | 0.0109(6) | 0.0132(7) | 0.0047(5) | 0.0008(5) | 0.0042(5) |
| C5 | 0.0119(7) | 0.0131(6) | 0.0137(7) | 0.0057(5) | 0.0026(5) | 0.0055(5) |
| C6 | 0.0122(7) | 0.0103(6) | 0.0114(6) | 0.0048(5) | 0.0015(5) | 0.0046(5) |
| C7 | 0.0118(7) | 0.0126(7) | 0.0134(7) | 0.0043(5) | 0.0008(5) | 0.0022(5) |
| C8 | 0.0110(7) | 0.0116(6) | 0.0119(7) | 0.0037(5) | 0.0016(5) | 0.0024(5) |
| N1 | 0.0129(6) | 0.0118(6) | 0.0122(6) | 0.0033(5) | 0.0014(5) | 0.0047(5) |
| N2 | 0.0132(6) | 0.0137(6) | 0.0138(6) | 0.0057(5) | 0.0016(5) | 0.0059(5) |
| N3 | 0.0108(6) | 0.0121(6) | 0.0118(6) | 0.0040(5) | 0.0017(4) | 0.0036(5) |
| N4 | 0.0099(6) | 0.0116(6) | 0.0163(6) | 0.0057(5) | -0.0003(5) | 0.0018(5) |
| N5 | 0.0119(6) | 0.0108(5) | 0.0132(6) | 0.0031(5) | 0.0011(5) | 0.0034(5) |
| N6 | 0.0136(6) | 0.0127(6) | 0.0130(6) | 0.0048(5) | 0.0018(5) | 0.0041(5) |
| N7 | 0.0139(6) | 0.0133(6) | 0.0148(6) | 0.0061(5) | 0.0016(5) | 0.0033(5) |
| N8 | 0.0129(6) | 0.0133(6) | 0.0128(6) | 0.0051(5) | 0.0023(5) | 0.0062(5) |
| N9 | 0.0138(6) | 0.0164(6) | 0.0170(6) | 0.0084(5) | 0.0039(5) | 0.0062(5) |
| N10 | 0.0129(6) | 0.0130(6) | 0.0146(6) | 0.0050(5) | 0.0020(5) | 0.0059(5) |
| N11 | 0.0121(6) | 0.0130(6) | 0.0129(6) | 0.0047(5) | 0.0006(5) | 0.0029(5) |
| N12 | 0.0117(6) | 0.0143(6) | 0.0141(6) | 0.0059(5) | 0.0010(5) | 0.0029(5) |
| N13 | 0.0116(6) | 0.0123(6) | 0.0113(6) | 0.0044(5) | 0.0023(4) | 0.0049(5) |
| N14 | 0.0139(6) | 0.0152(6) | 0.0170(6) | 0.0072(5) | 0.0056(5) | 0.0066(5) |
| N15 | 0.0130(6) | 0.0105(5) | 0.0140(6) | 0.0049(5) | 0.0023(5) | 0.0052(5) |
| N16 | 0.0142(6) | 0.0138(6) | 0.0123(6) | 0.0042(5) | 0.0023(5) | 0.0052(5) |
| N17 | 0.0161(6) | 0.0144(6) | 0.0150(6) | 0.0054(5) | 0.0030(5) | 0.0054(5) |
| N18 | 0.0118(6) | 0.0138(6) | 0.0122(6) | 0.0045(5) | 0.0024(5) | 0.0035(5) |
| N19 | 0.0121(6) | 0.0133(6) | 0.0189(6) | 0.0074(5) | 0.0015(5) | 0.0023(5) |
| N20 | 0.0120(6) | 0.0127(6) | 0.0135(6) | 0.0029(5) | 0.0010(5) | 0.0026(5) |
| O1 | 0.0143(5) | 0.0153(5) | 0.0250(6) | 0.0070(5) | 0.0033(4) | 0.0073(4) |
| O2 | 0.0229(6) | 0.0198(5) | 0.0144(5) | 0.0077(4) | -0.0005(4) | 0.0076(5) |
| O3 | 0.0217(6) | 0.0159(5) | 0.0133(5) | 0.0068(4) | 0.0021(4) | 0.0089(4) |
| O4 | 0.0213(6) | 0.0177(5) | 0.0139(5) | 0.0036(4) | 0.0059(4) | 0.0109(5) |
| O5 | 0.0124(5) | 0.0162(5) | 0.0254(6) | 0.0069(5) | 0.0033(4) | 0.0030(4) |
| O6 | 0.0212(6) | 0.0374(7) | 0.0143(5) | 0.0114(5) | 0.0031(5) | 0.0053(5) |
| O7 | 0.0167(5) | 0.0194(5) | 0.0138(5) | 0.0078(4) | 0.0055(4) | 0.0070(4) |
| O8 | 0.0135(5) | 0.0170(5) | 0.0156(5) | 0.0026(4) | -0.0020(4) | 0.0021(4) |
| O9 | 0.0121(5) | 0.0198(6) | 0.0263(6) | 0.0077(5) | 0.0032(4) | 0.0018(4) |
| O10 | 0.0215(6) | 0.0301(6) | 0.0149(5) | 0.0096(5) | 0.0052(4) | 0.0062(5) |
| O11 | 0.0166(5) | 0.0161(5) | 0.0132(5) | 0.0068(4) | 0.0054(4) | 0.0066(4) |
| O12 | 0.0144(5) | 0.0144(5) | 0.0137(5) | 0.0022(4) | -0.0015(4) | 0.0030(4) |
| O13 | 0.0176(6) | 0.0167(5) | 0.0295(6) | 0.0089(5) | 0.0060(5) | 0.0083(5) |
| O14 | 0.0226(6) | 0.0246(6) | 0.0168(5) | 0.0111(5) | 0.0021(4) | 0.0080(5) |
| O15 | 0.0213(6) | 0.0187(5) | 0.0155(5) | 0.0070(4) | 0.0012(4) | 0.0089(5) |
| O16 | 0.0185(6) | 0.0193(5) | 0.0144(5) | 0.0011(4) | 0.0045(4) | 0.0089(5) |
| O17 | 0.0263(7) | 0.0210(6) | 0.0360(7) | 0.0174(6) | 0.0144(6) | 0.0135(5) |
| O18 | 0.0154(5) | 0.0157(5) | 0.0189(6) | 0.0075(5) | -0.0016(4) | 0.0044(5) |
| O19 | 0.0237(6) | 0.0187(5) | 0.0148(6) | 0.0071(5) | 0.0061(5) | 0.0125(5) |
| O20 | 0.0152(6) | 0.0239(6) | 0.0123(5) | 0.0041(5) | 0.0035(5) | 0.0020(5) |
| O21 | 0.0178(6) | 0.0177(5) | 0.0164(6) | 0.0046(5) | -0.0024(5) | 0.0061(5) |
| O22 | 0.0198(6) | 0.0151(5) | 0.0286(6) | 0.0095(5) | 0.0068(5) | 0.0057(5) |
| O23 | 0.0197(6) | 0.0193(6) | 0.0157(6) | 0.0072(5) | 0.0053(4) | 0.0095(5) |

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| O24 | 0.0248(6) | 0.0143(5) | 0.0129(5) | 0.0033(4) | -0.0003(5) | 0.0071(5) |
| O25 | 0.0337(8) | 0.0233(6) | 0.0151(6) | 0.0066(5) | -0.0024(5) | -0.0089(6) |
| O26 | 0.0271(7) | 0.0337(7) | 0.0271(7) | 0.0185(6) | 0.0159(5) | 0.0194(6) |
| O27 | 0.0192(6) | 0.0213(6) | 0.0196(6) | -0.0010(5) | 0.0032(5) | 0.0074(5) |
| O28 | 0.0203(6) | 0.0171(6) | 0.0194(6) | 0.0032(5) | 0.0038(5) | 0.0067(5) |
| Sr1 | 0.01103(6) | 0.01069(6) | 0.00908(6) | 0.00391(5) | 0.00166(5) | 0.00457(5) |
| Sr2 | 0.01203(7) | 0.01247(6) | 0.00890(6) | 0.00421(5) | 0.00144(5) | 0.00368(5) |

Table S- 46: Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å$^2$) for **Sr(DNT)2·6H2O**.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H1 | 0.222(3) | 0.312(3) | 0.2591(18) | 0.077(10) |
| H2 | 0.338(3) | 0.299(2) | 0.2257(16) | 0.054(8) |
| H3 | 0.507(3) | 0.249(2) | 0.3452(15) | 0.056(7) |
| H4 | 0.522(3) | 0.145(2) | 0.3190(15) | 0.052(8) |
| H5 | 0.311(3) | -0.135(2) | 0.2411(15) | 0.047(7) |
| H6 | 0.286(2) | -0.1259(18) | 0.1635(14) | 0.038(6) |
| H7 | -0.123(2) | -0.0596(17) | 0.3403(13) | 0.027(5) |
| H8 | -0.162(3) | -0.114(2) | 0.2574(15) | 0.051(8) |
| H9 | -0.137(3) | 0.088(2) | 0.2458(15) | 0.050(8) |
| H10 | -0.103(3) | 0.1027(19) | 0.1731(15) | 0.044(7) |
| H11 | 0.960(3) | 0.771(2) | 0.2770(16) | 0.064(8) |
| H12 | 1.060(3) | 0.740(2) | 0.2191(16) | 0.060(8) |
| H13 | 1.171(3) | 0.500(2) | 0.2284(15) | 0.055(8) |
| H14 | 1.175(3) | 0.544(2) | 0.1612(16) | 0.061(8) |
| H15 | 1.056(2) | 0.3949(18) | 0.3391(14) | 0.034(6) |
| H16 | 0.974(2) | 0.298(2) | 0.2704(13) | 0.035(6) |
| H17 | 0.600(3) | 0.256(2) | 0.2277(15) | 0.055(8) |
| H18 | 0.588(3) | 0.253(2) | 0.1508(15) | 0.046(7) |
| H19 | 0.614(3) | 0.589(2) | 0.3099(16) | 0.056(8) |
| H20 | 0.663(3) | 0.646(2) | 0.2581(16) | 0.066(8) |
| H21 | 0.623(2) | 0.7144(19) | 0.1593(14) | 0.032(6) |
| H22 | 0.559(3) | 0.762(2) | 0.2243(15) | 0.051(7) |
| H23 | 0.321(3) | 0.713(2) | 0.2793(13) | 0.035(6) |
| H24 | 0.379(3) | 0.813(2) | 0.3393(15) | 0.047(7) |

## 2.8 Crystal Structure Report for $Ba(DNT)_2 \cdot 11H_2O$

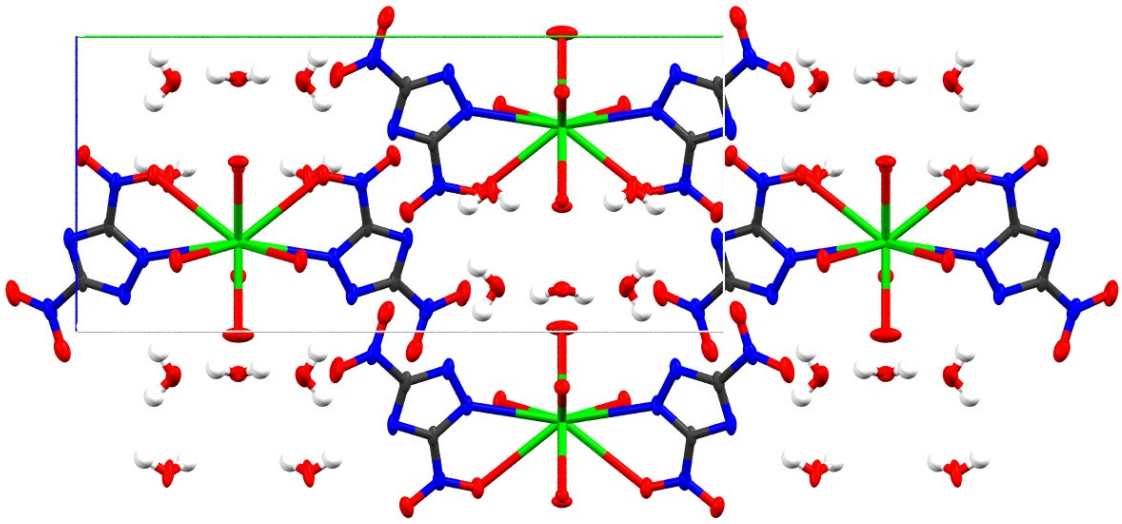

Figure S- 22: Projection of the packing of $Ba(DNT)_2 \cdot 11H_2O$ down the a axis.

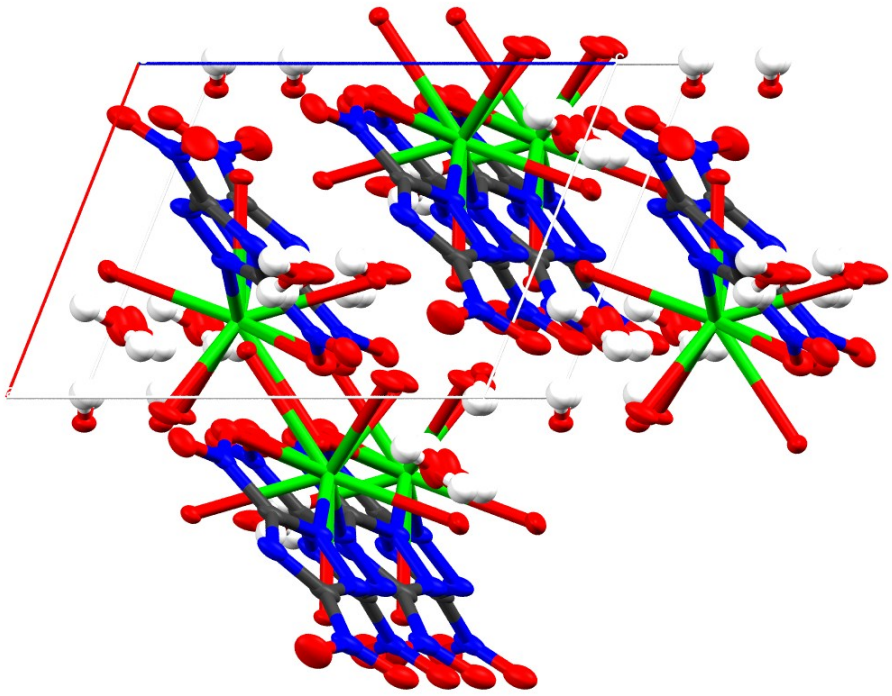

Figure S- 23: Projection of the packing of $Ba(DNT)_2 \cdot 11H_2O$ approximately down the b axis.

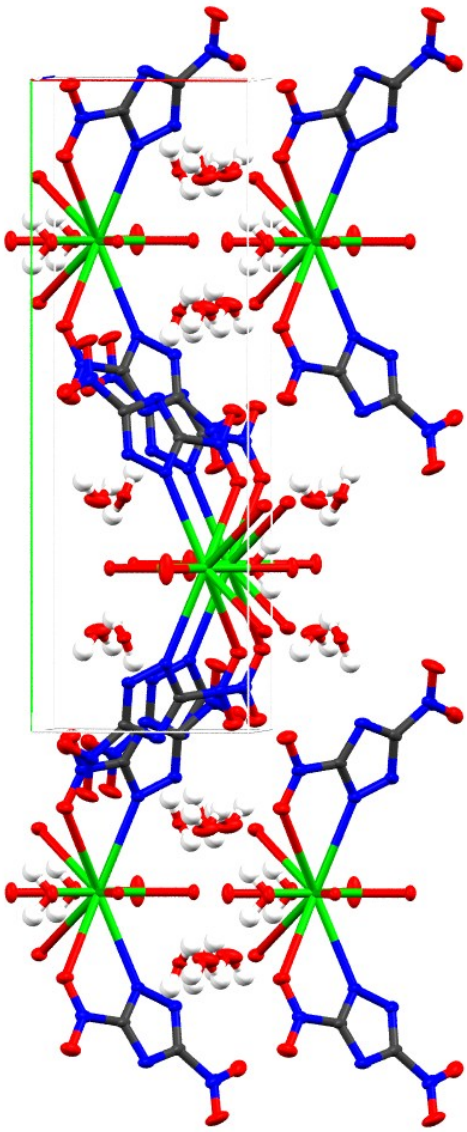

Figure S- 24: Projection of the packing of $Ba(DNT)_2 \cdot 11H_2O$ approximately down the c axis.

Table S- 47: Sample and crystal data for **Ba(DNT)2·11H2O**.

| | | |
|---|---|---|
| Identification code | MK16 | |
| Chemical formula | $C_4H_{22}BaN_{10}O_{19}$ | |
| Formula weight | 651.65 g/mol | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.092 x 0.123 x 0.149 mm | |
| Crystal system | monoclinic | |
| Space group | P 1 21/m 1 | |
| Unit cell dimensions | a = 6.9239(6) Å | α = 90° |
| | b = 18.7743(15) Å | β = 111.6350(10)° |
| | c = 9.2088(7) Å | γ = 90° |
| Volume | 1112.73(16) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.945 $g/cm^3$ | |
| Absorption coefficient | 1.891 $mm^{-1}$ | |
| F(000) | 648 | |

Table S- 48: Data collection and structure refinement for **Ba(DNT)2·11H2O**.

| | | |
|---|---|---|
| Theta range for data collection | 2.17 to 30.61° | |
| Index ranges | -9<=h<=9, -26<=k<=26, -13<=l<=13 | |
| Reflections collected | 26945 | |
| Independent reflections | 3476 [R(int) = 0.0424] | |
| Max. and min. transmission | 0.8450 and 0.7660 | |
| Structure solution technique | direct methods | |
| Structure solution program | SHELXTL XS 2013/1 (Bruker AXS) | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Refinement program | SHELXL-2014 (Sheldrick, 2014) | |
| Function minimized | $\Sigma\, w(F_o^2 - F_c^2)^2$ | |
| Data / restraints / parameters | 3476 / 7 / 178 | |
| Goodness-of-fit on $F^2$ | 1.204 | |
| Final R indices | 3214 data; I>2σ(I) | R1 = 0.0370, wR2 = 0.0831 |
| | all data | R1 = 0.0423, wR2 = 0.0846 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+6.3309P]$ where $P=(F_o^2+2F_c^2)/3$ | |
| Absolute structure parameter | 0.0(0) | |
| Largest diff. peak and hole | 1.396 and -3.222 $eÅ^{-3}$ | |
| R.M.S. deviation from mean | 0.146 $eÅ^{-3}$ | |

Table S- 49: Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for **Ba(DNT)2·11H2O**.

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| Ba01 | 0.23120(4) | 0.25 | 0.69872(3) | 0.01015(7) |
| C1 | 0.3504(6) | 0.44944(19) | 0.6451(5) | 0.0208(8) |
| C2 | 0.5841(6) | 0.4917(2) | 0.8279(5) | 0.0238(8) |
| N1 | 0.4088(5) | 0.39700(17) | 0.7498(4) | 0.0224(7) |
| N2 | 0.5658(5) | 0.42573(17) | 0.8733(4) | 0.0240(7) |
| N3 | 0.4546(5) | 0.51085(17) | 0.6860(5) | 0.0245(7) |
| N4 | 0.1845(5) | 0.43961(17) | 0.4955(4) | 0.0230(7) |
| N5 | 0.7383(6) | 0.54084(19) | 0.9272(5) | 0.0289(8) |
| O1 | 0.1348(5) | 0.48993(16) | 0.4044(4) | 0.0295(7) |
| O2 | 0.1022(5) | 0.38058(15) | 0.4694(4) | 0.0271(6) |
| O3 | 0.7603(6) | 0.59755(17) | 0.8700(5) | 0.0413(9) |
| O4 | 0.8370(5) | 0.52184(17) | 0.0632(4) | 0.0330(7) |
| O5 | 0.8596(6) | 0.25 | 0.4243(4) | 0.0230(8) |
| O6 | 0.9520(4) | 0.34633(15) | 0.7605(4) | 0.0273(6) |
| O7 | 0.3775(7) | 0.25 | 0.0118(5) | 0.0431(14) |
| O8 | 0.6591(5) | 0.25 | 0.8119(5) | 0.0196(7) |
| O9 | 0.3507(5) | 0.25 | 0.4439(4) | 0.0160(7) |
| O10 | 0.0768(6) | 0.25 | 0.1436(5) | 0.0227(8) |
| O11 | 0.6300(5) | 0.35821(16) | 0.4813(5) | 0.0354(8) |
| O12 | 0.7864(7) | 0.14983(17) | 0.1522(4) | 0.0387(8) |

Table S- 48: Bond lengths (Å) for **Ba(DNT)2·11H2O**.

| | | | |
|---|---|---|---|
| Ba01-O7 | 2.681(5) | Ba01-O8 | 2.755(4) |
| Ba01-O9 | 2.761(4) | Ba01-O6 | 2.853(3) |
| Ba01-O6 | 2.853(3) | Ba01-O5 | 2.865(4) |
| Ba01-N1 | 2.987(3) | Ba01-N1 | 2.987(3) |
| Ba01-O2 | 3.143(3) | Ba01-O2 | 3.143(3) |
| C1-N1 | 1.332(5) | C1-N3 | 1.338(5) |
| C1-N4 | 1.444(5) | C2-N2 | 1.329(5) |
| C2-N3 | 1.333(6) | C2-N5 | 1.451(5) |
| N1-N2 | 1.361(5) | N4-O1 | 1.225(4) |
| N4-O2 | 1.229(4) | N5-O3 | 1.222(5) |
| N5-O4 | 1.238(5) | | |

Table S- 49: Bond angles (°) for **Ba(DNT)2·11H2O**.

| | | | |
|---|---|---|---|
| O7-Ba01-O8 | 70.49(12) | O7-Ba01-O9 | 143.26(12) |
| O8-Ba01-O9 | 72.77(11) | O7-Ba01-O6 | 78.51(10) |
| O8-Ba01-O6 | 129.63(8) | O9-Ba01-O6 | 127.35(8) |
| O7-Ba01-O6 | 78.51(10) | O8-Ba01-O6 | 129.63(8) |
| O9-Ba01-O6 | 127.35(8) | O6-Ba01-O6 | 78.68(11) |
| O7-Ba01-O5 | 143.99(12) | O8-Ba01-O5 | 145.52(11) |
| O9-Ba01-O5 | 72.75(11) | O6-Ba01-O5 | 73.85(9) |
| O6-Ba01-O5 | 73.85(9) | O7-Ba01-N1 | 81.96(8) |
| O8-Ba01-N1 | 67.52(6) | O9-Ba01-N1 | 84.20(7) |
| O6-Ba01-N1 | 69.68(8) | O6-Ba01-N1 | 145.48(9) |
| O5-Ba01-N1 | 108.82(7) | O7-Ba01-N1 | 81.96(8) |
| O8-Ba01-N1 | 67.52(6) | O9-Ba01-N1 | 84.20(7) |
| O6-Ba01-N1 | 145.48(9) | O6-Ba01-N1 | 69.68(8) |
| O5-Ba01-N1 | 108.82(7) | N1-Ba01-N1 | 135.00(12) |
| O7-Ba01-O2 | 128.60(6) | O8-Ba01-O2 | 104.70(7) |
| O9-Ba01-O2 | 61.89(6) | O6-Ba01-O2 | 66.03(8) |
| O6-Ba01-O2 | 125.64(8) | O5-Ba01-O2 | 57.79(6) |
| N1-Ba01-O2 | 51.96(9) | N1-Ba01-O2 | 145.60(9) |
| O7-Ba01-O2 | 128.60(6) | O8-Ba01-O2 | 104.70(7) |
| O9-Ba01-O2 | 61.89(7) | O6-Ba01-O2 | 125.64(8) |
| O6-Ba01-O2 | 66.03(8) | O5-Ba01-O2 | 57.79(6) |
| N1-Ba01-O2 | 145.60(9) | N1-Ba01-O2 | 51.95(9) |
| O2-Ba01-O2 | 102.53(11) | N1-C1-N3 | 116.4(4) |
| N1-C1-N4 | 121.2(3) | N3-C1-N4 | 122.3(4) |
| N2-C2-N3 | 116.9(4) | N2-C2-N5 | 121.8(4) |
| N3-C2-N5 | 121.3(4) | C1-N1-N2 | 104.3(3) |
| C1-N1-Ba01 | 124.8(3) | N2-N1-Ba01 | 130.8(2) |
| C2-N2-N1 | 104.3(3) | C2-N3-C1 | 98.1(3) |
| O1-N4-O2 | 124.7(4) | O1-N4-C1 | 118.6(3) |
| O2-N4-C1 | 116.8(3) | O3-N5-O4 | 125.2(4) |
| O3-N5-C2 | 117.5(4) | O4-N5-C2 | 117.3(4) |
| N4-O2-Ba01 | 125.2(3) | | |

Table S- 50 : Anisotropic atomic displacement parameters (Å$^2$) for **Ba(DNT)2·11H2O**.The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Ba01 | 0.00940(12) | 0.00877(11) | 0.01259(12) | 0 | 0.00442(9) | 0 |
| C1 | 0.0184(17) | 0.0110(15) | 0.040(2) | -0.0017(15) | 0.0186(16) | -0.0003(13) |
| C2 | 0.0195(17) | 0.0134(16) | 0.046(2) | -0.0050(16) | 0.0206(17) | -0.0027(13) |
| N1 | 0.0167(14) | 0.0141(14) | 0.0384(19) | 0.0002(13) | 0.0126(14) | 0.0001(11) |
| N2 | 0.0174(15) | 0.0141(14) | 0.043(2) | -0.0034(14) | 0.0138(14) | -0.0003(12) |
| N3 | 0.0244(16) | 0.0121(14) | 0.046(2) | -0.0017(14) | 0.0234(16) | -0.0011(12) |
| N4 | 0.0231(16) | 0.0158(14) | 0.0384(19) | 0.0011(13) | 0.0212(15) | 0.0025(12) |
| N5 | 0.0234(17) | 0.0198(16) | 0.052(2) | -0.0109(16) | 0.0238(17) | -0.0047(13) |
| O1 | 0.0364(17) | 0.0188(14) | 0.0415(18) | 0.0066(13) | 0.0239(14) | 0.0040(12) |
| O2 | 0.0267(14) | 0.0162(13) | 0.0413(17) | 0.0014(12) | 0.0161(13) | -0.0017(11) |
| O3 | 0.048(2) | 0.0204(15) | 0.063(2) | -0.0093(15) | 0.0290(19) | -0.0164(14) |
| O4 | 0.0247(15) | 0.0259(15) | 0.052(2) | -0.0111(15) | 0.0185(15) | -0.0031(12) |
| O5 | 0.0143(17) | 0.039(2) | 0.0153(18) | 0 | 0.0046(14) | 0 |
| O6 | 0.0216(14) | 0.0170(13) | 0.0505(19) | -0.0040(13) | 0.0216(13) | -0.0005(11) |
| O7 | 0.021(2) | 0.090(4) | 0.021(2) | 0 | 0.0113(18) | 0 |
| O8 | 0.0119(16) | 0.0229(19) | 0.0240(19) | 0 | 0.0064(14) | 0 |
| O9 | 0.0138(16) | 0.0165(16) | 0.0195(18) | 0 | 0.0084(14) | 0 |
| O10 | 0.0143(18) | 0.030(2) | 0.023(2) | 0 | 0.0055(15) | 0 |
| O11 | 0.0188(14) | 0.0141(14) | 0.070(2) | 0.0082(15) | 0.0126(15) | 0.0019(11) |
| O12 | 0.065(3) | 0.0220(15) | 0.042(2) | -0.0056(14) | 0.0345(19) | -0.0071(16) |

Table S- 51 : Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å$^2$) for **Ba(DNT)2·11H2O**.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H1 | -0.009(6) | 0.284(2) | 0.126(6) | 0.04 |
| H2 | 0.686(8) | 0.330(2) | 0.441(6) | 0.04 |
| H3 | 0.591(8) | 0.3951(17) | 0.430(5) | 0.04 |
| H4 | 0.728(8) | 0.127(2) | 0.069(3) | 0.04 |
| H5 | 0.847(8) | 0.120(2) | 0.220(4) | 0.04 |

## 2.9 Crystal structure report for [Ag(NH$_3$)][DNT]

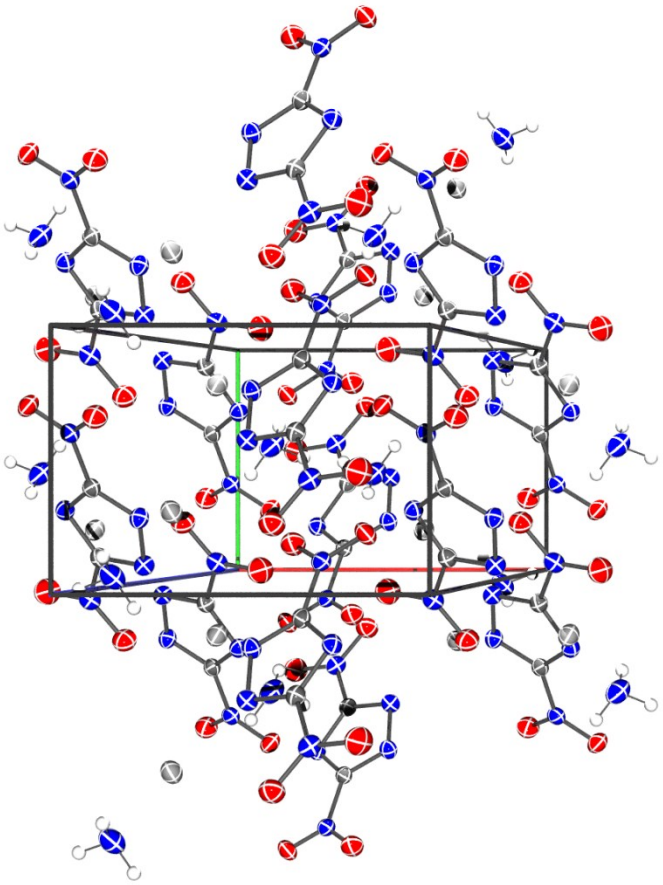

Figure S- 25: Projection of the packing of **[Ag(NH$_3$)][DNT]** normal to the 001 plane.

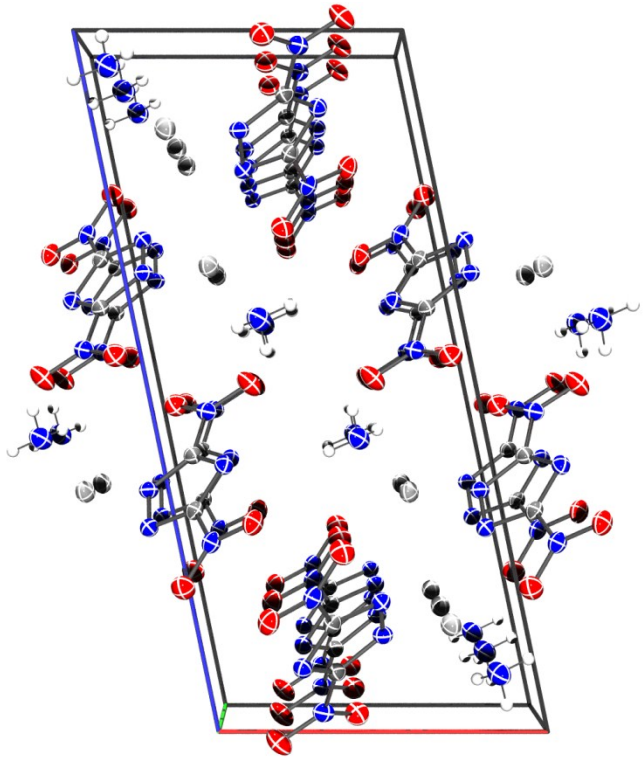

Figure S- 26 : Projection of the packing of **[Ag(NH$_3$)][DNT]** perpendicular to the 010 plane.

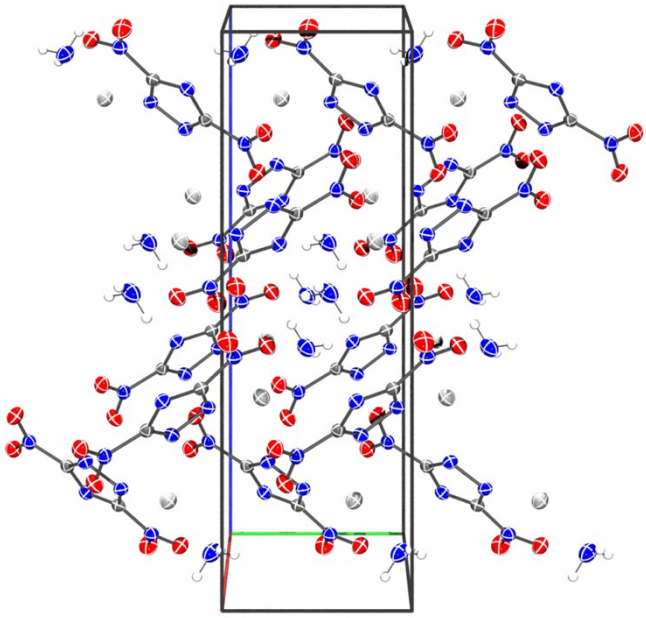

Figure S- 27 Projection of the packing of **[Ag(NH$_3$)][DNT]** perpendicular to the 100 plane.

Table S- 52: Sample and crystal data for **[Ag(NH$_3$)][DNT]**.

| | | |
|---|---|---|
| Identification code | AgDNT_NH3 | |
| Chemical formula | $C_2H_3AgN_6O_4$ | |
| Formula weight | 282.97 | |
| Temperature | 140(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.130 x 0.150 x 0.490 mm | |
| Crystal habit | clear orange prism | |
| Crystal system | monoclinic | |
| Space group | P 1 21/n 1 | |
| Unit cell dimensions | a = 7.8061(19) Å | α = 90° |
| | b = 5.5756(14) Å | β = 101.686(3)° |
| | c = 17.034(4) Å | γ = 90° |
| Volume | 726.0(3) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 2.589 g/cm$^3$ | |
| Absorption coefficient | 2.773 mm$^{-1}$ | |
| F(000) | 544 | |

Table S- 53: Data collection and structure refinement for **[Ag(NH$_3$)][DNT]**.

| | |
|---|---|
| Diffractometer | Bruker SMART APEX |
| Radiation source | fine-focus tube, MoKα |
| Theta range for data collection | 2.44 to 28.45° |
| Index ranges | -9<=h<=10, -7<=k<=6, -22<=l<=15 |
| Reflections collected | 4279 |
| Independent reflections | 1688 [R(int) = 0.0176] |
| Coverage of independent reflections | 91.8% |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.7140 and 0.3440 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXTL XT 2013/6 (Sheldrick, 2013) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXTL XLMP 2014/1 (Bruker AXS, 2013) |
| Function minimized | $\Sigma\, w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 1688 / 6 / 130 |
| Goodness-of-fit on $F^2$ | 1.084 |
| $\Delta/\sigma_{max}$ | 0.001 |
| Final R indices | 1604 data; I>2σ(I) R1 = 0.0185, wR2 = 0.0476 |
| | all data R1 = 0.0195, wR2 = 0.0482 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0245P)^2+0.4039P]$ where $P=(F_o^2+2F_c^2)/3$ |
| Largest diff. peak and hole | 0.440 and -0.623 eÅ$^{-3}$ |
| R.M.S. deviation from mean | 0.080 eÅ$^{-3}$ |

Table S- 54: Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for **[Ag(NH$_3$)][DNT].**

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| Ag1 | 0.73308(2) | 0.20046(3) | 0.33930(2) | 0.02589(7) |
| C1 | 0.0985(2) | 0.8952(4) | 0.39461(11) | 0.0194(3) |
| C2 | 0.0798(2) | 0.6116(3) | 0.32104(11) | 0.0188(3) |
| N1 | 0.9302(2) | 0.7305(3) | 0.29534(10) | 0.0206(3) |
| N2 | 0.9431(2) | 0.9230(3) | 0.34517(9) | 0.0203(3) |
| N3 | 0.1911(2) | 0.7033(3) | 0.38311(10) | 0.0209(3) |
| N4 | 0.1167(2) | 0.3945(3) | 0.28107(10) | 0.0217(3) |
| N5 | 0.1632(2) | 0.0719(3) | 0.45611(10) | 0.0236(3) |
| N6 | 0.6132(3) | 0.4410(4) | 0.41510(12) | 0.0325(4) |
| O1 | 0.2513(2) | 0.2850(3) | 0.30964(10) | 0.0275(3) |
| O2 | 0.0111(2) | 0.3318(3) | 0.22105(10) | 0.0303(3) |
| O3 | 0.3108(2) | 0.0437(3) | 0.49593(10) | 0.0366(4) |
| O4 | 0.0667(2) | 0.2395(3) | 0.46443(10) | 0.0300(3) |

Table S- 55: Bond lengths (Å) for **[Ag(NH$_3$)][DNT]**.

| | | | |
|---|---|---|---|
| Ag1-N6 | 2.198(2) | Ag1-N2 | 2.2415(16) |
| Ag1-N1 | 2.3934(18) | C1-N3 | 1.328(3) |
| C1-N2 | 1.338(2) | C1-N5 | 1.453(2) |
| C2-N3 | 1.327(2) | C2-N1 | 1.337(2) |
| C2-N4 | 1.446(3) | N1-N2 | 1.360(2) |
| N1-Ag1 | 2.3934(18) | N4-O1 | 1.227(2) |
| N4-O2 | 1.227(2) | N5-O3 | 1.223(2) |
| N5-O4 | 1.226(2) | N6-H1 | 0.84(2) |
| N6-H2 | 0.83(2) | N6-H3 | 0.84(2) |

Table S- 56: Bond angles (°) for **[Ag($NH_3$)][DNT]**.

| | | | |
|---|---|---|---|
| N6-Ag1-N2 | 142.14(7) | N6-Ag1-N1 | 108.21(7) |
| N2-Ag1-N1 | 109.51(6) | N3-C1-N2 | 116.87(17) |
| N3-C1-N5 | 122.19(16) | N2-C1-N5 | 120.92(17) |
| N3-C2-N1 | 117.20(17) | N3-C2-N4 | 122.46(16) |
| N1-C2-N4 | 120.34(16) | C2-N1-N2 | 103.77(15) |
| C2-N1-Ag1 | 122.65(13) | N2-N1-Ag1 | 127.68(12) |
| C1-N2-N1 | 104.14(15) | C1-N2-Ag1 | 132.05(13) |
| N1-N2-Ag1 | 123.79(12) | C2-N3-C1 | 98.03(16) |
| O1-N4-O2 | 124.42(17) | O1-N4-C2 | 117.77(16) |
| O2-N4-C2 | 117.81(16) | O3-N5-O4 | 124.47(18) |
| O3-N5-C1 | 117.62(17) | O4-N5-C1 | 117.91(16) |
| Ag1-N6-H1 | 117.(2) | Ag1-N6-H2 | 108.(3) |
| H1-N6-H2 | 109.(2) | Ag1-N6-H3 | 105.(3) |
| H1-N6-H3 | 110.(2) | H2-N6-H3 | 109.(2) |

Table S- 57: Anisotropic atomic displacement parameters (Å$^2$) for **[Ag(NH$_3$)][DNT]**.The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Ag1 | 0.02276(10) | 0.02645(11) | 0.02796(11) | -0.00232(5) | 0.00395(7) | 0.00261(5) |
| C1 | 0.0195(8) | 0.0210(9) | 0.0177(8) | 0.0014(7) | 0.0038(6) | -0.0010(7) |
| C2 | 0.0187(8) | 0.0192(9) | 0.0198(8) | 0.0015(7) | 0.0067(6) | -0.0003(7) |
| N1 | 0.0198(8) | 0.0228(8) | 0.0197(8) | -0.0018(6) | 0.0047(6) | 0.0010(6) |
| N2 | 0.0219(7) | 0.0217(8) | 0.0172(7) | -0.0006(6) | 0.0036(6) | 0.0011(6) |
| N3 | 0.0192(8) | 0.0219(8) | 0.0216(8) | 0.0032(6) | 0.0040(6) | 0.0010(6) |
| N4 | 0.0217(7) | 0.0192(8) | 0.0260(8) | 0.0012(6) | 0.0089(6) | -0.0014(6) |
| N5 | 0.0255(8) | 0.0236(8) | 0.0208(8) | 0.0006(6) | 0.0031(6) | -0.0027(7) |
| N6 | 0.0314(9) | 0.0322(10) | 0.0319(10) | -0.0053(8) | 0.0019(8) | 0.0080(8) |
| O1 | 0.0251(7) | 0.0251(8) | 0.0338(8) | 0.0023(6) | 0.0098(6) | 0.0071(6) |
| O2 | 0.0301(8) | 0.0283(8) | 0.0313(8) | -0.0077(6) | 0.0036(6) | -0.0007(6) |
| O3 | 0.0309(8) | 0.0373(9) | 0.0354(8) | -0.0047(7) | -0.0081(6) | -0.0015(7) |
| O4 | 0.0323(8) | 0.0274(8) | 0.0301(8) | -0.0047(6) | 0.0056(6) | 0.0006(6) |

Table S- 58: Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å$^2$) for **[Ag(NH$_3$)][DNT]**.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H1 | 0.513(3) | 1.491(6) | 0.3959(18) | 0.061(10) |
| H2 | 0.679(4) | 1.558(5) | 0.427(2) | 0.076(12) |
| H3 | 0.612(5) | 1.362(7) | 0.4566(18) | 0.104(17) |

# 2.10 Crystal Structure Report for $[NH_4][DNT]$

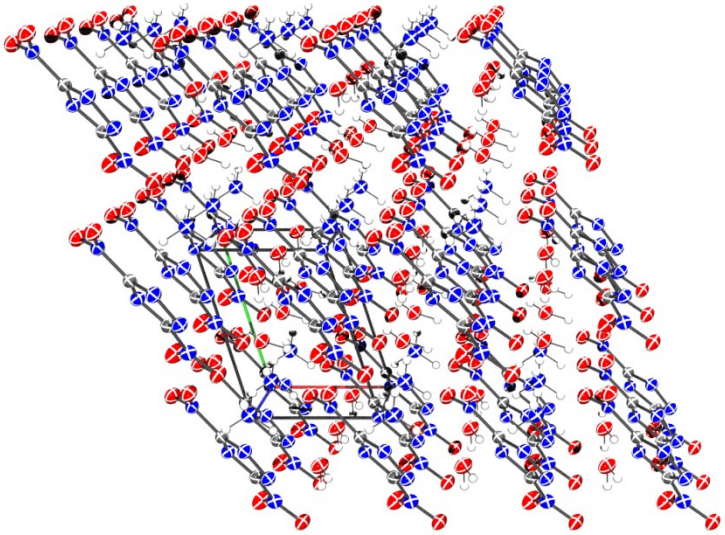

Figure S- 28 : Projection of the packing of **[NH4][DNT]** perpendicular to the 001 plane.

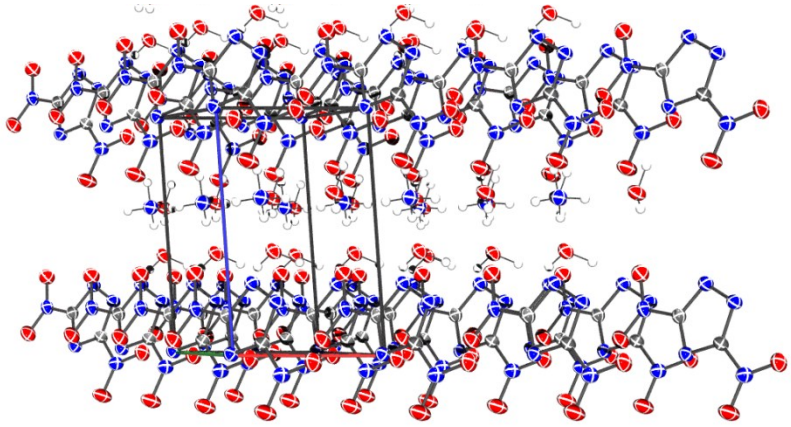

Figure S- 29 : Projection of the packing of **[NH4][DNT]** perpendicular to the 010 plane.

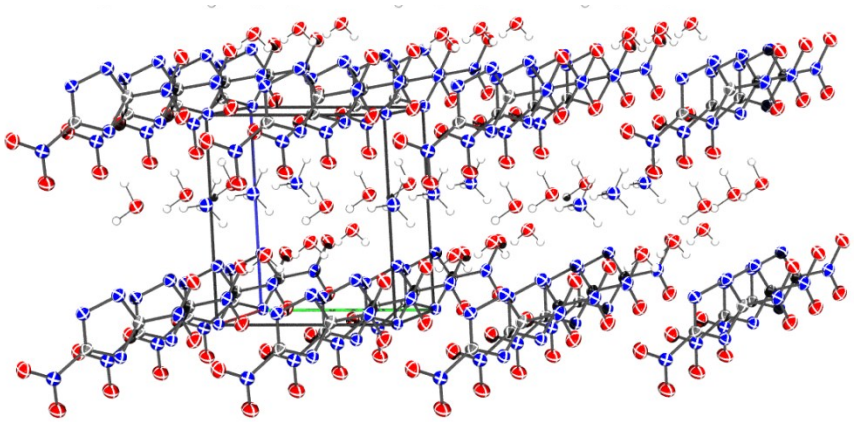

Figure S- 30 : Projection of the packing of **[NH4][DNT]** perpendicular to the 100 plane.

Table S- 59: Sample and crystal data for **[NH4][DNT]**.

| | | |
|---|---|---|
| Identification code | NH4DNT | |
| Chemical formula | $C_2H_8N_6O_6$ | |
| Formula weight | 212.14 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.080 x 0.230 x 0.290 mm | |
| Crystal habit | clear orange plate | |
| Crystal system | triclinic | |
| Space group | P 1 | |
| Unit cell dimensions | a = 4.653(3) Å | α = 93.105(7)° |
| | b = 6.461(4) Å | β = 93.948(7)° |
| | c = 7.619(4) Å | γ = 108.360(7)° |
| Volume | 216.2(2) $Å^3$ | |
| Z | 1 | |
| Density (calculated) | 1.630 $g/cm^3$ | |
| Absorption coefficient | 0.158 $mm^{-1}$ | |
| F(000) | 110 | |

Table S- 60: Data collection and structure refinement for **[NH4][DNT]**.

| | |
|---|---|
| Diffractometer | Bruker SMART APEX |
| Radiation source | fine-focus tube, MoKα |
| Theta range for data collection | 2.69 to 28.49° |
| Index ranges | -6<=h<=5, -8<=k<=8, -9<=l<=9 |
| Reflections collected | 2547 |
| Independent reflections | 1599 [R(int) = 0.0122] |
| Coverage of independent reflections | 91.7% |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.9880 and 0.9560 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXTL XT 2013/6 (Sheldrick, 2013) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXTL XLMP 2014/1 (Bruker AXS, 2013) |
| Function minimized | $\Sigma\, w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 1599 / 3 / 159 |
| Goodness-of-fit on $F^2$ | 1.075 |
| Final R indices | 1510 data; I>2σ(I) R1 = 0.0264, wR2 = 0.0610 |
| | all data R1 = 0.0291, wR2 = 0.0627 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0323P)^2+0.0243P]$ where $P=(F_o^2+2F_c^2)/3$ |
| Absolute structure parameter | -1.0(7) |
| Largest diff. peak and hole | 0.182 and -0.155 eÅ$^{-3}$ |
| R.M.S. deviation from mean | 0.037 eÅ$^{-3}$ |

Table S- 61: Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for **[NH4][DNT]**.U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| C1 | 0.0235(5) | 0.1202(4) | 0.1594(3) | 0.0218(5) |
| C2 | 0.1479(5) | 0.8759(4) | 0.0501(3) | 0.0223(5) |
| N1 | 0.2711(4) | 0.9042(3) | 0.2164(3) | 0.0245(4) |
| N2 | 0.1871(5) | 0.0687(3) | 0.2909(3) | 0.0250(4) |
| N3 | 0.9884(5) | 0.0060(3) | 0.0048(3) | 0.0228(4) |
| N4 | 0.8892(4) | 0.2930(3) | 0.1865(3) | 0.0249(4) |
| N5 | 0.1904(4) | 0.7128(3) | 0.9260(3) | 0.0267(5) |
| N6 | 0.3952(5) | 0.3379(3) | 0.6457(3) | 0.0273(5) |
| O1 | 0.7380(4) | 0.3287(3) | 0.0606(2) | 0.0329(4) |
| O2 | 0.9359(4) | 0.3919(3) | 0.3327(2) | 0.0322(4) |
| O3 | 0.0579(5) | 0.6860(3) | 0.7775(2) | 0.0390(5) |
| O4 | 0.3569(4) | 0.6097(3) | 0.9779(2) | 0.0322(4) |
| O5 | 0.6036(4) | 0.6935(3) | 0.4284(2) | 0.0282(4) |
| O6 | 0.7718(4) | 0.0695(3) | 0.6591(2) | 0.0300(4) |

Table S- 62: Bond lengths (Å) for **[NH4][DNT]**.

| | | | |
|---|---|---|---|
| C1-N3 | 1.327(3) | C1-N2 | 1.336(3) |
| C1-N4 | 1.453(3) | C2-N3 | 1.329(3) |
| C2-N1 | 1.333(3) | C2-N5 | 1.446(3) |
| N1-N2 | 1.353(3) | N4-O2 | 1.224(3) |
| N4-O1 | 1.226(3) | N5-O3 | 1.227(3) |
| N5-O4 | 1.230(3) | N6-H1 | 0.94(4) |
| N6-H2 | 0.95(3) | N6-H3 | 0.91(3) |
| N6-H4 | 0.92(3) | O5-H5 | 0.78(4) |
| O5-H6 | 0.94(5) | O6-H7 | 0.87(3) |
| O6-H8 | 0.92(5) | | |

Table S- 63: Bond angles (°) for **[NH4][DNT]**.

| | | | |
|---|---|---|---|
| N3-C1-N2 | 117.1(2) | N3-C1-N4 | 122.0(2) |
| N2-C1-N4 | 120.9(2) | N3-C2-N1 | 116.6(2) |
| N3-C2-N5 | 122.2(2) | N1-C2-N5 | 121.13(19) |
| C2-N1-N2 | 104.54(19) | C1-N2-N1 | 103.7(2) |
| C1-N3-C2 | 98.0(2) | O2-N4-O1 | 125.0(2) |
| O2-N4-C1 | 117.77(18) | O1-N4-C1 | 117.2(2) |
| O3-N5-O4 | 124.6(2) | O3-N5-C2 | 118.2(2) |
| O4-N5-C2 | 117.23(19) | H1-N6-H2 | 112.(3) |
| H1-N6-H3 | 107.(3) | H2-N6-H3 | 111.(3) |
| H1-N6-H4 | 113.(3) | H2-N6-H4 | 104.(3) |
| H3-N6-H4 | 111.(3) | H5-O5-H6 | 118.(4) |
| H7-O6-H8 | 103.(3) | | |

Table S- 64: Anisotropic atomic displacement parameters (Å$^2$) for **[NH4][DNT]**.The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0211(10) | 0.0207(10) | 0.0238(13) | 0.0033(9) | 0.0012(9) | 0.0071(8) |
| C2 | 0.0235(12) | 0.0227(9) | 0.0206(11) | 0.0029(8) | -0.0004(9) | 0.0078(8) |
| N1 | 0.0281(11) | 0.0256(9) | 0.0215(10) | 0.0015(8) | -0.0005(8) | 0.0117(8) |
| N2 | 0.0275(10) | 0.0271(10) | 0.0227(11) | 0.0028(8) | 0.0012(8) | 0.0123(8) |
| N3 | 0.0242(9) | 0.0218(9) | 0.0229(11) | 0.0011(8) | 0.0002(8) | 0.0087(7) |
| N4 | 0.0229(10) | 0.0250(9) | 0.0286(12) | 0.0055(9) | 0.0009(8) | 0.0100(8) |
| N5 | 0.0298(11) | 0.0264(9) | 0.0242(12) | 0.0012(8) | 0.0020(9) | 0.0094(9) |
| N6 | 0.0304(12) | 0.0270(10) | 0.0261(12) | 0.0015(9) | 0.0017(9) | 0.0120(9) |
| O1 | 0.0342(10) | 0.0344(9) | 0.0340(11) | 0.0071(8) | -0.0020(8) | 0.0171(8) |
| O2 | 0.0368(10) | 0.0304(8) | 0.0311(11) | -0.0053(8) | -0.0012(8) | 0.0154(7) |
| O3 | 0.0531(12) | 0.0433(11) | 0.0252(11) | -0.0051(8) | -0.0088(9) | 0.0257(9) |
| O4 | 0.0338(10) | 0.0335(9) | 0.0344(11) | 0.0012(8) | -0.0008(8) | 0.0192(8) |
| O5 | 0.0294(10) | 0.0307(9) | 0.0270(10) | 0.0061(7) | -0.0016(8) | 0.0136(7) |
| O6 | 0.0380(10) | 0.0300(9) | 0.0244(10) | 0.0018(7) | -0.0043(8) | 0.0161(7) |

Table S- 65: Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å$^2$) for **[NH4][DNT]**.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H1 | 0.524(8) | 0.252(6) | 0.639(5) | 0.049(10) |
| H2 | 0.411(6) | 0.408(5) | 0.761(4) | 0.031(8) |
| H3 | 0.448(7) | 0.438(5) | 0.565(4) | 0.042(8) |
| H4 | 0.194(8) | 0.256(5) | 0.627(4) | 0.040(8) |
| H5 | 0.507(9) | 0.741(6) | 0.364(5) | 0.049(11) |
| H6 | 0.755(11) | 0.644(7) | 0.382(6) | 0.079(14) |
| H7 | 0.722(7) | -0.052(5) | 0.592(4) | 0.030(8) |
| H8 | 0.824(10) | 0.028(7) | 0.767(6) | 0.081(14) |

## 2.11 Crystal Structure Report for $[C(NH_2)_3][DNT]$

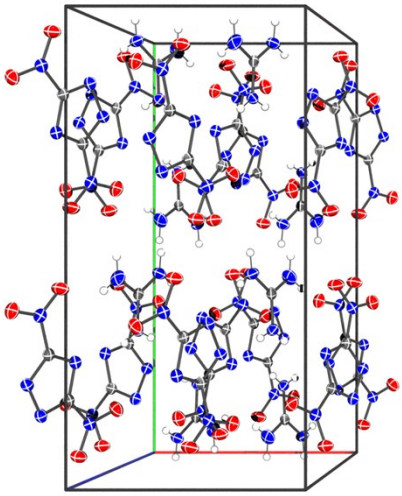

Figure S- 31: Projection of the packing of **[C(NH2)3][DNT]** perpendicular to the 001 plane.

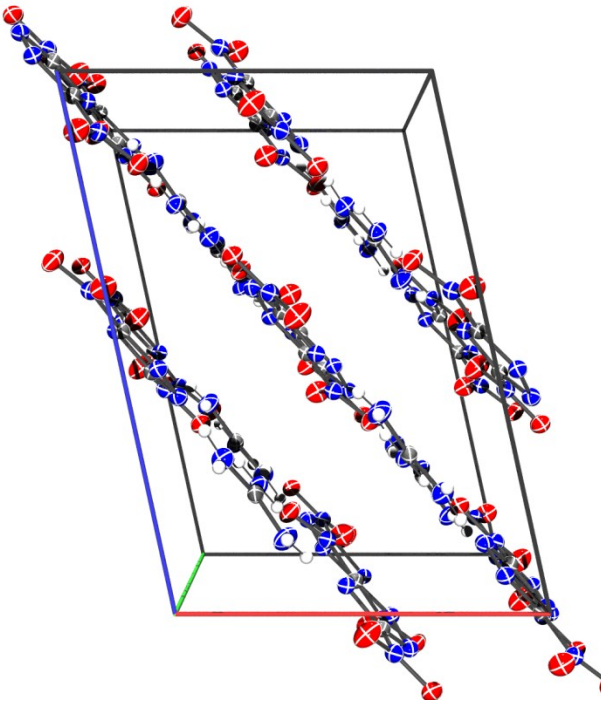

Figure S- 32 : Projection of the packing of **[C(NH2)3][DNT]** perpendicular to the 010 plane.

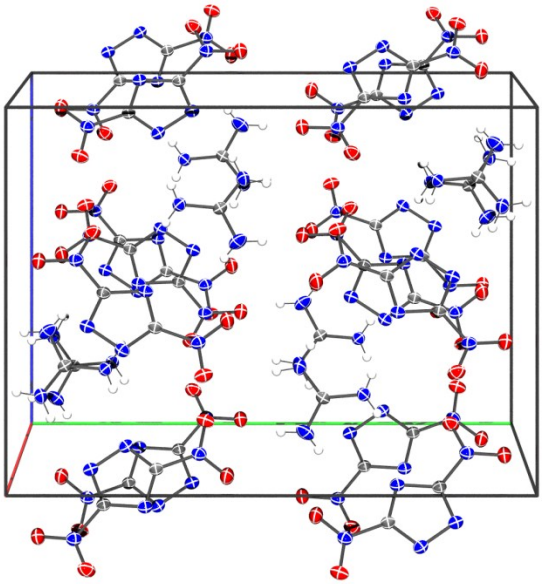

Figure S- 33: Projection of the packing of **[C(NH2)3][DNT]** perpendicular to the 100 plane.

Table S- 66: Sample and crystal data for **[C(NH2)3][DNT]**.

| | | |
|---|---|---|
| Identification code | GuaniDNT | |
| Chemical formula | $C_3H_6N_8O_4$ | |
| Formula weight | 218.16 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.274 x 0.295 x 0.801 mm | |
| Crystal system | monoclinic | |
| Space group | C 1 2/c 1 | |
| Unit cell dimensions | a = 8.3235(7) Å | α = 90° |
| | b = 16.7996(14) Å | β = 102.3250(13)° |
| | c = 12.3068(10) Å | γ = 90° |
| Volume | 1681.2(2) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.724 $g/cm^3$ | |
| Absorption coefficient | 0.155 $mm^{-1}$ | |
| F(000) | 896 | |

Table S- 67: Data collection and structure refinement for **[C(NH2)3][DNT]**.

| | |
|---|---|
| Diffractometer | Bruker APEX DUO |
| Radiation source | fine-focus tube, MoKα |
| Theta range for data collection | 2.42 to 30.52° |
| Index ranges | -11<=h<=11, -23<=k<=24, -17<=l<=17 |
| Reflections collected | 20271 |
| Independent reflections | 2562 [R(int) = 0.0333] |
| Coverage of independent reflections | 99.3% |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.9590 and 0.8860 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXTL XT 2013/6 (Sheldrick, 2013) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXTL XLMP 2014/1 (Bruker AXS, 2013) |
| Function minimized | $\Sigma w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 2562 / 0 / 160 |
| Goodness-of-fit on $F^2$ | 1.075 |
| Final R indices | 2221 data; I>2σ(I) R1 = 0.0420, wR2 = 0.1147 |
| | all data R1 = 0.0486, wR2 = 0.1189 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0585P)^2+1.5987P]$ where $P=(F_o^2+2F_c^2)/3$ |
| Largest diff. peak and hole | 0.486 and -0.262 $eÅ^{-3}$ |
| R.M.S. deviation from mean | 0.055 $eÅ^{-3}$ |

Table S- 68: Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for **[C(NH2)3][DNT]**.

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| C1 | 0.45529(14) | 0.21803(7) | 0.55973(10) | 0.0183(2) |
| C2 | 0.50191(15) | 0.31605(7) | 0.47779(9) | 0.0181(2) |
| C3 | 0.22225(14) | 0.40070(7) | 0.78750(10) | 0.0182(2) |
| N1 | 0.42001(13) | 0.34343(7) | 0.55183(9) | 0.0212(2) |
| N2 | 0.38860(14) | 0.27727(7) | 0.60685(9) | 0.0211(2) |
| N3 | 0.52994(13) | 0.23721(7) | 0.47756(8) | 0.0198(2) |
| N4 | 0.43571(14) | 0.13733(7) | 0.59504(9) | 0.0219(2) |
| N5 | 0.55743(14) | 0.36971(7) | 0.40095(9) | 0.0218(2) |
| N6 | 0.28742(15) | 0.44451(7) | 0.71836(10) | 0.0249(2) |
| N7 | 0.16520(17) | 0.43552(10) | 0.86842(12) | 0.0322(3) |
| N8 | 0.21329(14) | 0.32243(7) | 0.77699(10) | 0.0209(2) |
| O1 | 0.49918(15) | 0.08366(6) | 0.55042(10) | 0.0341(3) |
| O2 | 0.35507(13) | 0.12595(7) | 0.66590(8) | 0.0275(2) |
| O3 | 0.64830(13) | 0.34261(7) | 0.34287(9) | 0.0291(2) |
| O4 | 0.51029(14) | 0.43882(6) | 0.39762(9) | 0.0301(2) |

Table S- 69: Bond lengths (Å) for **[C(NH2)3][DNT]**.

| | | | |
|---|---|---|---|
| C1-N2 | 1.3313(16) | C1-N3 | 1.3345(16) |
| C1-N4 | 1.4434(16) | C2-N1 | 1.3311(16) |
| C2-N3 | 1.3450(16) | C2-N5 | 1.4516(16) |
| C3-N8 | 1.3217(17) | C3-N6 | 1.3256(17) |
| C3-N7 | 1.3271(17) | N1-N2 | 1.3556(16) |
| N4-O2 | 1.2237(15) | N4-O1 | 1.2319(16) |
| N5-O4 | 1.2234(15) | N5-O3 | 1.2334(15) |
| N6-H1 | 0.78(3) | N6-H2 | 0.83(2) |
| N7-H3 | 0.79(3) | N7-H4 | 0.77(2) |
| N8-H5 | 0.80(2) | N8-H6 | 0.76(2) |

Table S- 70: Bond angles (°) for **[C(NH2)3][DNT]**.

| | | | |
|---|---|---|---|
| N2-C1-N3 | 117.03(11) | N2-C1-N4 | 119.12(11) |
| N3-C1-N4 | 123.75(11) | N1-C2-N3 | 117.14(11) |
| N1-C2-N5 | 120.80(11) | N3-C2-N5 | 122.06(11) |
| N8-C3-N6 | 120.78(12) | N8-C3-N7 | 119.36(13) |
| N6-C3-N7 | 119.86(14) | C2-N1-N2 | 103.89(10) |
| C1-N2-N1 | 104.63(10) | C1-N3-C2 | 97.30(10) |
| O2-N4-O1 | 123.78(12) | O2-N4-C1 | 118.40(11) |
| O1-N4-C1 | 117.81(11) | O4-N5-O3 | 124.26(12) |
| O4-N5-C2 | 117.82(11) | O3-N5-C2 | 117.91(11) |
| C3-N6-H1 | 117.8(16) | C3-N6-H2 | 121.1(16) |
| H1-N6-H2 | 121.(2) | C3-N7-H3 | 117.(2) |
| C3-N7-H4 | 119.7(16) | H3-N7-H4 | 122.(3) |
| C3-N8-H5 | 119.2(15) | C3-N8-H6 | 113.7(15) |
| H5-N8-H6 | 127.(2) | | |

Table S- 71: Anisotropic atomic displacement parameters (Å$^2$) for **[C(NH2)3][DNT]**.The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0169(5) | 0.0211(5) | 0.0164(5) | -0.0010(4) | 0.0023(4) | -0.0003(4) |
| C2 | 0.0168(5) | 0.0209(5) | 0.0159(5) | -0.0003(4) | 0.0018(4) | 0.0006(4) |
| C3 | 0.0144(5) | 0.0217(6) | 0.0185(5) | -0.0026(4) | 0.0033(4) | 0.0002(4) |
| N1 | 0.0206(5) | 0.0241(5) | 0.0189(5) | -0.0019(4) | 0.0044(4) | 0.0011(4) |
| N2 | 0.0206(5) | 0.0227(5) | 0.0195(5) | -0.0026(4) | 0.0032(4) | 0.0006(4) |
| N3 | 0.0187(5) | 0.0229(5) | 0.0176(5) | -0.0005(4) | 0.0035(4) | 0.0008(4) |
| N4 | 0.0213(5) | 0.0244(5) | 0.0196(5) | 0.0009(4) | 0.0033(4) | -0.0017(4) |
| N5 | 0.0215(5) | 0.0240(5) | 0.0194(5) | 0.0006(4) | 0.0037(4) | 0.0012(4) |
| N6 | 0.0288(6) | 0.0192(5) | 0.0280(6) | 0.0002(4) | 0.0086(5) | -0.0038(4) |
| N7 | 0.0346(7) | 0.0352(7) | 0.0305(6) | -0.0095(5) | 0.0153(5) | 0.0039(5) |
| N8 | 0.0217(5) | 0.0203(5) | 0.0221(5) | -0.0017(4) | 0.0076(4) | -0.0034(4) |
| O1 | 0.0478(7) | 0.0207(5) | 0.0393(6) | -0.0009(4) | 0.0217(5) | 0.0022(4) |
| O2 | 0.0269(5) | 0.0348(5) | 0.0219(5) | 0.0043(4) | 0.0075(4) | -0.0028(4) |
| O3 | 0.0313(5) | 0.0317(5) | 0.0283(5) | 0.0059(4) | 0.0150(4) | 0.0065(4) |
| O4 | 0.0396(6) | 0.0203(5) | 0.0319(5) | 0.0022(4) | 0.0111(4) | 0.0026(4) |

Table S- 72: Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å$^2$) for **[C(NH2)3][DNT]**.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H1 | 0.299(3) | 0.4901(15) | 0.7310(18) | 0.046(6) |

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H2 | 0.322(3) | 0.4238(14) | 0.6664(19) | 0.039(6) |
| H3 | 0.159(3) | 0.482(2) | 0.866(2) | 0.067(9) |
| H4 | 0.120(3) | 0.4103(13) | 0.9053(18) | 0.034(5) |
| H5 | 0.175(3) | 0.2971(13) | 0.8200(17) | 0.034(5) |
| H6 | 0.255(2) | 0.3062(11) | 0.7319(16) | 0.024(4) |

# 2.12 Crystal Structure Report for [aminoguanidine][DNT]

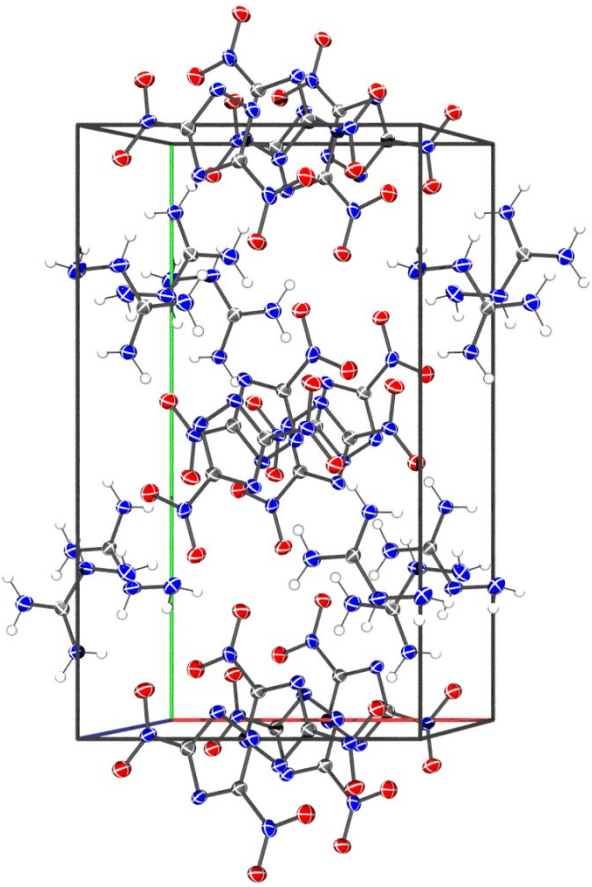

Figure S- 34 : Projection of the packing of **[aminoguanidine][DNT]** perpendicular to the 001 plane.

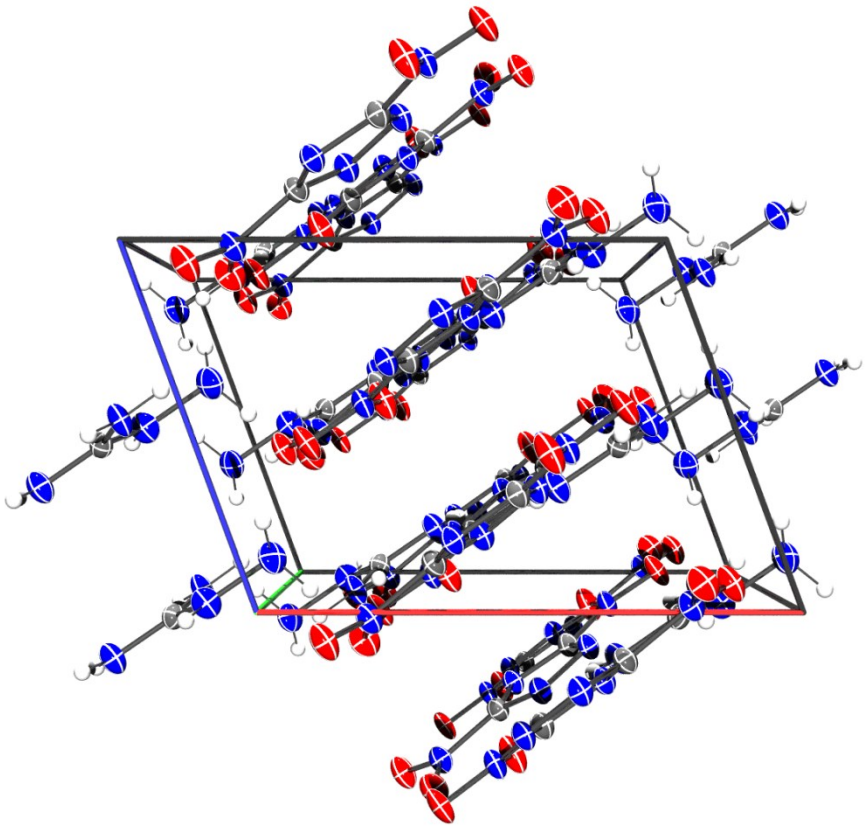

Figure S- 35 : Projection of the packing of [aminoguanidine][DNT] perpendicular to the 010 plane.

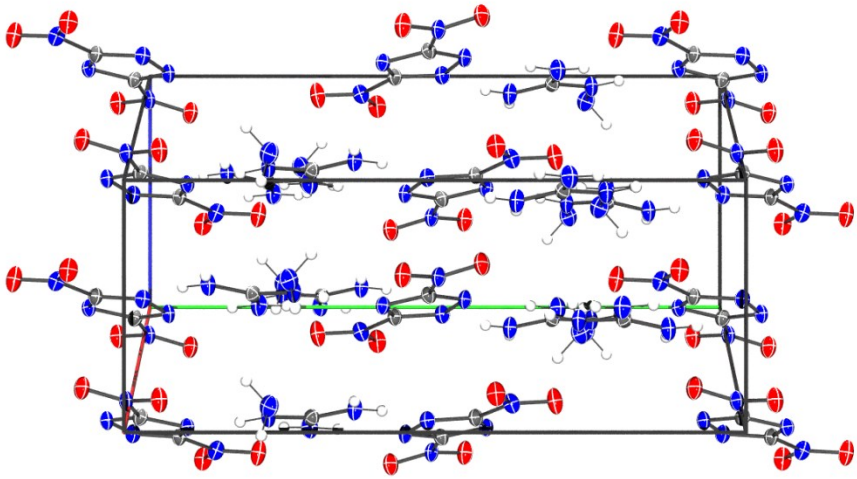

Figure S- 36 : Projection of the packing of **[aminoguanidine][DNT]** perpendicular to the 100 plane.

Table S- 73 : Sample and crystal data for **[aminoguanidine][DNT]**.

| | | |
|---|---|---|
| Identification code | XMK20b_01 | |
| Chemical formula | $C_3H_7N_9O_4$ | |
| Formula weight | 233.18 g/mol | |
| Temperature | 100(2) K | |
| Wavelength | 1.54178 Å | |
| Crystal size | 0.096 x 0.116 x 0.182 mm | |
| Crystal habit | colorless blade | |
| Crystal system | monoclinic | |
| Space group | P 1 21/c 1 | |
| Unit cell dimensions | a = 9.0616(3) Å | α = 90° |
| | b = 16.2452(5) Å | β = 110.189(3)° |
| | c = 6.5935(2) Å | γ = 90° |
| Volume | 910.98(5) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.700 $g/cm^3$ | |
| Absorption coefficient | 1.338 $mm^{-1}$ | |
| F(000) | 480 | |

Table S- 74 : Data collection and structure refinement for **[aminoguanidine][DNT]**.

| | |
|---|---|
| Diffractometer | Bruker APEX DUO |
| Radiation source | IuS microsource, CuKα |
| Theta range for data collection | 2.72 to 72.18° |
| Index ranges | -11<=h<=11, -19<=k<=18, -7<=l<=7 |
| Reflections collected | 12104 |
| Independent reflections | 1692 [R(int) = 0.0474] |
| Coverage of independent reflections | 93.7% |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.8820 and 0.7930 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXTL XT 2014/3 (Sheldrick, 2014) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXL-2014 (Sheldrick, 2014) |
| Function minimized | $\Sigma\, w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 1692 / 35 / 201 |
| Goodness-of-fit on $F^2$ | 1.220 |
| Final R indices | 1440 data; I>2σ(I) R1 = 0.0790, wR2 = 0.2765 |
| | all data R1 = 0.0884, wR2 = 0.2846 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.1444P)^2+3.2934P]$ where $P=(F_o^2+2F_c^2)/3$ |
| Largest diff. peak and hole | 0.446 and -0.423 $eÅ^{-3}$ |
| R.M.S. deviation from mean | 0.111 $eÅ^{-3}$ |

Table S- 75 :Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for **[aminoguanidine][DNT]**.

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| C3 | 0.7907(6) | 0.2022(3) | 0.4460(8) | 0.0196(10) |
| N6 | 0.6410(5) | 0.2084(3) | 0.3259(7) | 0.0266(10) |
| N7 | 0.8563(5) | 0.1302(3) | 0.5165(7) | 0.0239(10) |
| N8 | 0.8763(5) | 0.2710(2) | 0.4945(7) | 0.0255(10) |
| N9 | 0.0367(5) | 0.2656(3) | 0.6234(8) | 0.0288(11) |
| C1_a | 0.4444(9) | 0.4319(4) | 0.180(3) | 0.0187(14) |
| C2_a | 0.6420(9) | 0.4896(4) | 0.3681(19) | 0.0191(15) |
| N1_a | 0.5378(5) | 0.5500(3) | 0.2983(7) | 0.0199(10) |
| N2_a | 0.4049(5) | 0.5124(3) | 0.1712(7) | 0.0203(10) |
| N3_a | 0.5908(5) | 0.4132(3) | 0.2998(7) | 0.0191(10) |
| N4_a | 0.3280(5) | 0.3735(3) | 0.0597(9) | 0.0221(11) |
| N5_a | 0.7988(5) | 0.5059(3) | 0.5178(7) | 0.0212(10) |
| O1_a | 0.1973(4) | 0.4002(3) | 0.9518(7) | 0.0283(10) |
| O2_a | 0.3655(5) | 0.3006(2) | 0.0702(8) | 0.0299(10) |
| O3_a | 0.8287(5) | 0.5766(2) | 0.5855(7) | 0.0285(10) |
| O4_a | 0.8913(4) | 0.4481(2) | 0.5710(7) | 0.0288(10) |
| C1A_b | 0.464(10) | 0.431(3) | 0.19(3) | 0.0187(14) |
| C2A_b | 0.645(8) | 0.495(2) | 0.39(2) | 0.0191(15) |
| N1A_b | 0.702(4) | 0.4191(19) | 0.398(7) | 0.0199(10) |
| N2A_b | 0.576(4) | 0.3742(19) | 0.280(7) | 0.0203(10) |
| N3A_b | 0.500(4) | 0.5084(18) | 0.247(7) | 0.0191(10) |
| N4A_b | 0.313(4) | 0.400(2) | 0.049(11) | 0.0221(11) |
| N5A_b | 0.750(4) | 0.5623(16) | 0.494(7) | 0.0212(10) |
| O1A_b | 0.307(5) | 0.326(2) | 0.006(8) | 0.0283(10) |
| O2A_b | 0.206(4) | 0.450(2) | 0.974(7) | 0.0299(10) |
| O3A_b | 0.876(4) | 0.545(2) | 0.635(7) | 0.0285(10) |
| O4A_b | 0.695(4) | 0.6315(17) | 0.456(7) | 0.0288(10) |

Table S- 76: Bond lengths (Å) for **[aminoguanidine][DNT]**.

| | | | |
|---|---|---|---|
| C3-N6 | 1.317(6) | C3-N7 | 1.322(6) |
| C3-N8 | 1.335(6) | N6-H1 | 0.86(2) |
| N6-H2 | 0.87(2) | N7-H3 | 0.88(2) |
| N7-H4 | 0.87(2) | N8-N9 | 1.411(6) |
| N8-H5 | 0.87(2) | N9-H9 | 0.89(2) |
| N9-H10 | 0.89(2) | C1_a-N3_a | 1.323(7) |
| C1_a-N2_a | 1.351(8) | C1_a-N4_a | 1.439(7) |
| C1_a-C2_a | 2.021(7) | C2_a-N1_a | 1.330(8) |
| C2_a-N3_a | 1.347(7) | C2_a-N5_a | 1.447(7) |
| N1_a-N2_a | 1.353(6) | N4_a-O2_a | 1.227(6) |
| N4_a-O1_a | 1.231(6) | N5_a-O4_a | 1.227(6) |
| N5_a-O3_a | 1.228(6) | C1A_b-N3A_b | 1.326(19) |
| C1A_b-N2A_b | 1.35(2) | C1A_b-N4A_b | 1.443(19) |
| C1A_b-C2A_b | 2.020(18) | C2A_b-N1A_b | 1.33(2) |
| C2A_b-N3A_b | 1.35(2) | C2A_b-N5A_b | 1.451(19) |
| N1A_b-N2A_b | 1.351(19) | N4A_b-O2A_b | 1.229(19) |
| N4A_b-O1A_b | 1.235(19) | N5A_b-O4A_b | 1.219(19) |
| N5A_b-O3A_b | 1.232(19) | | |

Table S- 77 : Bond angles (°) for **[aminoguanidine][DNT]**.

| | | | |
|---|---|---|---|
| N6-C3-N7 | 121.6(4) | N6-C3-N8 | 118.2(4) |
| N7-C3-N8 | 120.2(4) | C3-N6-H1 | 115.(4) |
| C3-N6-H2 | 129.(4) | H1-N6-H2 | 115.(6) |
| C3-N7-H3 | 116.(4) | C3-N7-H4 | 118.(4) |
| H3-N7-H4 | 126.(6) | C3-N8-N9 | 119.0(4) |
| C3-N8-H5 | 120.(4) | N9-N8-H5 | 121.(4) |
| N8-N9-H9 | 105.(4) | N8-N9-H10 | 105.(4) |
| H9-N9-H10 | 115.(6) | N3_a-C1_a-N2_a | 116.5(5) |
| N3_a-C1_a-N4_a | 124.8(6) | N2_a-C1_a-N4_a | 118.7(5) |
| N3_a-C1_a-C2_a | 41.3(3) | N2_a-C1_a-C2_a | 75.2(4) |
| N4_a-C1_a-C2_a | 166.0(5) | N1_a-C2_a-N3_a | 116.3(5) |
| N1_a-C2_a-N5_a | 120.9(5) | N3_a-C2_a-N5_a | 122.7(5) |
| N1_a-C2_a-C1_a | 75.9(4) | N3_a-C2_a-C1_a | 40.4(3) |

| | | | |
|---|---|---|---|
| N5_a-C2_a-C1_a | 162.9(5) | C2_a-N1_a-N2_a | 104.8(4) |
| C1_a-N2_a-N1_a | 104.1(4) | C1_a-N3_a-C2_a | 98.4(5) |
| O2_a-N4_a-O1_a | 124.4(4) | O2_a-N4_a-C1_a | 118.0(4) |
| O1_a-N4_a-C1_a | 117.6(5) | O4_a-N5_a-O3_a | 124.7(4) |
| O4_a-N5_a-C2_a | 117.9(4) | O3_a-N5_a-C2_a | 117.5(4) |
| N3A_b-C1A_b-N2A_b | 116.2(18) | N3A_b-C1A_b-N4A_b | 127.(3) |
| N2A_b-C1A_b-N4A_b | 117.(3) | N3A_b-C1A_b-C2A_b | 41.5(10) |
| N2A_b-C1A_b-C2A_b | 74.7(14) | N4A_b-C1A_b-C2A_b | 167.(8) |
| N1A_b-C2A_b-N3A_b | 116.(2) | N1A_b-C2A_b-N5A_b | 120.(3) |
| N3A_b-C2A_b-N5A_b | 122.(3) | N1A_b-C2A_b-C1A_b | 76.1(15) |
| N3A_b-C2A_b-C1A_b | 40.5(9) | N5A_b-C2A_b-C1A_b | 162.(5) |
| C2A_b-N1A_b-N2A_b | 104.0(19) | N1A_b-N2A_b-C1A_b | 104.3(19) |
| C1A_b-N3A_b-C2A_b | 98.0(15) | O2A_b-N4A_b-O1A_b | 126.(3) |
| O2A_b-N4A_b-C1A_b | 118.(2) | O1A_b-N4A_b-C1A_b | 116.(2) |
| O4A_b-N5A_b-O3A_b | 125.(3) | O4A_b-N5A_b-C2A_b | 117.(2) |
| O3A_b-N5A_b-C2A_b | 118.(3) | | |

Table S- 78: Anisotropic atomic displacement parameters (Å$^2$) for **[aminoguanidine][DNT]**.The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C3 | 0.019(2) | 0.018(2) | 0.022(2) | -0.0014(17) | 0.0080(18) | -0.0026(17) |
| N6 | 0.020(2) | 0.022(2) | 0.033(2) | 0.0019(17) | 0.0028(18) | 0.0014(16) |
| N7 | 0.015(2) | 0.0171(19) | 0.034(2) | -0.0016(16) | 0.0015(17) | -0.0006(15) |
| N8 | 0.028(2) | 0.015(2) | 0.032(2) | -0.0004(16) | 0.0079(18) | -0.0024(16) |
| N9 | 0.024(2) | 0.026(2) | 0.034(2) | -0.0056(18) | 0.0070(19) | -0.0087(17) |
| C1_a | 0.017(3) | 0.016(2) | 0.022(3) | -0.0012(17) | 0.005(3) | -0.0011(18) |
| C2_a | 0.017(2) | 0.018(2) | 0.020(4) | -0.0020(19) | 0.0039(19) | -0.0008(18) |
| N1_a | 0.018(2) | 0.014(2) | 0.026(2) | 0.0004(17) | 0.0050(17) | -0.0020(16) |
| N2_a | 0.015(2) | 0.019(2) | 0.025(2) | 0.0002(17) | 0.0040(18) | 0.0024(16) |
| N3_a | 0.016(2) | 0.016(2) | 0.023(2) | -0.0003(17) | 0.0042(17) | -0.0025(17) |
| N4_a | 0.013(2) | 0.022(3) | 0.027(2) | -0.003(2) | 0.0023(17) | 0.0017(19) |
| N5_a | 0.019(2) | 0.015(2) | 0.027(2) | 0.0001(17) | 0.0044(18) | -0.0030(16) |
| O1_a | 0.0141(19) | 0.026(2) | 0.035(2) | -0.0015(16) | -0.0041(16) | 0.0011(15) |
| O2_a | 0.0176(19) | 0.0190(19) | 0.045(2) | -0.0053(17) | 0.0004(17) | 0.0014(15) |
| O3_a | 0.027(2) | 0.019(2) | 0.035(2) | -0.0045(17) | 0.0055(19) | -0.0053(16) |
| O4_a | 0.0190(19) | 0.0205(19) | 0.040(2) | 0.0026(16) | 0.0009(16) | 0.0010(15) |
| C1A_b | 0.017(3) | 0.016(2) | 0.022(3) | -0.0012(17) | 0.005(3) | -0.0011(18) |
| C2A_b | 0.017(2) | 0.018(2) | 0.020(4) | -0.0020(19) | 0.0039(19) | -0.0008(18) |
| N1A_b | 0.018(2) | 0.014(2) | 0.026(2) | 0.0004(17) | 0.0050(17) | -0.0020(16) |
| N2A_b | 0.015(2) | 0.019(2) | 0.025(2) | 0.0002(17) | 0.0040(18) | 0.0024(16) |
| N3A_b | 0.016(2) | 0.016(2) | 0.023(2) | -0.0003(17) | 0.0042(17) | -0.0025(17) |
| N4A_b | 0.013(2) | 0.022(3) | 0.027(2) | -0.003(2) | 0.0023(17) | 0.0017(19) |
| N5A_b | 0.019(2) | 0.015(2) | 0.027(2) | 0.0001(17) | 0.0044(18) | -0.0030(16) |
| O1A_b | 0.0141(19) | 0.026(2) | 0.035(2) | -0.0015(16) | -0.0041(16) | 0.0011(15) |
| O2A_b | 0.0176(19) | 0.0190(19) | 0.045(2) | -0.0053(17) | 0.0004(17) | 0.0014(15) |
| O3A_b | 0.027(2) | 0.019(2) | 0.035(2) | -0.0045(17) | 0.0055(19) | -0.0053(16) |
| O4A_b | 0.0190(19) | 0.0205(19) | 0.040(2) | 0.0026(16) | 0.0009(16) | 0.0010(15) |

Table S- 79 : Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å$^2$) for **[aminoguanidine][DNT]**.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H1 | 0.592(7) | 0.162(2) | 0.292(10) | 0.032 |
| H2 | 0.581(6) | 0.252(3) | 0.294(10) | 0.032 |
| H3 | 0.795(6) | 0.087(2) | 0.476(9) | 0.029 |
| H4 | 0.955(3) | 0.130(4) | 0.599(8) | 0.029 |
| H5 | 0.832(7) | 0.318(2) | 0.451(10) | 0.031 |
| H9 | 1.089(7) | 0.277(4) | 0.535(9) | 0.035 |
| H10 | 1.049(8) | 0.302(3) | 0.730(8) | 0.035 |

# 2.13 Crystal Structure Report for [$HNEt_3$][DNT]

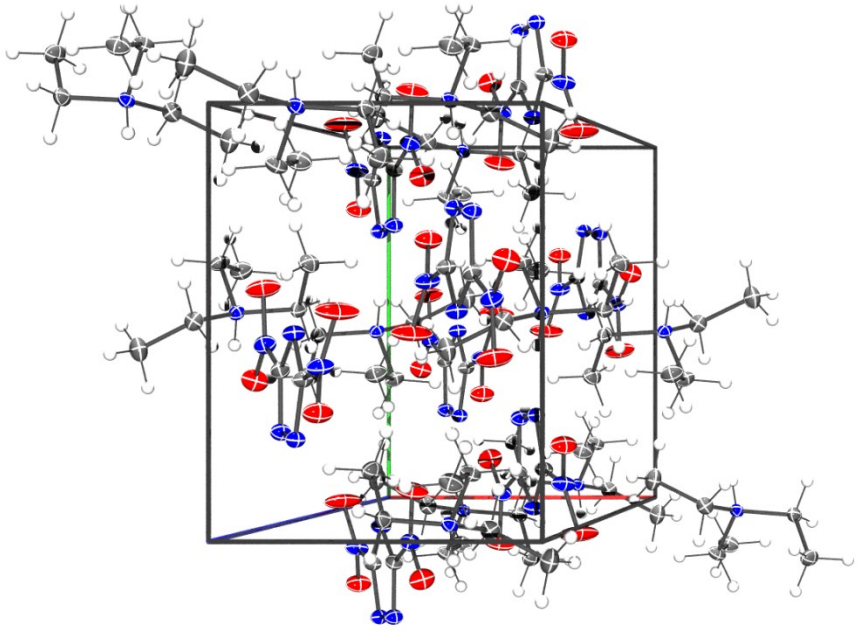

Figure S- 37 : Projection of the packing in **[HNEt3][DNT]** perpendicular to the 001 plane.

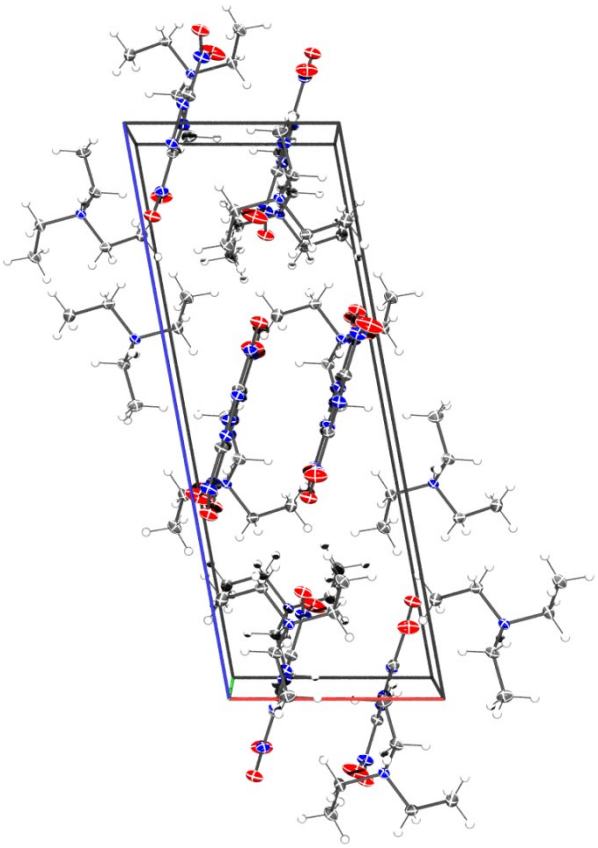

Figure S- 38: Projection of the packing in **[HNEt3][DNT]** perpendicular to the 010 plane.

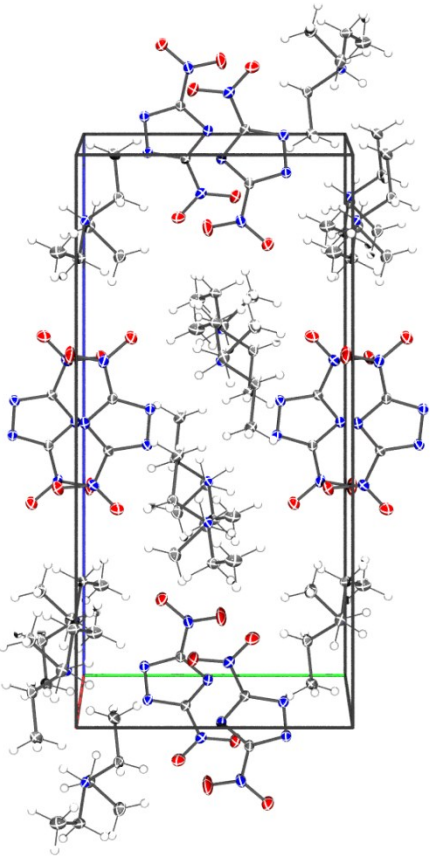

Figure S- 39: Projection of the packing in **[HNEt3][DNT]** perpendicular to the 100 plane.

Table S- 80: Sample and crystal data for **[HNEt3][DNT]**.

| | | |
|---|---|---|
| Identification code | Et3NHDNT | |
| Chemical formula | $C_8H_{16}N_6O_4$ | |
| Formula weight | 260.27 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.232 x 0.293 x 0.402 mm | |
| Crystal habit | clear pale yellow prism | |
| Crystal system | monoclinic | |
| Space group | P 1 21/n 1 | |
| Unit cell dimensions | a = 7.0842(5) Å | α = 90° |
| | b = 9.3195(6) Å | β = 100.3110(11)° |
| | c = 19.3391(13) Å | γ = 90° |
| Volume | 1256.17(15) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.376 $g/cm^3$ | |
| Absorption coefficient | 0.111 $mm^{-1}$ | |
| F(000) | 552 | |

Table S- 81: Data collection and structure refinement for **[HNEt3][DNT]**.

| | | |
|---|---|---|
| Diffractometer | Bruker APEX DUO | |
| Radiation source | fine-focus tube, MoKα | |
| Theta range for data collection | 2.14 to 30.65° | |
| Index ranges | -10<=h<=9, -13<=k<=13, -27<=l<=27 | |
| Reflections collected | 29946 | |
| Independent reflections | 3841 [R(int) = 0.0325] | |
| Absorption correction | multi-scan | |
| Max. and min. transmission | 0.9750 and 0.9570 | |
| Structure solution technique | direct methods | |
| Structure solution program | SHELXTL XT 2013/6 (Sheldrick, 2013) | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Refinement program | SHELXTL XLMP 2014/1 (Bruker AXS, 2013) | |
| Function minimized | $\Sigma w(F_o^2 - F_c^2)^2$ | |
| Data / restraints / parameters | 3841 / 0 / 169 | |
| Goodness-of-fit on $F^2$ | 1.042 | |
| $\Delta/\sigma_{max}$ | 0.001 | |
| Final R indices | 3189 data; I>2σ(I) | R1 = 0.0397, wR2 = 0.0959 |
| | all data | R1 = 0.0508, wR2 = 0.1022 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0434P)^2+0.5128P]$ where $P=(F_o^2+2F_c^2)/3$ | |
| Largest diff. peak and hole | 0.623 and -0.484 $eÅ^{-3}$ | |
| R.M.S. deviation from mean | 0.047 $eÅ^{-3}$ | |

Table S- 82: Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for **[HNEt3][DNT]**.U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| x/a | y/b | z/c | U(eq) |
|---|---|---|---|

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| C1 | 0.82004(14) | 0.12816(10) | 0.56321(5) | 0.01597(19) |
| C2 | 0.69179(14) | 0.11022(11) | 0.46243(5) | 0.01575(19) |
| C3 | 0.24304(15) | 0.35101(11) | 0.41424(5) | 0.0177(2) |
| C4 | 0.22214(17) | 0.36755(12) | 0.49031(6) | 0.0226(2) |
| C5 | 0.94241(14) | 0.46655(11) | 0.34903(6) | 0.0178(2) |
| C6 | 0.87516(16) | 0.35571(12) | 0.29252(6) | 0.0215(2) |
| C7 | 0.25477(15) | 0.49687(12) | 0.30698(5) | 0.0183(2) |
| C8 | 0.44980(16) | 0.56698(14) | 0.32843(6) | 0.0252(2) |
| N1 | 0.69958(12) | 0.25202(9) | 0.47367(4) | 0.01647(17) |
| N2 | 0.78518(12) | 0.26379(9) | 0.54215(4) | 0.01586(17) |
| N3 | 0.76506(13) | 0.02513(9) | 0.51615(5) | 0.01835(18) |
| N4 | 0.60249(14) | 0.05214(10) | 0.39467(5) | 0.01969(18) |
| N5 | 0.91361(15) | 0.09765(10) | 0.63454(5) | 0.0223(2) |
| N6 | 0.15806(12) | 0.47643(9) | 0.36969(4) | 0.01362(16) |
| O1 | 0.59269(16) | 0.92108(9) | 0.38865(5) | 0.0341(2) |
| O2 | 0.54033(13) | 0.13713(9) | 0.34776(4) | 0.02656(19) |
| O3 | 0.97036(18) | 0.97504(9) | 0.64869(5) | 0.0447(3) |
| O4 | 0.93216(13) | 0.19736(9) | 0.67694(4) | 0.02596(19) |

Table S- 83: Bond lengths (Å) for **[HNEt3][DNT]**.

| | | | |
|---|---|---|---|
| C1-N3 | 1.3323(13) | C1-N2 | 1.3374(12) |
| C1-N5 | 1.4476(13) | C2-N3 | 1.3359(13) |
| C2-N1 | 1.3388(13) | C2-N4 | 1.4538(13) |
| C3-N6 | 1.5117(13) | C3-C4 | 1.5125(14) |
| C3-H3A | 0.99 | C3-H3B | 0.99 |
| C4-H4A | 0.98 | C4-H4B | 0.98 |
| C4-H4C | 0.98 | C5-N6 | 1.5111(13) |
| C5-C6 | 1.5173(14) | C5-H5A | 0.99 |
| C5-H5B | 0.99 | C6-H6A | 0.98 |
| C6-H6B | 0.98 | C6-H6C | 0.98 |
| C7-N6 | 1.5080(13) | C7-C8 | 1.5174(15) |
| C7-H7A | 0.99 | C7-H7B | 0.99 |
| C8-H8A | 0.98 | C8-H8B | 0.98 |
| C8-H8C | 0.98 | N1-N2 | 1.3589(12) |
| N4-O2 | 1.2253(12) | N4-O1 | 1.2277(12) |
| N5-O3 | 1.2258(12) | N5-O4 | 1.2308(12) |
| N6-H1 | 0.903(14) | | |

Table S- 84: Bond angles (°) for **[HNEt3][DNT]**.

| | | | |
|---|---|---|---|
| N3-C1-N2 | 117.24(9) | N3-C1-N5 | 122.50(9) |
| N2-C1-N5 | 120.26(9) | N3-C2-N1 | 117.44(9) |
| N3-C2-N4 | 121.72(9) | N1-C2-N4 | 120.83(9) |
| N6-C3-C4 | 112.16(8) | N6-C3-H3A | 109.2 |
| C4-C3-H3A | 109.2 | N6-C3-H3B | 109.2 |
| C4-C3-H3B | 109.2 | H3A-C3-H3B | 107.9 |
| C3-C4-H4A | 109.5 | C3-C4-H4B | 109.5 |

| | | | |
|---|---|---|---|
| H4A-C4-H4B | 109.5 | C3-C4-H4C | 109.5 |
| H4A-C4-H4C | 109.5 | H4B-C4-H4C | 109.5 |
| N6-C5-C6 | 113.84(8) | N6-C5-H5A | 108.8 |
| C6-C5-H5A | 108.8 | N6-C5-H5B | 108.8 |
| C6-C5-H5B | 108.8 | H5A-C5-H5B | 107.7 |
| C5-C6-H6A | 109.5 | C5-C6-H6B | 109.5 |
| H6A-C6-H6B | 109.5 | C5-C6-H6C | 109.5 |
| H6A-C6-H6C | 109.5 | H6B-C6-H6C | 109.5 |
| N6-C7-C8 | 110.92(8) | N6-C7-H7A | 109.5 |
| C8-C7-H7A | 109.5 | N6-C7-H7B | 109.5 |
| C8-C7-H7B | 109.5 | H7A-C7-H7B | 108.0 |
| C7-C8-H8A | 109.5 | C7-C8-H8B | 109.5 |
| H8A-C8-H8B | 109.5 | C7-C8-H8C | 109.5 |
| H8A-C8-H8C | 109.5 | H8B-C8-H8C | 109.5 |
| C2-N1-N2 | 103.66(8) | C1-N2-N1 | 104.26(8) |
| C1-N3-C2 | 97.40(8) | O2-N4-O1 | 124.48(9) |
| O2-N4-C2 | 117.87(9) | O1-N4-C2 | 117.65(9) |
| O3-N5-O4 | 124.29(10) | O3-N5-C1 | 118.15(9) |
| O4-N5-C1 | 117.56(9) | C7-N6-C5 | 112.24(8) |
| C7-N6-C3 | 111.35(8) | C5-N6-C3 | 112.60(8) |
| C7-N6-H1 | 106.2(8) | C5-N6-H1 | 106.3(8) |
| C3-N6-H1 | 107.7(8) | | |

Table S- 85: Anisotropic atomic displacement parameters (Å$^2$) for **[HNEt3][DNT]**.The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0188(4) | 0.0121(4) | 0.0160(4) | 0.0000(3) | 0.0004(3) | -0.0007(3) |
| C2 | 0.0176(4) | 0.0142(4) | 0.0152(4) | -0.0018(3) | 0.0023(3) | -0.0015(3) |
| C3 | 0.0208(5) | 0.0138(4) | 0.0170(4) | 0.0003(3) | -0.0006(4) | 0.0045(4) |
| C4 | 0.0307(6) | 0.0193(5) | 0.0181(5) | 0.0038(4) | 0.0053(4) | 0.0034(4) |
| C5 | 0.0143(4) | 0.0165(4) | 0.0213(5) | -0.0028(4) | 0.0000(4) | 0.0011(4) |
| C6 | 0.0207(5) | 0.0190(5) | 0.0224(5) | -0.0031(4) | -0.0027(4) | -0.0028(4) |
| C7 | 0.0201(5) | 0.0210(5) | 0.0138(4) | -0.0006(4) | 0.0031(4) | 0.0010(4) |
| C8 | 0.0195(5) | 0.0337(6) | 0.0232(5) | -0.0016(5) | 0.0057(4) | -0.0037(4) |
| N1 | 0.0189(4) | 0.0139(4) | 0.0154(4) | -0.0013(3) | -0.0001(3) | -0.0001(3) |
| N2 | 0.0179(4) | 0.0129(4) | 0.0154(4) | -0.0001(3) | -0.0006(3) | 0.0003(3) |
| N3 | 0.0235(4) | 0.0128(4) | 0.0182(4) | -0.0011(3) | 0.0022(3) | -0.0014(3) |
| N4 | 0.0244(4) | 0.0178(4) | 0.0168(4) | -0.0034(3) | 0.0034(3) | -0.0024(3) |
| N5 | 0.0311(5) | 0.0135(4) | 0.0194(4) | 0.0023(3) | -0.0034(4) | -0.0018(4) |
| N6 | 0.0142(4) | 0.0123(4) | 0.0134(4) | -0.0016(3) | 0.0001(3) | 0.0013(3) |
| O1 | 0.0601(6) | 0.0165(4) | 0.0237(4) | -0.0061(3) | 0.0023(4) | -0.0084(4) |
| O2 | 0.0344(5) | 0.0254(4) | 0.0172(4) | -0.0017(3) | -0.0028(3) | 0.0033(3) |
| O3 | 0.0785(8) | 0.0137(4) | 0.0318(5) | 0.0044(3) | -0.0178(5) | 0.0048(4) |
| O4 | 0.0368(5) | 0.0182(4) | 0.0193(4) | -0.0029(3) | -0.0048(3) | -0.0011(3) |

Table S- 86: Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å$^2$) for **[HNEt3][DNT]**.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H3A | 0.3808 | 0.3424 | 0.4116 | 0.021 |
| H3B | 0.1784 | 0.2616 | 0.3952 | 0.021 |
| H4A | 0.2777 | 0.2838 | 0.5171 | 0.034 |
| H4B | 0.0859 | 0.3752 | 0.4933 | 0.034 |
| H4C | 0.2893 | 0.4544 | 0.5098 | 0.034 |
| H5A | -0.1082 | 0.5617 | 0.3320 | 0.021 |
| H5B | -0.1123 | 0.4426 | 0.3913 | 0.021 |
| H6A | -0.0721 | 0.2616 | 0.3082 | 0.032 |
| H6B | -0.0805 | 0.3829 | 0.2491 | 0.032 |
| H6C | -0.2653 | 0.3511 | 0.2837 | 0.032 |
| H7A | 0.1731 | 0.5577 | 0.2717 | 0.022 |
| H7B | 0.2704 | 0.4026 | 0.2851 | 0.022 |
| H8A | 0.4339 | 0.6619 | 0.3484 | 0.038 |
| H8B | 0.5111 | 0.5771 | 0.2871 | 0.038 |
| H8C | 0.5303 | 0.5072 | 0.3636 | 0.038 |
| H1 | 0.1823(19) | 0.5567(15) | 0.3959(7) | 0.016 |

## 2.14 Crystal Structure Report for monoclinic $[H_2NEt_2][DNT]$

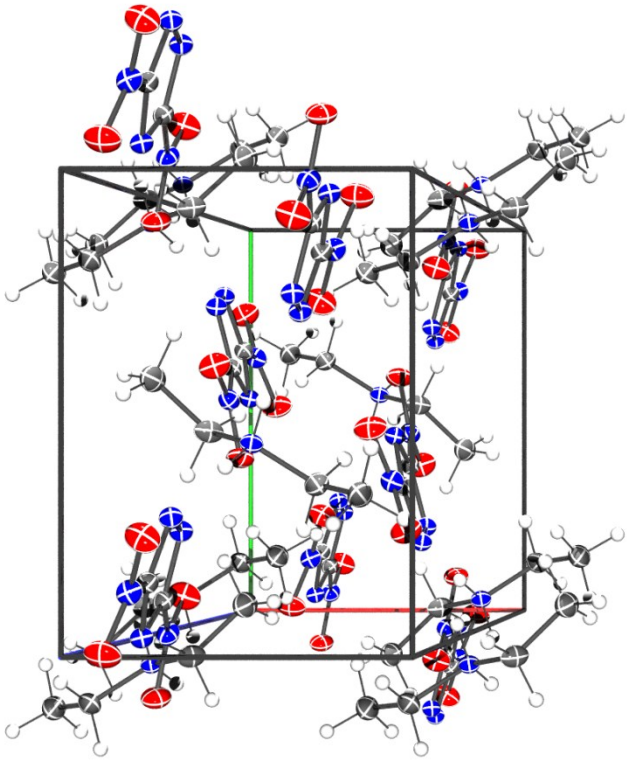

Figure S- 40 : Projection of the packing of monoclinic [H2NEt2][DNT] perpendicular to the 001 plane.

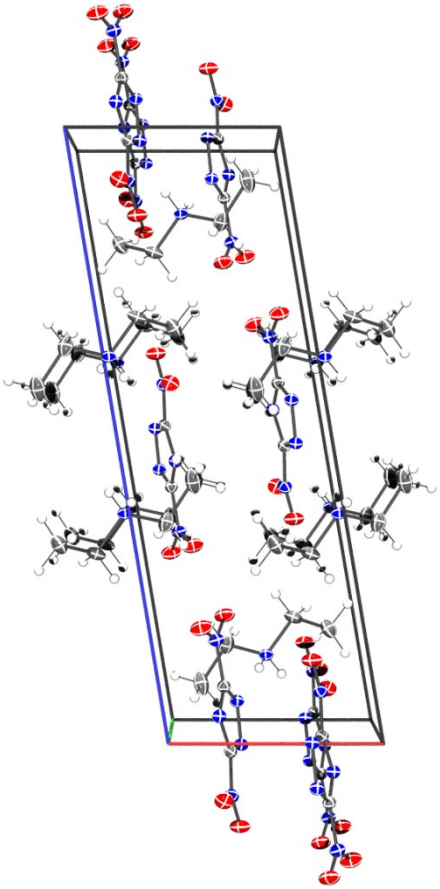

Figure S- 41: Projection of the packing of monoclinic [H2NEt2][DNT] perpendicular to the 010 plane.

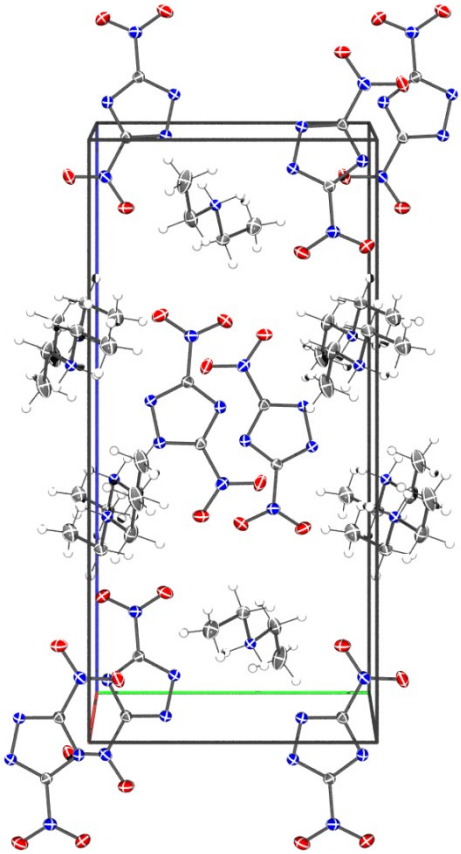

Figure S- 42: Projection of the packing of monoclinic [H2NEt2][DNT] perpendicular to the 100 plane.

Table S- 87: Sample and crystal data for **monoclinic [H2NEt2][**DNT].

| | | |
|---|---|---|
| Identification code | Et2NH2DNT | |
| Chemical formula | $C_6H_{12}N_6O_4$ | |
| Formula weight | 232.22 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.162 x 0.258 x 0.499 mm | |
| Crystal habit | clear yellow prism | |
| Crystal system | monoclinic | |
| Space group | P 1 21/n 1 | |
| Unit cell dimensions | a = 6.4659(4) Å | α = 90° |
| | b = 8.9964(6) Å | β = 99.5420(10)° |
| | c = 18.8357(12) Å | γ = 90° |
| Volume | 1080.51(12) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.427 $g/cm^3$ | |
| Absorption coefficient | 0.120 $mm^{-1}$ | |
| F(000) | 488 | |

Table S- 88: Data collection and structure refinement for **monoclinic [H2NEt2][**DNT].

| | | |
|---|---|---|
| Diffractometer | Bruker APEX DUO | |
| Radiation source | fine-focus tube, MoKα | |
| Theta range for data collection | 2.19 to 29.13° | |
| Index ranges | -8<=h<=8, -12<=k<=12, -25<=l<=25 | |
| Reflections collected | 24237 | |
| Independent reflections | 2903 [R(int) = 0.0293] | |
| Absorption correction | multi-scan | |
| Structure solution technique | direct methods | |
| Structure solution program | SHELXTL XT 2013/6 (Sheldrick, 2013) | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Refinement program | SHELXTL XLMP 2014/1 (Bruker AXS, 2013) | |
| Function minimized | $\Sigma\, w(F_o^2 - F_c^2)^2$ | |
| Data / restraints / parameters | 2903 / 1 / 153 | |
| Goodness-of-fit on $F^2$ | 1.034 | |
| $\Delta/\sigma_{max}$ | 0.001 | |
| Final R indices | 2518 data; I>2σ(I) | R1 = 0.0318, wR2 = 0.0795 |
| | all data | R1 = 0.0385, wR2 = 0.0842 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0412P)^2+0.2954P]$ where $P=(F_o^2+2F_c^2)/3$ | |
| Largest diff. peak and hole | 0.243 and -0.255 $eÅ^{-3}$ | |
| R.M.S. deviation from mean | 0.042 $eÅ^{-3}$ | |

Table S- 89: Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for monoclinic [H2NEt2][DNT].U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| C1 | 0.19931(14) | 0.65943(10) | 0.41238(5) | 0.01626(18) |
| N1 | 0.24316(12) | 0.54448(8) | 0.45680(4) | 0.01731(16) |
| O1 | 0.25774(14) | 0.52846(9) | 0.31310(4) | 0.03106(19) |
| C2 | 0.21905(13) | 0.61371(10) | 0.51739(5) | 0.01596(17) |
| N2 | 0.15157(12) | 0.78805(9) | 0.44110(4) | 0.01712(16) |
| O2 | 0.14070(13) | 0.75549(9) | 0.29801(4) | 0.03017(18) |
| C3 | 0.15829(16) | 0.14918(12) | 0.35719(6) | 0.0272(2) |
| N3 | 0.16548(12) | 0.75706(9) | 0.51241(4) | 0.01724(16) |
| O3 | 0.28330(12) | 0.40435(8) | 0.58728(4) | 0.02662(17) |
| C4 | 0.31718(17) | 0.16944(13) | 0.42490(7) | 0.0359(3) |
| N4 | 0.19974(13) | 0.64661(9) | 0.33560(4) | 0.02061(17) |
| O4 | 0.23233(13) | 0.61343(9) | 0.63962(4) | 0.02976(18) |
| C5 | 0.81035(17) | 0.03608(11) | 0.30799(5) | 0.0237(2) |
| N5 | 0.24791(13) | 0.53792(9) | 0.58637(4) | 0.01948(17) |
| C6 | 0.65249(17) | 0.92288(12) | 0.32433(6) | 0.0294(2) |
| N6 | 0.97388(12) | 0.06248(9) | 0.37277(4) | 0.01627(16) |

Table S- 90: Bond lengths (Å) for monoclinic [H2NEt2][DNT].

| | | | |
|---|---|---|---|
| C1-N1 | 1.3308(12) | C1-N2 | 1.3349(12) |
| C1-N4 | 1.4513(11) | N1-C2 | 1.3319(12) |
| O1-N4 | 1.2259(11) | C2-N3 | 1.3346(12) |
| C2-N5 | 1.4516(11) | N2-N3 | 1.3602(11) |
| O2-N4 | 1.2317(11) | C3-N6 | 1.4941(12) |
| C3-C4 | 1.5103(16) | C3-H3A | 0.99 |
| C3-H3B | 0.99 | O3-N5 | 1.2228(11) |
| C4-H4A | 0.98 | C4-H4B | 0.98 |
| C4-H4C | 0.98 | O4-N5 | 1.2294(11) |
| C5-N6 | 1.4952(12) | C5-C6 | 1.5092(15) |
| C5-H5A | 0.99 | C5-H5B | 0.99 |
| C6-H6A | 0.98 | C6-H6B | 0.98 |
| C6-H6C | 0.98 | N6-H2N | 0.900(11) |
| N6-H1N | 0.900(11) | | |

Table S- 91: Bond angles (°) for **monoclinic [H2NEt2][**DNT].

| | | | |
|---|---|---|---|
| N1-C1-N2 | 117.28(8) | N1-C1-N4 | 121.96(8) |
| N2-C1-N4 | 120.76(8) | C1-N1-C2 | 97.60(7) |
| N1-C2-N3 | 117.22(8) | N1-C2-N5 | 122.09(8) |
| N3-C2-N5 | 120.68(8) | C1-N2-N3 | 103.92(7) |
| N6-C3-C4 | 110.51(9) | N6-C3-H3A | 109.5 |
| C4-C3-H3A | 109.5 | N6-C3-H3B | 109.5 |
| C4-C3-H3B | 109.5 | H3A-C3-H3B | 108.1 |
| C2-N3-N2 | 103.97(7) | C3-C4-H4A | 109.5 |
| C3-C4-H4B | 109.5 | H4A-C4-H4B | 109.5 |
| C3-C4-H4C | 109.5 | H4A-C4-H4C | 109.5 |
| H4B-C4-H4C | 109.5 | O1-N4-O2 | 125.04(8) |
| O1-N4-C1 | 117.69(8) | O2-N4-C1 | 117.27(8) |
| N6-C5-C6 | 110.58(8) | N6-C5-H5A | 109.5 |
| C6-C5-H5A | 109.5 | N6-C5-H5B | 109.5 |
| C6-C5-H5B | 109.5 | H5A-C5-H5B | 108.1 |
| O3-N5-O4 | 124.89(8) | O3-N5-C2 | 118.05(8) |
| O4-N5-C2 | 117.06(8) | C5-C6-H6A | 109.5 |
| C5-C6-H6B | 109.5 | H6A-C6-H6B | 109.5 |
| C5-C6-H6C | 109.5 | H6A-C6-H6C | 109.5 |
| H6B-C6-H6C | 109.5 | C3-N6-C5 | 113.71(8) |
| C3-N6-H2N | 109.1(8) | C5-N6-H2N | 109.0(8) |
| C3-N6-H1N | 109.0(8) | C5-N6-H1N | 108.6(8) |
| H2N-N6-H1N | 107.2(11) | | |

Table S- 92: Torsion angles (°) for **monoclinic [H2NEt2][**DNT].

| | | | |
|---|---|---|---|
| N2-C1-N1-C2 | -0.22(10) | N4-C1-N1-C2 | -179.34(8) |
| C1-N1-C2-N3 | 0.07(10) | C1-N1-C2-N5 | 179.68(8) |
| N1-C1-N2-N3 | 0.29(11) | N4-C1-N2-N3 | 179.42(8) |
| N1-C2-N3-N2 | 0.09(10) | N5-C2-N3-N2 | -179.53(8) |
| C1-N2-N3-C2 | -0.21(9) | N1-C1-N4-O1 | -5.46(13) |
| N2-C1-N4-O1 | 175.46(9) | N1-C1-N4-O2 | 174.24(9) |
| N2-C1-N4-O2 | -4.85(13) | N1-C2-N5-O3 | -4.36(13) |
| N3-C2-N5-O3 | 175.25(8) | N1-C2-N5-O4 | 176.46(8) |
| N3-C2-N5-O4 | -3.93(13) | C4-C3-N6-C5 | -179.28(8) |
| C6-C5-N6-C3 | 168.42(8) | | |

Table S- 93: Anisotropic atomic displacement parameters (Å$^2$) for **monoclinic [H2NEt2]+**[DNT].The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0173(4) | 0.0164(4) | 0.0154(4) | -0.0007(3) | 0.0032(3) | -0.0013(3) |
| N1 | 0.0188(4) | 0.0152(4) | 0.0178(4) | -0.0002(3) | 0.0028(3) | -0.0009(3) |
| O1 | 0.0477(5) | 0.0246(4) | 0.0224(4) | -0.0060(3) | 0.0103(3) | 0.0029(3) |
| C2 | 0.0161(4) | 0.0155(4) | 0.0160(4) | 0.0012(3) | 0.0018(3) | -0.0016(3) |
| N2 | 0.0194(4) | 0.0162(4) | 0.0156(3) | 0.0007(3) | 0.0023(3) | -0.0003(3) |
| O2 | 0.0417(4) | 0.0298(4) | 0.0198(3) | 0.0074(3) | 0.0074(3) | 0.0070(3) |
| C3 | 0.0252(5) | 0.0210(5) | 0.0376(6) | 0.0065(4) | 0.0111(4) | -0.0013(4) |
| N3 | 0.0197(4) | 0.0165(4) | 0.0152(3) | 0.0004(3) | 0.0022(3) | -0.0001(3) |
| O3 | 0.0337(4) | 0.0173(3) | 0.0281(4) | 0.0068(3) | 0.0029(3) | -0.0004(3) |
| C4 | 0.0224(5) | 0.0246(5) | 0.0588(8) | -0.0121(5) | 0.0011(5) | -0.0034(4) |
| N4 | 0.0241(4) | 0.0214(4) | 0.0167(4) | -0.0003(3) | 0.0048(3) | -0.0014(3) |
| O4 | 0.0425(4) | 0.0301(4) | 0.0165(3) | 0.0002(3) | 0.0045(3) | 0.0047(3) |
| C5 | 0.0317(5) | 0.0203(5) | 0.0163(4) | -0.0003(3) | -0.0046(4) | 0.0023(4) |
| N5 | 0.0199(4) | 0.0196(4) | 0.0186(4) | 0.0028(3) | 0.0018(3) | -0.0014(3) |
| C6 | 0.0232(5) | 0.0275(5) | 0.0344(6) | -0.0048(4) | -0.0038(4) | -0.0005(4) |
| N6 | 0.0202(4) | 0.0143(3) | 0.0142(3) | 0.0003(3) | 0.0026(3) | 0.0010(3) |

Table S- 94**:** Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å$^2$) for **monoclinic [H2NEt2]+**[DNT].

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H3A | 0.1110 | 0.2477 | 0.3374 | 0.033 |
| H3B | 0.2242 | 0.0962 | 0.3206 | 0.033 |
| H4A | 0.2552 | 0.2287 | 0.4596 | 0.054 |
| H4B | 0.4409 | 0.2208 | 0.4132 | 0.054 |
| H4C | 0.3585 | 0.0720 | 0.4458 | 0.054 |
| H5A | -0.1220 | 0.0000 | 0.2678 | 0.028 |
| H5B | -0.2621 | 0.1307 | 0.2929 | 0.028 |
| H6A | -0.2777 | -0.1731 | 0.3352 | 0.044 |
| H6B | -0.4588 | -0.0878 | 0.2825 | 0.044 |
| H6C | -0.4086 | -0.0440 | 0.3659 | 0.044 |
| H2N | -0.0847(18) | 0.1109(13) | 0.4062(6) | 0.02 |
| H1N | 0.0185(18) | -0.0261(12) | 0.3916(6) | 0.02 |

## 2.15 Crystal Structure Report for triclinic $[H_2NEt_2][DNT]$

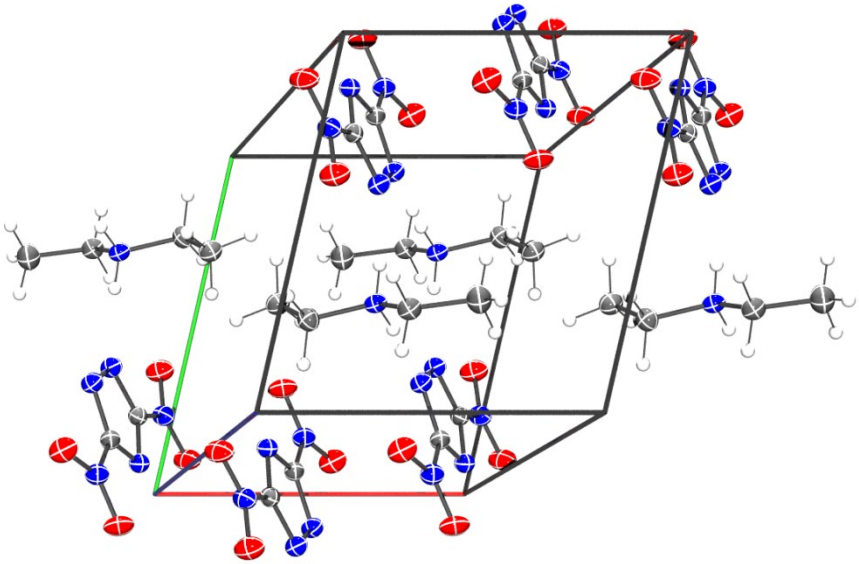

Figure S- 43: Projection of the packing of **triclinic [H2NEt2][DNT]** perpendicular to the 001 plane.

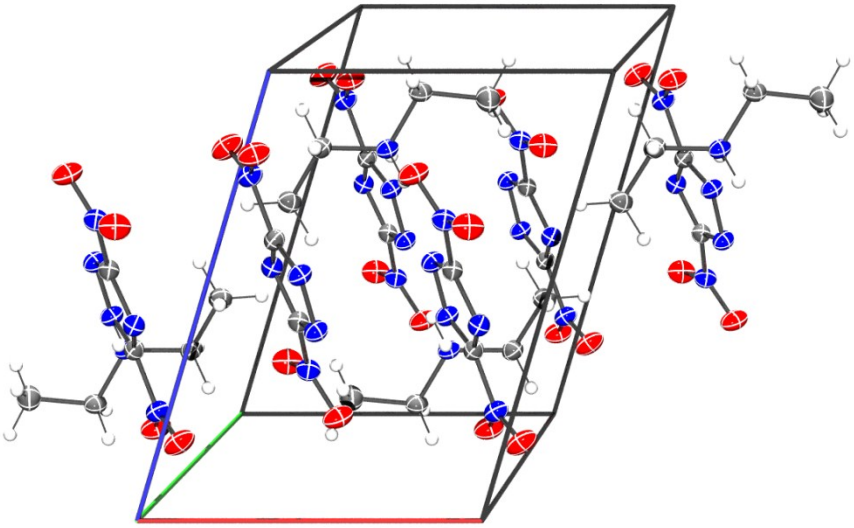

Figure S- 44: Projection of the packing of **triclinic [H2NEt2][DNT]** perpendicular to the 010 plane.

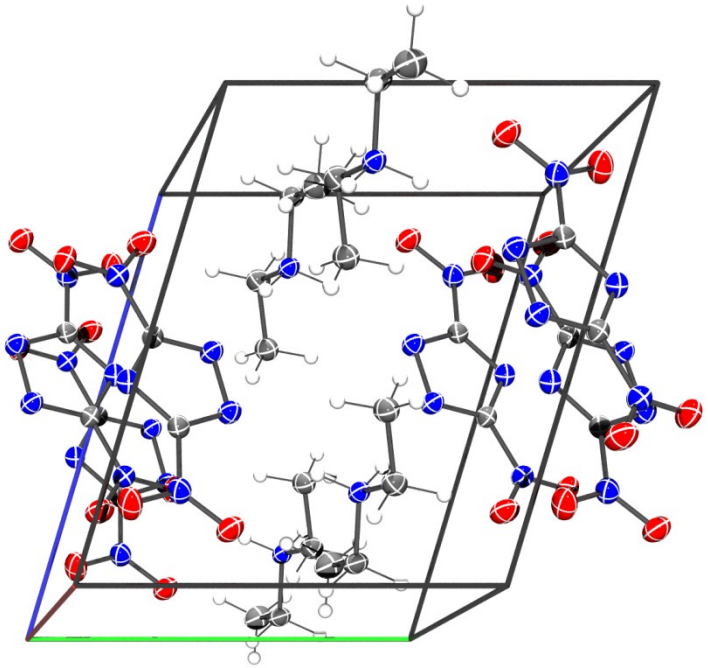

Figure S- 45: Projection of the packing of perpendicular to the 100 plane.

Table S- 95: Sample and crystal data for **triclinic [H2NEt2][DNT]**.

| | | |
|---|---|---|
| Identification code | XMK18 | |
| Chemical formula | $C_6H_{12}N_6O_4$ | |
| Formula weight | 232.20 | |
| Temperature | 100(2) K | |
| Wavelength | 1.54178 Å | |
| Crystal size | 0.132 x 0.209 x 0.257 mm | |
| Crystal habit | yellow blade | |
| Crystal system | triclinic | |
| Space group | P -1 | |
| Unit cell dimensions | a = 7.3101(9) Å | α = 73.347(3)° |
| | b = 8.1876(10) Å | β = 73.673(2)° |
| | c = 9.9470(12) Å | γ = 77.130(3)° |
| Volume | 540.79(11) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.426 $g/cm^3$ | |
| Absorption coefficient | 1.036 $mm^{-1}$ | |
| F(000) | 244 | |

Table S- 96: Data collection and structure refinement for **triclinic [H2NEt2][DNT]**.

| | |
|---|---|
| Diffractometer | Bruker APEX DUO |
| Radiation source | IuS microsource, CuKα |
| Theta range for data collection | 4.77 to 63.18° |
| Index ranges | -8<=h<=8, -9<=k<=9, -10<=l<=11 |
| Reflections collected | 8580 |
| Independent reflections | 1606 [R(int) = 0.0255] |
| Structure solution technique | direct methods |
| Structure solution program | SHELXTL XT 2013/5 (Sheldrick, 2013) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXTL XLMP 2014/1 (Bruker AXS, 2013) |
| Function minimized | $\Sigma\, w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 1606 / 0 / 153 |
| Goodness-of-fit on $F^2$ | 1.029 |
| Final R indices | 1486 data; I>2σ(I) R1 = 0.0267, wR2 = 0.0671 |
| | all data R1 = 0.0292, wR2 = 0.0689 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0318P)^2+0.1977P]$ where $P=(F_o^2+2F_c^2)/3$ |
| Largest diff. peak and hole | 0.135 and -0.153 eÅ$^{-3}$ |
| R.M.S. deviation from mean | 0.032 eÅ$^{-3}$ |

Table S- 97: Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for **triclinic [H2NEt2][DNT]**.U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| C1 | 0.30428(18) | 0.96776(15) | 0.44942(13) | 0.0203(3) |
| C2 | 0.19128(18) | 0.85170(16) | 0.65347(13) | 0.0205(3) |
| N1 | 0.17401(15) | 0.00668(13) | 0.56371(11) | 0.0225(3) |
| N2 | 0.07672(16) | 0.81592(14) | 0.80045(12) | 0.0253(3) |
| N3 | 0.31868(15) | 0.72668(13) | 0.60306(11) | 0.0232(3) |
| N4 | 0.39540(16) | 0.80537(13) | 0.46418(11) | 0.0229(3) |
| N5 | 0.34971(16) | 0.09380(14) | 0.31357(11) | 0.0245(3) |
| O1 | 0.95924(14) | 0.93369(12) | 0.84262(10) | 0.0346(3) |
| O2 | 0.10349(14) | 0.66748(12) | 0.87414(10) | 0.0324(3) |
| O3 | 0.25239(15) | 0.23739(12) | 0.30009(10) | 0.0329(3) |
| O4 | 0.48527(14) | 0.04807(12) | 0.21908(10) | 0.0336(3) |
| C3 | 0.3960(2) | 0.6689(2) | 0.11641(16) | 0.0342(4) |
| C4 | 0.59929(19) | 0.69976(17) | 0.09498(13) | 0.0246(3) |
| C5 | 0.84965(19) | 0.69389(17) | 0.22467(14) | 0.0253(3) |
| C6 | 0.9130(2) | 0.61250(17) | 0.36410(14) | 0.0268(3) |
| N6 | 0.65847(16) | 0.64737(14) | 0.23511(11) | 0.0211(3) |

Table S- 98: Bond lengths (Å) for **triclinic [H2NEt2][DNT]**.

| | | | |
|---|---|---|---|
| C1-N1 | 1.3283(16) | C1-N4 | 1.3348(16) |
| C1-N5 | 1.4500(17) | C2-N1 | 1.3289(16) |
| C2-N3 | 1.3317(16) | C2-N2 | 1.4492(17) |
| N2-O1 | 1.2262(14) | N2-O2 | 1.2316(14) |
| N3-N4 | 1.3613(15) | N5-O3 | 1.2235(14) |
| N5-O4 | 1.2322(14) | C3-C4 | 1.509(2) |
| C4-N6 | 1.4926(17) | C5-N6 | 1.4973(18) |
| C5-C6 | 1.5086(19) | | |

Table S- 99: Bond angles (°) for **triclinic [H2NEt2][DNT]**.

| | | | |
|---|---|---|---|
| N1-C1-N4 | 117.11(11) | N1-C1-N5 | 122.62(11) |
| N4-C1-N5 | 120.27(11) | N1-C2-N3 | 117.35(11) |
| N1-C2-N2 | 122.51(11) | N3-C2-N2 | 120.14(11) |
| C1-N1-C2 | 97.75(10) | O1-N2-O2 | 124.50(11) |
| O1-N2-C2 | 118.33(11) | O2-N2-C2 | 117.16(10) |
| C2-N3-N4 | 103.83(10) | C1-N4-N3 | 103.96(10) |
| O3-N5-O4 | 124.41(11) | O3-N5-C1 | 118.42(11) |
| O4-N5-C1 | 117.17(10) | N6-C4-C3 | 110.90(11) |
| N6-C5-C6 | 110.30(11) | C4-N6-C5 | 113.74(10) |

Table S- 100: Anisotropic atomic displacement parameters ($Å^2$) for **triclinic [H2NEt2][DNT]**.The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0205(7) | 0.0192(6) | 0.0210(7) | -0.0038(5) | -0.0052(5) | -0.0029(5) |
| C2 | 0.0198(7) | 0.0204(6) | 0.0215(6) | -0.0062(5) | -0.0032(5) | -0.0038(5) |
| N1 | 0.0224(6) | 0.0200(6) | 0.0249(6) | -0.0063(5) | -0.0046(5) | -0.0031(5) |
| N2 | 0.0265(6) | 0.0235(6) | 0.0246(6) | -0.0079(5) | -0.0001(5) | -0.0055(5) |
| N3 | 0.0233(6) | 0.0217(6) | 0.0208(6) | -0.0033(4) | -0.0018(4) | -0.0024(5) |
| N4 | 0.0232(6) | 0.0209(5) | 0.0209(6) | -0.0027(4) | -0.0026(4) | -0.0020(5) |
| N5 | 0.0282(6) | 0.0219(6) | 0.0224(6) | -0.0039(5) | -0.0065(5) | -0.0032(5) |
| O1 | 0.0356(6) | 0.0266(5) | 0.0354(6) | -0.0140(4) | 0.0080(4) | -0.0043(4) |
| O2 | 0.0399(6) | 0.0251(5) | 0.0240(5) | -0.0012(4) | -0.0009(4) | -0.0029(4) |
| O3 | 0.0442(6) | 0.0187(5) | 0.0315(5) | -0.0022(4) | -0.0101(4) | 0.0010(4) |
| O4 | 0.0366(6) | 0.0314(5) | 0.0232(5) | -0.0021(4) | 0.0009(4) | -0.0016(4) |
| C3 | 0.0324(8) | 0.0376(8) | 0.0317(8) | -0.0019(6) | -0.0095(6) | -0.0092(7) |
| C4 | 0.0276(8) | 0.0247(7) | 0.0191(7) | -0.0018(5) | -0.0052(5) | -0.0040(6) |
| C5 | 0.0242(7) | 0.0279(7) | 0.0229(7) | -0.0060(5) | -0.0021(5) | -0.0068(6) |
| C6 | 0.0281(7) | 0.0263(7) | 0.0254(7) | -0.0072(6) | -0.0064(6) | -0.0014(6) |
| N6 | 0.0231(6) | 0.0183(6) | 0.0181(6) | -0.0030(5) | -0.0017(5) | -0.0014(5) |

Table S- 101: Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å$^2$) for **triclinic [H2NEt2][DNT]**.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H3B | 0.3867 | 0.5472 | 0.1633 | 0.051 |
| H3C | 0.3630 | 0.6978 | 0.0226 | 0.051 |
| H3A | 0.3063 | 0.7415 | 0.1773 | 0.051 |
| H4B | 0.6887 | 0.6329 | 0.0277 | 0.03 |
| H4A | 0.6073 | 0.8236 | 0.0514 | 0.03 |
| H5A | 0.8394 | 0.8209 | 0.2038 | 0.03 |
| H5B | 0.9470 | 0.6533 | 0.1445 | 0.03 |
| H6B | 1.0273 | 0.6582 | 0.3615 | 0.04 |
| H6C | 0.9443 | 0.4871 | 0.3763 | 0.04 |
| H6A | 0.8085 | 0.6393 | 0.4450 | 0.04 |
| H1 | 0.569(2) | 0.700(2) | 0.3006(17) | 0.032 |
| H2 | 0.662(2) | 0.532(2) | 0.2719(17) | 0.032 |

## 2.16 Crystal Structure Report for $[C_5H_6N][DNT]$

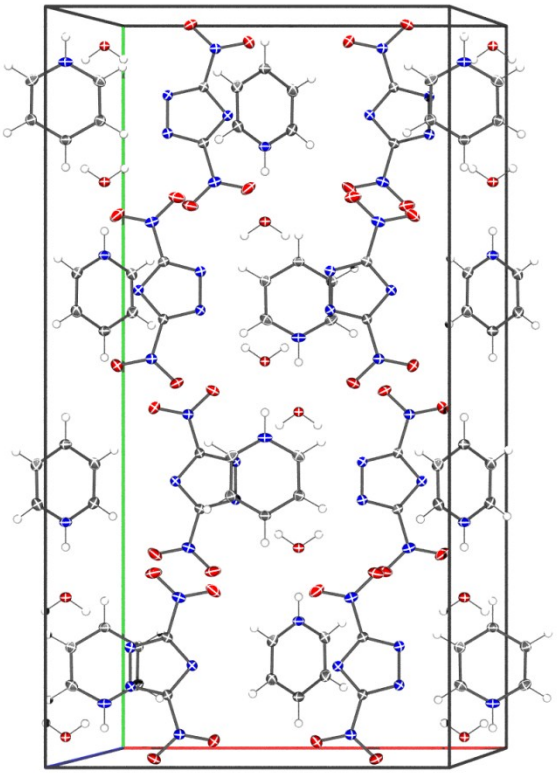

Figure S- 46: Projection of the packing of **[C5H6N][DNT]** perpendicular to the 001 plane.

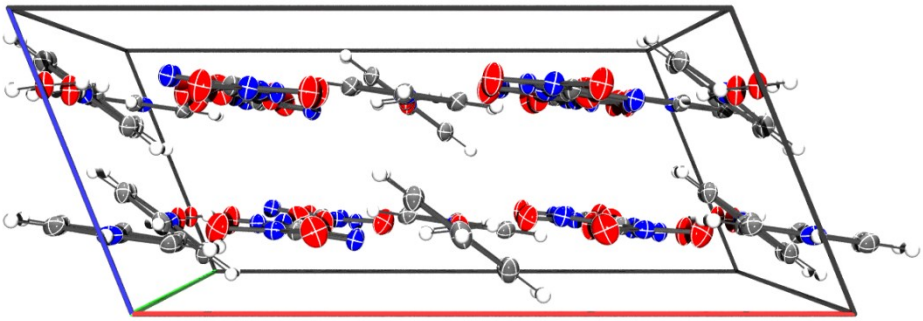

Figure S- 47: Projection of the packing of **[C5H6N][DNT]** perpendicular to the 010 plane.

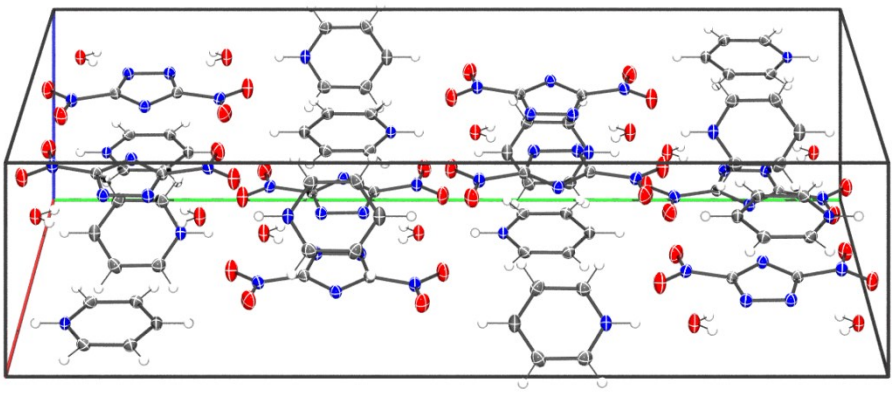

Figure S- 48: Projection of the packing of **[C5H6N][DNT]** perpendicular to the 100 plane.

Table S- 102: Sample and crystal data for **[C5H6N][DNT]**.

| | | |
|---|---|---|
| Identification code | PyrDNT | |
| Chemical formula | $C_7H_8N_6O_5$ | |
| Formula weight | 256.19 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.200 x 0.361 x 0.485 mm | |
| Crystal habit | clear orange prism | |
| Crystal system | monoclinic | |
| Space group | C 1 2/c 1 | |
| Unit cell dimensions | a = 13.9051(6) Å | α = 90° |
| | b = 26.2532(12) Å | β = 111.9480(7)° |
| | c = 6.3689(3) Å | γ = 90° |
| Volume | 2156.48(17) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.578 $g/cm^3$ | |
| Absorption coefficient | 0.136 $mm^{-1}$ | |
| F(000) | 1056 | |

Table S- 103: Data collection and structure refinement for **[C5H6N][DNT]**.

| | |
|---|---|
| Diffractometer | Bruker APEX DUO |
| Radiation source | fine-focus tube, MoKα |
| Theta range for data collection | 1.55 to 30.55° |
| Index ranges | -19<=h<=19, -37<=k<=36, -9<=l<=9 |
| Reflections collected | 26448 |
| Independent reflections | 3279 [R(int) = 0.0274] |
| Coverage of independent reflections | 99.0% |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.9730 and 0.9370 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXTL XT 2013/6 (Sheldrick, 2013) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXTL XLMP 2014/1 (Bruker AXS, 2013) |
| Function minimized | $\Sigma\, w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 3279 / 0 / 174 |
| Goodness-of-fit on $F^2$ | 1.064 |
| Final R indices | 2729 data; I>2σ(I) R1 = 0.0345, wR2 = 0.0974 |
| | all data R1 = 0.0425, wR2 = 0.1042 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0581P)^2+0.7631P]$ where $P=(F_o^2+2F_c^2)/3$ |
| Largest diff. peak and hole | 0.400 and -0.271 eÅ$^{-3}$ |
| R.M.S. deviation from mean | 0.048 eÅ$^{-3}$ |

Table S- 104: Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for **[C5H6N][DNT]**.U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| C1 | 0.24371(7) | 0.33320(3) | 0.23954(14) | 0.01535(17) |
| C2 | 0.24375(6) | 0.40971(3) | 0.24424(14) | 0.01510(17) |
| C3 | 0.04673(7) | 0.34465(3) | 0.62966(15) | 0.02008(18) |
| C4 | 0.04841(7) | 0.39712(4) | 0.62805(16) | 0.02154(19) |
| C5 | 0.0 | 0.42351(5) | 0.75 | 0.0216(3) |
| C6 | 0.57873(7) | 0.40782(3) | 0.72123(14) | 0.01873(18) |
| C7 | 0.58060(7) | 0.35528(3) | 0.72116(14) | 0.01768(17) |
| C8 | 0.5 | 0.32875(5) | 0.75 | 0.0173(2) |
| N1 | 0.18551(6) | 0.37115(3) | 0.26559(13) | 0.01647(16) |
| N2 | 0.32959(6) | 0.34592(3) | 0.20560(13) | 0.01778(16) |
| N3 | 0.32984(6) | 0.39769(3) | 0.20870(13) | 0.01712(16) |
| N4 | 0.21586(6) | 0.28019(3) | 0.24785(12) | 0.01905(17) |
| N5 | 0.21609(6) | 0.46257(3) | 0.25740(13) | 0.01876(16) |
| N6 | 0.0 | 0.31993(4) | 0.75 | 0.0186(2) |
| N7 | 0.5 | 0.43253(4) | 0.75 | 0.0185(2) |
| O1 | 0.13107(6) | 0.27141(3) | 0.25770(14) | 0.03168(19) |
| O2 | 0.27825(6) | 0.24766(3) | 0.24498(14) | 0.03254(19) |
| O3 | 0.13245(6) | 0.47157(3) | 0.27208(14) | 0.02777(18) |
| O4 | 0.27912(6) | 0.49495(3) | 0.25281(14) | 0.02775(18) |
| O1W | 0.5 | 0.28002(4) | 0.25 | 0.0246(2) |
| O2W | 0.5 | 0.46591(3) | 0.25 | 0.01942(19) |

Table S- 105: Bond lengths (Å) for **[C5H6N][DNT]**.

| | | | |
|---|---|---|---|
| C1-N1 | 1.3324(11) | C1-N2 | 1.3331(11) |
| C1-N4 | 1.4509(11) | C2-N1 | 1.3347(10) |
| C2-N3 | 1.3365(11) | C2-N5 | 1.4509(11) |
| C3-N6 | 1.3429(10) | C3-C4 | 1.3777(13) |
| C3-H3 | 0.95 | C4-C5 | 1.3882(11) |
| C4-H4 | 0.95 | C5-C4 | 1.3882(11) |
| C5-H5 | 0.95 | C6-N7 | 1.3426(10) |
| C6-C7 | 1.3797(12) | C6-H6 | 0.95 |
| C7-C8 | 1.3889(10) | C7-H7 | 0.95 |
| C8-C7 | 1.3889(10) | C8-H8 | 0.95 |
| N2-N3 | 1.3592(11) | N4-O2 | 1.2225(11) |
| N4-O1 | 1.2257(11) | N5-O3 | 1.2241(10) |
| N5-O4 | 1.2290(10) | N6-C3 | 1.3428(10) |
| N6-H1 | 0.866(18) | N7-C6 | 1.3426(10) |
| N7-H2 | 0.880(18) | O1W-H1W | 0.868(13) |
| O2W-H2W | 0.837(12) | | |

Table S- 106: Bond angles (°) for **[C5H6N][DNT]**.

| | | | |
|---|---|---|---|
| N1-C1-N2 | 117.10(8) | N1-C1-N4 | 121.99(8) |
| N2-C1-N4 | 120.91(8) | N1-C2-N3 | 117.00(8) |
| N1-C2-N5 | 122.38(7) | N3-C2-N5 | 120.61(7) |
| N6-C3-C4 | 120.04(8) | N6-C3-H3 | 120.0 |
| C4-C3-H3 | 120.0 | C3-C4-C5 | 118.80(8) |
| C3-C4-H4 | 120.6 | C5-C4-H4 | 120.6 |
| C4-C5-C4 | 120.12(12) | C4-C5-H5 | 119.9 |
| C4-C5-H5 | 119.9 | N7-C6-C7 | 119.97(8) |
| N7-C6-H6 | 120.0 | C7-C6-H6 | 120.0 |
| C6-C7-C8 | 119.02(8) | C6-C7-H7 | 120.5 |
| C8-C7-H7 | 120.5 | C7-C8-C7 | 119.80(11) |
| C7-C8-H8 | 120.1 | C7-C8-H8 | 120.1 |
| C1-N1-C2 | 97.73(7) | C1-N2-N3 | 104.22(7) |
| C2-N3-N2 | 103.95(7) | O2-N4-O1 | 124.82(8) |
| O2-N4-C1 | 117.97(8) | O1-N4-C1 | 117.21(8) |
| O3-N5-O4 | 125.08(8) | O3-N5-C2 | 117.96(7) |
| O4-N5-C2 | 116.96(7) | C3-N6-C3 | 122.19(11) |
| C3-N6-H1 | 118.90(5) | C3-N6-H1 | 118.91(5) |
| C6-N7-C6 | 122.23(11) | C6-N7-H2 | 118.89(5) |
| C6-N7-H2 | 118.88(5) | | |

Table S- 107: Anisotropic atomic displacement parameters (Å$^2$) for **[C5H6N][DNT]**.The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0164(4) | 0.0135(4) | 0.0160(4) | 0.0004(3) | 0.0059(3) | -0.0013(3) |
| C2 | 0.0146(4) | 0.0143(4) | 0.0174(4) | -0.0002(3) | 0.0071(3) | -0.0006(3) |
| C3 | 0.0186(4) | 0.0205(4) | 0.0228(4) | -0.0008(3) | 0.0097(3) | 0.0027(3) |
| C4 | 0.0197(4) | 0.0199(4) | 0.0277(5) | 0.0055(3) | 0.0118(4) | 0.0005(3) |
| C5 | 0.0184(6) | 0.0136(5) | 0.0319(7) | 0 | 0.0084(5) | 0 |
| C6 | 0.0229(4) | 0.0178(4) | 0.0166(4) | 0.0001(3) | 0.0086(3) | -0.0042(3) |
| C7 | 0.0198(4) | 0.0171(4) | 0.0185(4) | -0.0009(3) | 0.0100(3) | 0.0002(3) |
| C8 | 0.0213(6) | 0.0126(5) | 0.0203(5) | 0 | 0.0102(5) | 0 |
| N1 | 0.0157(3) | 0.0149(3) | 0.0195(3) | 0.0004(2) | 0.0074(3) | -0.0010(2) |
| N2 | 0.0180(3) | 0.0153(3) | 0.0218(4) | -0.0001(3) | 0.0095(3) | -0.0002(3) |
| N3 | 0.0171(3) | 0.0148(3) | 0.0218(3) | -0.0002(3) | 0.0099(3) | -0.0007(3) |
| N4 | 0.0234(4) | 0.0151(3) | 0.0174(3) | 0.0007(3) | 0.0062(3) | -0.0030(3) |
| N5 | 0.0198(4) | 0.0145(3) | 0.0238(4) | 0.0002(3) | 0.0102(3) | 0.0000(3) |
| N6 | 0.0190(5) | 0.0120(5) | 0.0230(5) | 0 | 0.0059(4) | 0 |
| N7 | 0.0273(6) | 0.0111(4) | 0.0158(5) | 0 | 0.0066(4) | 0 |
| O1 | 0.0351(4) | 0.0219(4) | 0.0451(5) | -0.0026(3) | 0.0231(4) | -0.0113(3) |
| O2 | 0.0335(4) | 0.0153(3) | 0.0465(5) | 0.0019(3) | 0.0122(4) | 0.0045(3) |
| O3 | 0.0244(4) | 0.0209(3) | 0.0438(4) | -0.0006(3) | 0.0195(3) | 0.0040(3) |
| O4 | 0.0299(4) | 0.0155(3) | 0.0429(4) | -0.0006(3) | 0.0195(3) | -0.0056(3) |
| O1W | 0.0221(5) | 0.0129(4) | 0.0428(6) | 0 | 0.0169(4) | 0 |
| O2W | 0.0168(4) | 0.0128(4) | 0.0313(5) | 0 | 0.0120(4) | 0 |

Table S- 108: Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for **[C5H6N][DNT]**.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H3 | 0.0787 | 0.3260 | 0.5456 | 0.024 |
| H4 | 0.0821 | 0.4149 | 0.5450 | 0.026 |
| H5 | 0.0000 | 0.4597 | 0.7500 | 0.026 |
| H6 | 0.6331 | 0.4265 | 0.7009 | 0.022 |
| H7 | 0.6362 | 0.3375 | 0.7017 | 0.021 |
| H8 | 0.5000 | 0.2926 | 0.7500 | 0.021 |
| H1 | 0.0000 | 0.2869(7) | 0.7500 | 0.022 |
| H2 | 0.5000 | 0.4661(7) | 0.7500 | 0.022 |
| H1W | 0.4460(10) | 0.2985(5) | 0.235(2) | 0.029 |
| H2W | 0.5513(9) | 0.4477(5) | 0.263(2) | 0.023 |

# 2.17 Crystal Structure Report for [CH4N5][DNT]

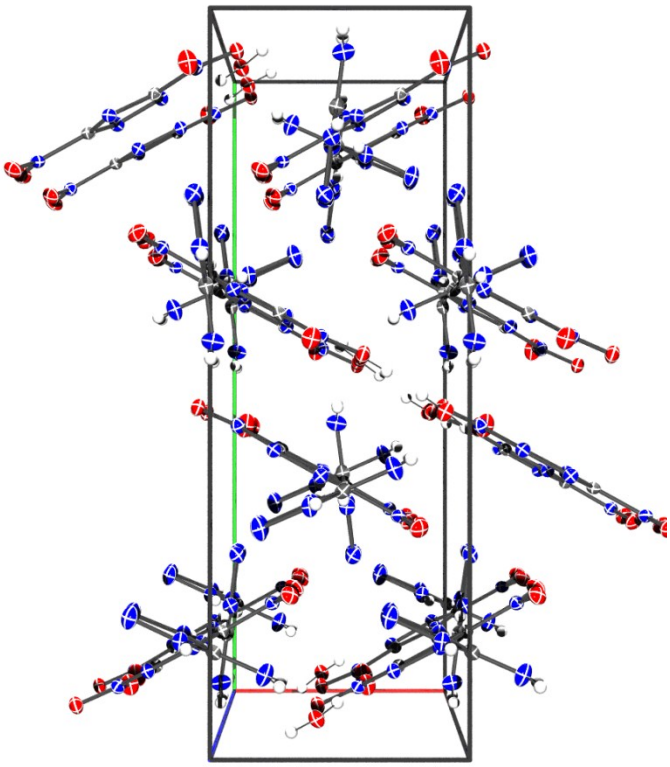

Figure S- 49 : Projection of the packing of **[CH4N5][DNT]** perpendicular to the 001 plane.

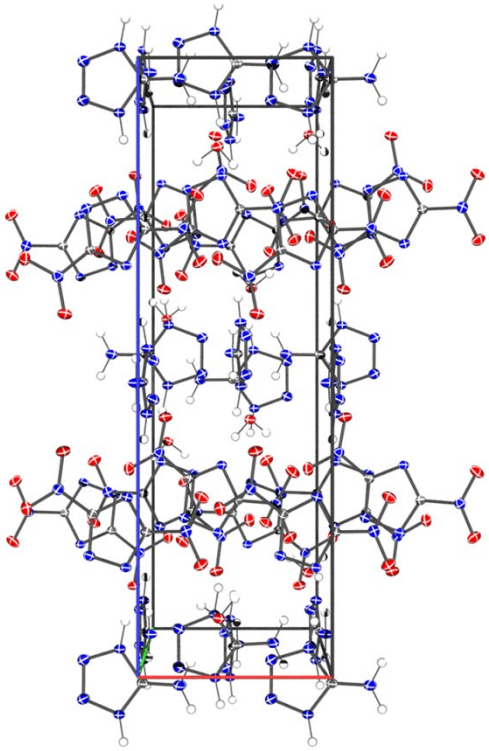

Figure S- 50: Projection of the packing of **[CH4N5][DNT]** perpendicular to the 010 plane.

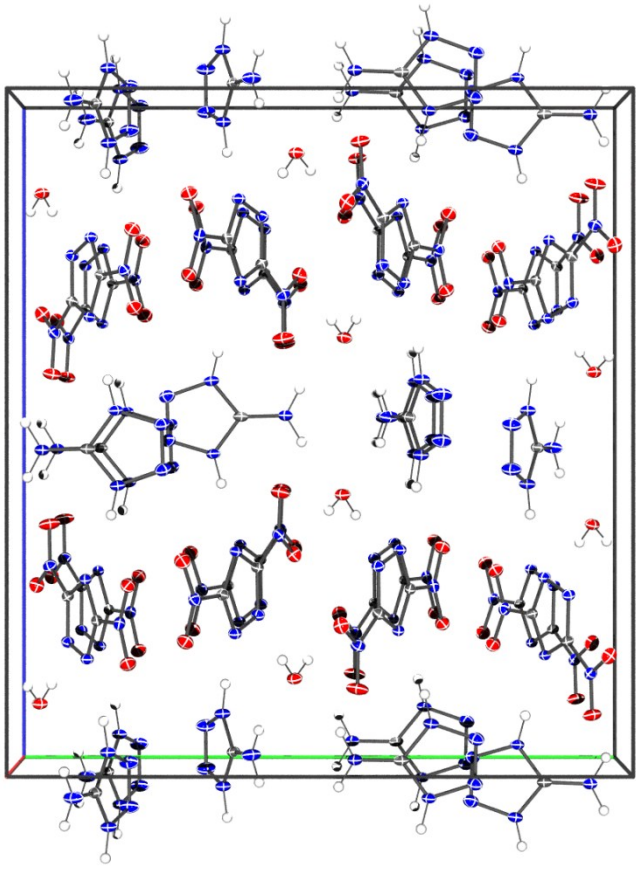

Figure S- 51 : Projection of the packing of **[CH4N5][DNT]** perpendicular to the 100 plane.

A clear colourless prism-like specimen of $C_3H_6N_{10}O_5$, approximate dimensions 0.090 mm x 0.120 mm x 0.230 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker APEX DUO system equipped with a TRIUMPH curved-crystal monochromator and a MoKα fine-focus tube (λ = 0.71073 Å).

The total exposure time was 10.00 hours. The frames were integrated with the Bruker SAINT software package using a SAINT V8.34A (Bruker AXS, 2013) algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 35316 reflections to a maximum θ angle of 30.51° (0.70 Å resolution), of which 6290 were independent (average redundancy 5.615, completeness = 99.6%, $R_{int}$ = 3.44%, $R_{sig}$ = 2.93%) and 5417 (86.12%) were greater than $2\sigma(F^2)$. The final cell constants of a = 6.0692(3) Å, b = 17.6181(8) Å, c = 19.4400(9) Å, volume = 2078.68(17) $Å^3$, are based upon the refinement of the XYZ-centroids of 9366 reflections above 20 σ(I) with 4.624° < 2θ < 60.98°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.852. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9660 and 0.9860.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 21 21 21, with Z = 8 for the formula unit, $C_3H_6N_{10}O_5$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 373 variables converged at R1 = 3.72%, for the observed data and wR2 = 8.36% for all data. The goodness-of-fit was 1.060. The largest peak in the final difference electron density synthesis was 0.296 $e^-/Å^3$ and the largest hole was -0.318 $e^-/Å^3$ with an RMS deviation of 0.060 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.676 $g/cm^3$ and F(000), 1072 $e^-$.

Table S- 109: Sample and crystal data for **[CH4N5][DNT]**.

| | | |
|---|---|---|
| Identification code | ATDNT | |
| Chemical formula | $C_3H_6N_{10}O_5$ | |
| Formula weight | 262.18 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.090 x 0.120 x 0.230 mm | |
| Crystal habit | clear colourless prism | |
| Crystal system | orthorhombic | |
| Space group | P 21 21 21 | |
| Unit cell dimensions | a = 6.0692(3) Å | α = 90° |
| | b = 17.6181(8) Å | β = 90° |
| | c = 19.4400(9) Å | γ = 90° |
| Volume | 2078.68(17) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.676 $g/cm^3$ | |
| Absorption coefficient | 0.153 $mm^{-1}$ | |
| F(000) | 1072 | |

Table S- 110: Data collection and structure refinement for **[CH4N5][DNT]**.

| | |
|---|---|
| Diffractometer | Bruker APEX DUO |
| Radiation source | fine-focus tube, MoKα |
| Theta range for data collection | 1.56 to 30.51° |
| Index ranges | -8<=h<=8, -25<=k<=25, -27<=l<=27 |
| Reflections collected | 35316 |
| Independent reflections | 6290 [R(int) = 0.0344] |
| Coverage of independent reflections | 99.6% |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.9860 and 0.9660 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXTL XT 2013/6 (Sheldrick, 2013) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXL-2014 (Sheldrick, 2014) |
| Function minimized | $\Sigma\, w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 6290 / 0 / 373 |
| Goodness-of-fit on $F^2$ | 1.060 |
| Final R indices | 5417 data; I>2σ(I) R1 = 0.0372, wR2 = 0.0797 |
| | all data R1 = 0.0472, wR2 = 0.0836 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0444P)^2+0.2528P]$ where $P=(F_o^2+2F_c^2)/3$ |
| Absolute structure parameter | -0.2(4) |
| Largest diff. peak and hole | 0.296 and -0.318 eÅ$^{-3}$ |
| R.M.S. deviation from mean | 0.060 eÅ$^{-3}$ |

Table S- 111: Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for **[CH4N5][DNT]**.U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| C1 | 0.9710(3) | 0.64438(10) | 0.27244(9) | 0.0114(3) |
| C2 | 0.2484(3) | 0.59199(11) | 0.24074(9) | 0.0119(3) |
| C3 | 0.5169(3) | 0.34935(10) | 0.27161(9) | 0.0117(3) |
| C4 | 0.2419(3) | 0.40125(10) | 0.30702(9) | 0.0116(3) |
| C5 | 0.5130(3) | 0.37020(10) | 0.52366(10) | 0.0139(3) |
| C6 | 0.9890(3) | 0.64163(10) | 0.52275(10) | 0.0134(3) |
| N1 | 0.2634(3) | 0.59140(9) | 0.30905(8) | 0.0134(3) |
| N2 | 0.0763(3) | 0.62674(9) | 0.33033(7) | 0.0131(3) |
| N3 | 0.0686(3) | 0.62438(9) | 0.21390(7) | 0.0122(3) |
| N4 | 0.7621(3) | 0.68427(9) | 0.27348(8) | 0.0138(3) |
| N5 | 0.4199(3) | 0.55868(9) | 0.19874(8) | 0.0151(3) |
| N6 | 0.2197(3) | 0.40226(9) | 0.23892(8) | 0.0133(3) |
| N7 | 0.4052(3) | 0.36731(9) | 0.21547(8) | 0.0131(3) |
| N8 | 0.4254(3) | 0.36897(9) | 0.33163(7) | 0.0119(3) |
| N9 | 0.7232(3) | 0.30848(9) | 0.26778(8) | 0.0141(3) |
| N10 | 0.0761(3) | 0.43441(9) | 0.35125(8) | 0.0143(3) |
| N11 | 0.5325(3) | 0.32559(9) | 0.46805(8) | 0.0145(3) |
| N12 | 0.5581(3) | 0.25176(10) | 0.48803(8) | 0.0170(3) |
| N13 | 0.5580(3) | 0.24980(10) | 0.55358(8) | 0.0182(3) |
| N14 | 0.5303(3) | 0.32229(10) | 0.57677(8) | 0.0156(3) |
| N15 | 0.4858(3) | 0.44411(9) | 0.52530(9) | 0.0194(3) |
| N16 | 0.1101(3) | 0.65974(9) | 0.46753(8) | 0.0151(3) |
| N17 | 0.3066(3) | 0.68982(11) | 0.48829(8) | 0.0210(4) |
| N18 | 0.3083(3) | 0.69049(11) | 0.55382(8) | 0.0213(4) |
| N19 | 0.1143(3) | 0.66092(10) | 0.57657(8) | 0.0156(3) |
| N20 | 0.7913(3) | 0.61139(10) | 0.52340(10) | 0.0211(3) |
| O1 | 0.6781(2) | 0.69957(8) | 0.21751(7) | 0.0185(3) |
| O2 | 0.6826(2) | 0.69920(8) | 0.32981(7) | 0.0198(3) |
| O3 | 0.3948(3) | 0.55813(9) | 0.13646(7) | 0.0253(3) |
| O4 | 0.5813(2) | 0.53239(8) | 0.22935(7) | 0.0181(3) |
| O5 | 0.8114(2) | 0.29071(8) | 0.32264(7) | 0.0206(3) |
| O6 | 0.7969(3) | 0.29462(8) | 0.21049(7) | 0.0197(3) |
| O7 | 0.1124(3) | 0.43737(9) | 0.41296(7) | 0.0217(3) |
| O8 | 0.9082(2) | 0.45854(8) | 0.32253(7) | 0.0185(3) |
| O9 | 0.5850(3) | 0.53765(9) | 0.40768(7) | 0.0164(3) |
| O10 | 0.5921(3) | 0.54048(8) | 0.64083(7) | 0.0161(3) |

Table S- 112: Bond lengths (Å) for **[CH4N5][DNT]**.

| | | | |
|---|---|---|---|
| C1-N3 | 1.330(2) | C1-N2 | 1.331(2) |
| C1-N4 | 1.449(2) | C2-N1 | 1.331(2) |
| C2-N3 | 1.338(2) | C2-N5 | 1.447(2) |
| C3-N7 | 1.323(2) | C3-N8 | 1.338(2) |
| C3-N9 | 1.446(2) | C4-N6 | 1.331(2) |
| C4-N8 | 1.339(2) | C4-N10 | 1.447(2) |
| C5-N15 | 1.313(2) | C5-N14 | 1.338(2) |
| C5-N11 | 1.342(2) | C6-N20 | 1.313(2) |
| C6-N19 | 1.338(2) | C6-N16 | 1.340(2) |
| N1-N2 | 1.359(2) | N4-O2 | 1.225(2) |
| N4-O1 | 1.231(2) | N5-O3 | 1.220(2) |
| N5-O4 | 1.236(2) | N6-N7 | 1.362(2) |
| N9-O6 | 1.225(2) | N9-O5 | 1.234(2) |
| N10-O7 | 1.221(2) | N10-O8 | 1.237(2) |
| N11-N12 | 1.366(2) | N11-H1 | 0.90(3) |
| N12-N13 | 1.275(2) | N13-N14 | 1.365(2) |
| N14-H2 | 0.86(3) | N15-H3 | 0.89(3) |
| N15-H4 | 0.88(3) | N16-N17 | 1.366(2) |
| N16-H5 | 0.93(2) | N17-N18 | 1.274(2) |
| N18-N19 | 1.361(2) | N19-H6 | 0.89(3) |
| N20-H7 | 0.86(3) | N20-H8 | 0.86(3) |
| O9-H11 | 0.81(3) | O9-H12 | 0.87(3) |
| O10-H9 | 0.82(3) | O10-H10 | 0.87(3) |

Table S- 113: Bond angles (°) for **[CH4N5][DNT].**

| | | | |
|---|---|---|---|
| N3-C1-N2 | 116.57(16) | N3-C1-N4 | 122.00(15) |
| N2-C1-N4 | 121.42(16) | N1-C2-N3 | 116.62(17) |
| N1-C2-N5 | 120.72(17) | N3-C2-N5 | 122.67(15) |
| N7-C3-N8 | 116.43(16) | N7-C3-N9 | 121.34(15) |
| N8-C3-N9 | 122.20(16) | N6-C4-N8 | 116.45(16) |
| N6-C4-N10 | 121.02(17) | N8-C4-N10 | 122.52(15) |
| N15-C5-N14 | 128.10(18) | N15-C5-N11 | 127.69(18) |
| N14-C5-N11 | 104.21(16) | N20-C6-N19 | 127.97(18) |
| N20-C6-N16 | 127.29(18) | N19-C6-N16 | 104.74(15) |
| C2-N1-N2 | 104.07(15) | C1-N2-N1 | 104.53(14) |
| C1-N3-C2 | 98.22(14) | O2-N4-O1 | 125.43(16) |
| O2-N4-C1 | 117.45(15) | O1-N4-C1 | 117.11(15) |
| O3-N5-O4 | 125.00(17) | O3-N5-C2 | 118.25(16) |
| O4-N5-C2 | 116.75(14) | C4-N6-N7 | 104.07(15) |
| C3-N7-N6 | 104.81(14) | C3-N8-C4 | 98.24(14) |
| O6-N9-O5 | 125.26(17) | O6-N9-C3 | 117.53(15) |
| O5-N9-C3 | 117.21(15) | O7-N10-O8 | 125.27(17) |
| O7-N10-C4 | 118.41(16) | O8-N10-C4 | 116.31(15) |
| C5-N11-N12 | 109.79(14) | C5-N11-H1 | 127.4(17) |
| N12-N11-H1 | 121.9(16) | N13-N12-N11 | 108.05(17) |

| | | | |
|---|---|---|---|
| N12-N13-N14 | 107.75(17) | C5-N14-N13 | 110.19(15) |
| C5-N14-H2 | 127.(2) | N13-N14-H2 | 122.(2) |
| C5-N15-H3 | 119.3(17) | C5-N15-H4 | 118.5(17) |
| H3-N15-H4 | 121.(2) | C6-N16-N17 | 109.55(15) |
| C6-N16-H5 | 130.0(17) | N17-N16-H5 | 120.4(17) |
| N18-N17-N16 | 107.81(17) | N17-N18-N19 | 108.34(17) |
| C6-N19-N18 | 109.56(15) | C6-N19-H6 | 131.(2) |
| N18-N19-H6 | 120.(2) | C6-N20-H7 | 118.8(19) |
| C6-N20-H8 | 120.4(19) | H7-N20-H8 | 120.(2) |
| H11-O9-H12 | 103.(3) | H9-O10-H10 | 104.(3) |

Table S- 114: Anisotropic atomic displacement parameters (Å$^2$) for **[CH4N5][DNT]**.The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0132(8) | 0.0103(8) | 0.0108(8) | 0.0002(6) | -0.0006(7) | -0.0005(6) |
| C2 | 0.0117(8) | 0.0125(9) | 0.0114(8) | -0.0014(6) | 0.0001(7) | -0.0007(7) |
| C3 | 0.0127(8) | 0.0121(9) | 0.0102(7) | -0.0005(6) | 0.0002(7) | -0.0003(6) |
| C4 | 0.0120(8) | 0.0131(9) | 0.0096(7) | -0.0009(6) | -0.0003(7) | -0.0007(7) |
| C5 | 0.0130(7) | 0.0198(9) | 0.0089(7) | -0.0003(7) | 0.0003(7) | -0.0016(6) |
| C6 | 0.0151(7) | 0.0153(8) | 0.0099(7) | -0.0009(7) | -0.0007(8) | 0.0031(6) |
| N1 | 0.0145(7) | 0.0145(8) | 0.0113(7) | 0.0009(5) | -0.0012(6) | 0.0000(6) |
| N2 | 0.0148(7) | 0.0146(8) | 0.0098(6) | 0.0001(5) | -0.0003(6) | 0.0006(6) |
| N3 | 0.0143(7) | 0.0120(7) | 0.0103(6) | -0.0002(5) | -0.0012(6) | 0.0002(6) |
| N4 | 0.0146(7) | 0.0109(8) | 0.0160(7) | -0.0011(6) | -0.0008(7) | 0.0001(6) |
| N5 | 0.0141(7) | 0.0169(8) | 0.0141(7) | -0.0015(6) | 0.0003(6) | -0.0013(7) |
| N6 | 0.0133(7) | 0.0149(8) | 0.0117(7) | -0.0004(6) | -0.0009(6) | 0.0005(6) |
| N7 | 0.0146(7) | 0.0143(8) | 0.0104(7) | 0.0000(5) | -0.0009(6) | 0.0004(6) |
| N8 | 0.0136(7) | 0.0131(8) | 0.0089(6) | -0.0006(5) | -0.0001(6) | 0.0003(6) |
| N9 | 0.0142(7) | 0.0135(8) | 0.0145(7) | -0.0010(6) | -0.0010(6) | -0.0001(6) |
| N10 | 0.0145(7) | 0.0139(8) | 0.0145(7) | -0.0016(5) | 0.0011(6) | -0.0002(6) |
| N11 | 0.0168(7) | 0.0181(8) | 0.0086(7) | 0.0006(6) | 0.0006(6) | 0.0009(6) |
| N12 | 0.0177(7) | 0.0195(8) | 0.0138(8) | 0.0012(6) | 0.0019(6) | 0.0024(6) |
| N13 | 0.0185(8) | 0.0217(9) | 0.0143(7) | 0.0021(6) | 0.0027(7) | 0.0022(7) |
| N14 | 0.0175(8) | 0.0202(9) | 0.0090(7) | 0.0012(6) | 0.0008(6) | 0.0001(6) |
| N15 | 0.0295(8) | 0.0186(8) | 0.0100(6) | -0.0002(7) | 0.0005(8) | -0.0020(6) |
| N16 | 0.0149(7) | 0.0211(8) | 0.0093(7) | -0.0003(6) | 0.0001(6) | -0.0008(6) |
| N17 | 0.0169(7) | 0.0315(10) | 0.0146(8) | -0.0012(7) | 0.0012(7) | -0.0047(7) |
| N18 | 0.0168(8) | 0.0337(11) | 0.0134(8) | -0.0008(7) | 0.0014(7) | -0.0059(8) |
| N19 | 0.0149(8) | 0.0230(9) | 0.0088(7) | -0.0006(6) | -0.0001(6) | -0.0012(6) |
| N20 | 0.0185(8) | 0.0329(10) | 0.0118(7) | -0.0012(7) | -0.0007(8) | -0.0074(6) |
| O1 | 0.0215(7) | 0.0178(7) | 0.0161(6) | 0.0007(5) | -0.0054(6) | 0.0046(6) |
| O2 | 0.0218(7) | 0.0210(8) | 0.0165(7) | -0.0022(5) | 0.0065(6) | 0.0025(6) |
| O3 | 0.0237(8) | 0.0401(10) | 0.0120(6) | -0.0047(6) | 0.0025(6) | 0.0042(7) |
| O4 | 0.0134(6) | 0.0195(7) | 0.0214(7) | 0.0001(5) | -0.0015(6) | 0.0027(5) |
| O5 | 0.0227(8) | 0.0208(8) | 0.0183(7) | -0.0002(5) | -0.0083(6) | 0.0054(6) |

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| O6 | 0.0211(7) | 0.0207(8) | 0.0172(7) | -0.0022(5) | 0.0059(6) | 0.0035(6) |
| O7 | 0.0232(7) | 0.0301(8) | 0.0118(6) | -0.0034(5) | 0.0017(6) | 0.0024(6) |
| O8 | 0.0132(6) | 0.0200(7) | 0.0224(7) | -0.0025(5) | -0.0009(6) | 0.0027(6) |
| O9 | 0.0164(6) | 0.0213(7) | 0.0115(6) | 0.0003(5) | -0.0004(6) | 0.0032(6) |
| O10 | 0.0167(6) | 0.0205(8) | 0.0112(6) | -0.0014(5) | 0.0010(6) | 0.0032(6) |

Table S- 115: Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for **[CH4N5][DNT]**.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H1 | 0.509(5) | 0.3384(15) | 0.4239(13) | 0.030(7) |
| H2 | 0.516(5) | 0.3328(17) | 0.6196(15) | 0.046(9) |
| H3 | 0.489(5) | 0.4703(15) | 0.4860(14) | 0.033(7) |
| H4 | 0.490(5) | 0.4671(15) | 0.5652(14) | 0.033(7) |
| H5 | 0.081(4) | 0.6529(13) | 0.4212(12) | 0.022(6) |
| H6 | 0.091(5) | 0.6559(15) | 0.6217(14) | 0.037(8) |
| H7 | -0.268(5) | 0.5981(16) | 0.4850(15) | 0.036(8) |
| H8 | -0.270(5) | 0.5988(15) | 0.5616(15) | 0.031(7) |
| H9 | 0.510(5) | 0.5599(16) | 0.6693(15) | 0.036(8) |
| H10 | 0.694(5) | 0.5193(16) | 0.6658(14) | 0.034(8) |
| H11 | 0.675(5) | 0.5150(17) | 0.3845(16) | 0.040(9) |
| H12 | 0.502(5) | 0.5592(16) | 0.3767(14) | 0.038(8) |

# 2.18 Crystal Structure Report for $[PPh_4][DNT]$

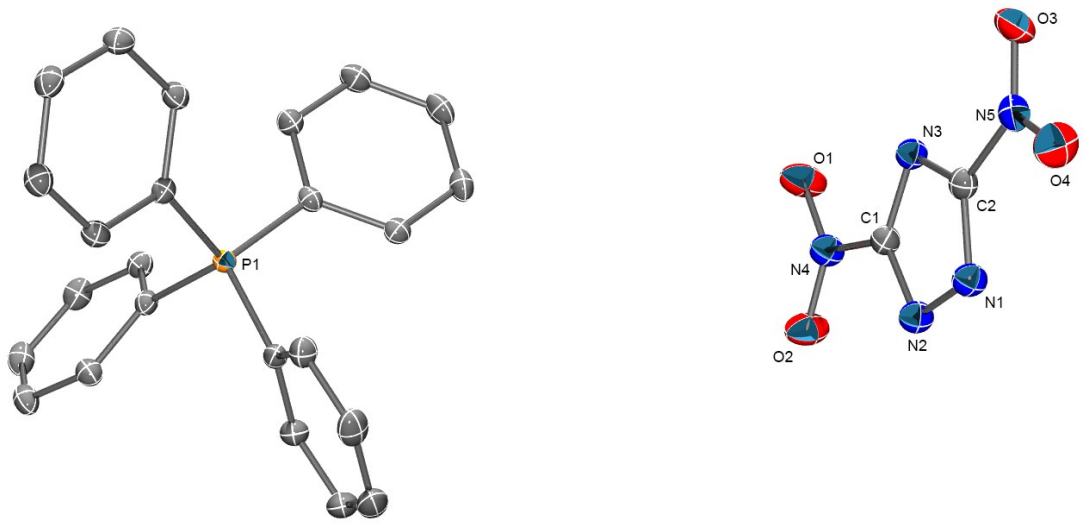


Figure S- 52: Molecular structure of **[PPh4][DNT**]. Thermal ellipsoids are shown at the 50% probability level.Hydrogen atoms were omitted for clarity.

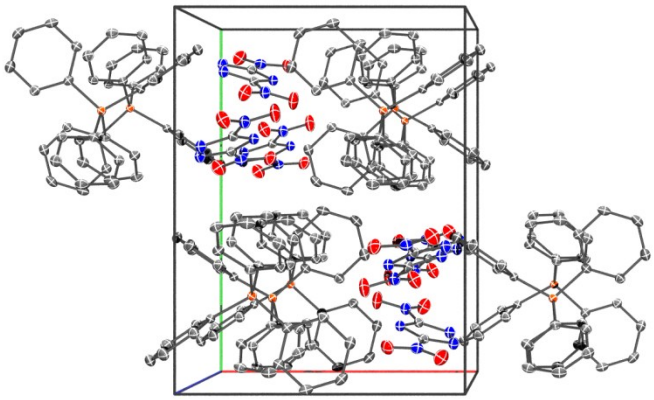

Figure S- 53: Projection of the packing of **[PPh4][DNT**] perpendicular to the 001 plane. Hydrogen atoms were omitted for clarity.

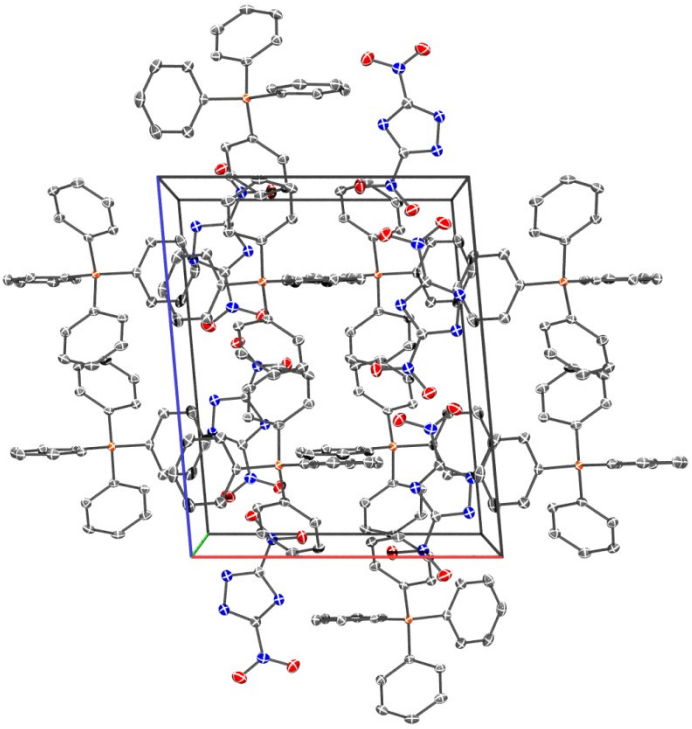

Figure S- 54: Projection of the packing of $[PPh_4][DNT]$ perpendicular to the 010 plane. Hydrogen atoms were omitted for clarity.

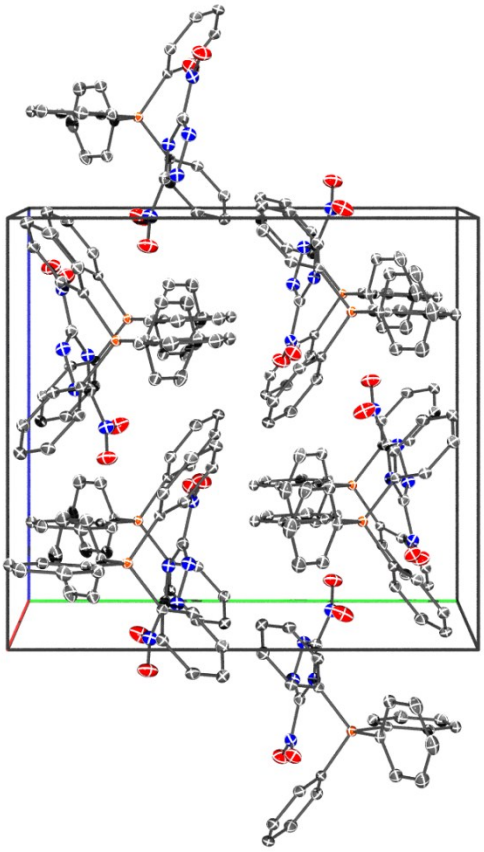

Figure S- 55: Projection of the packing of **[PPh4][DNT**] perpendicular to the 100 plane. Hydrogen atoms were omitted for clarity.

Table S- 116: Sample and crystal data for **[PPh4][DNT**].

| | | |
|---|---|---|
| Identification code | XGC2_83imp | |
| Chemical formula | $C_{26}H_{20}N_5O_4P$ | |
| Formula weight | 497.44 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.141 x 0.257 x 0.286 mm | |
| Crystal system | monoclinic | |
| Space group | P 1 21/c 1 | |
| Unit cell dimensions | a = 11.2261(5) Å | α = 90° |
| | b = 15.0086(7) Å | β = 95.0410(10)° |
| | c = 13.8078(6) Å | γ = 90° |
| Volume | 2317.45(18) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.426 $g/cm^3$ | |
| Absorption coefficient | 0.164 $mm^{-1}$ | |
| F(000) | 1032 | |

Table S- 117: Data collection and structure refinement for **[PPh4][DNT**].

| | | |
|---|---|---|
| Theta range for data collection | 1.82 to 28.50° | |
| Index ranges | -15<=h<=15, -20<=k<=20, -18<=l<=18 | |
| Reflections collected | 50180 | |
| Independent reflections | 5872 [R(int) = 0.0558] | |
| Absorption correction | multi-scan | |
| Structure solution technique | direct methods | |
| Structure solution program | SHELXTL XS 2013/1 (Bruker AXS) | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Refinement program | SHELXL-2013 (Sheldrick, 2013) | |
| Function minimized | $\Sigma\, w(F_o^2 - F_c^2)^2$ | |
| Data / restraints / parameters | 5872 / 0 / 325 | |
| Goodness-of-fit on $F^2$ | 1.010 | |
| Final R indices | 4600 data; I>2σ(I) | R1 = 0.0373, wR2 = 0.0837 |
| | all data | R1 = 0.0557, wR2 = 0.0923 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0397P)^2+1.1073P]$ where $P=(F_o^2+2F_c^2)/3$ | |
| Largest diff. peak and hole | 0.345 and -0.264 $eÅ^{-3}$ | |
| R.M.S. deviation from mean | 0.050 $eÅ^{-3}$ | |

Table S- 118: Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for **[PPh4][DNT]**.U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| C1 | 0.18798(13) | 0.83189(10) | 0.41096(10) | 0.0179(3) |
| C2 | 0.16020(13) | 0.86982(10) | 0.27150(11) | 0.0189(3) |
| N1 | 0.24200(11) | 0.79766(9) | 0.50288(10) | 0.0237(3) |
| N2 | 0.07446(11) | 0.85853(9) | 0.40219(9) | 0.0220(3) |
| N3 | 0.05531(11) | 0.88386(9) | 0.30725(9) | 0.0225(3) |
| N4 | 0.17766(12) | 0.89031(9) | 0.17114(9) | 0.0232(3) |
| N5 | 0.24882(11) | 0.83772(8) | 0.33237(9) | 0.0198(3) |
| O1 | 0.08945(11) | 0.91145(9) | 0.11693(9) | 0.0348(3) |
| O2 | 0.28021(11) | 0.88604(8) | 0.14647(9) | 0.0309(3) |
| O3 | 0.17919(11) | 0.79380(9) | 0.57105(8) | 0.0347(3) |
| O4 | 0.34716(10) | 0.77480(9) | 0.50725(9) | 0.0370(3) |
| C3 | 0.16079(12) | 0.29597(9) | 0.72413(10) | 0.0154(3) |
| C4 | 0.10023(13) | 0.31497(10) | 0.63402(11) | 0.0197(3) |
| C5 | 0.99732(14) | 0.36710(10) | 0.62991(12) | 0.0255(3) |
| C6 | 0.95720(14) | 0.40039(11) | 0.71473(13) | 0.0273(4) |
| C7 | 0.01652(14) | 0.38114(10) | 0.80449(12) | 0.0255(3) |
| C8 | 0.11880(13) | 0.32871(10) | 0.80968(11) | 0.0202(3) |
| C9 | 0.31069(12) | 0.17108(9) | 0.83993(10) | 0.0151(3) |
| C10 | 0.20910(13) | 0.12228(9) | 0.86069(10) | 0.0176(3) |
| C11 | 0.21724(14) | 0.06479(10) | 0.93989(10) | 0.0208(3) |
| C12 | 0.32438(15) | 0.05564(10) | 0.99734(10) | 0.0226(3) |
| C13 | 0.42336(14) | 0.10529(10) | 0.97801(11) | 0.0216(3) |
| C14 | 0.41768(13) | 0.16334(9) | 0.89936(10) | 0.0177(3) |
| C15 | 0.41948(12) | 0.31892(9) | 0.73757(9) | 0.0150(3) |
| C16 | 0.39146(13) | 0.40975(9) | 0.74134(10) | 0.0168(3) |
| C17 | 0.48220(14) | 0.47281(10) | 0.74699(10) | 0.0205(3) |
| C18 | 0.60041(14) | 0.44596(10) | 0.74780(11) | 0.0225(3) |
| C19 | 0.62893(14) | 0.35603(10) | 0.74394(11) | 0.0221(3) |
| C20 | 0.53935(13) | 0.29228(10) | 0.73921(10) | 0.0183(3) |
| C21 | 0.30728(12) | 0.16568(9) | 0.62837(10) | 0.0146(3) |
| C22 | 0.40426(13) | 0.16498(10) | 0.57166(10) | 0.0181(3) |
| C23 | 0.40796(14) | 0.10232(10) | 0.49772(10) | 0.0205(3) |
| C24 | 0.31570(14) | 0.04131(10) | 0.47992(11) | 0.0211(3) |
| C25 | 0.21772(13) | 0.04348(10) | 0.53501(11) | 0.0202(3) |
| C26 | 0.21321(13) | 0.10492(10) | 0.60948(10) | 0.0171(3) |
| P1 | 0.30090(3) | 0.23838(2) | 0.73171(3) | 0.01296(8) |

Table S- 119: Bond lengths (Å) for **[PPh4][DNT**].

| | | | |
|---|---|---|---|
| C1-N2 | 1.3310(19) | C1-N5 | 1.3348(19) |
| C1-N1 | 1.4516(19) | C2-N3 | 1.3330(19) |
| C2-N5 | 1.3347(19) | C2-N4 | 1.4494(19) |
| N1-O4 | 1.2258(17) | N1-O3 | 1.2261(17) |
| N2-N3 | 1.3637(18) | N4-O1 | 1.2294(17) |
| N4-O2 | 1.2306(17) | C3-C4 | 1.394(2) |
| C3-C8 | 1.399(2) | C3-P1 | 1.7897(14) |
| C4-C5 | 1.392(2) | C4-H5 | 0.95 |
| C5-C6 | 1.384(2) | C5-H4 | 0.95 |
| C6-C7 | 1.385(2) | C6-H3 | 0.95 |
| C7-C8 | 1.389(2) | C7-H2 | 0.95 |
| C8-H1 | 0.95 | C9-C14 | 1.3987(19) |
| C9-C10 | 1.4059(19) | C9-P1 | 1.7990(14) |
| C10-C11 | 1.390(2) | C10-H6 | 0.95 |
| C11-C12 | 1.388(2) | C11-H7 | 0.95 |
| C12-C13 | 1.383(2) | C12-H8 | 0.95 |
| C13-C14 | 1.389(2) | C13-H9 | 0.95 |
| C14-H10 | 0.95 | C15-C16 | 1.4010(19) |
| C15-C20 | 1.4021(19) | C15-P1 | 1.7946(14) |
| C16-C17 | 1.388(2) | C16-H11 | 0.95 |
| C17-C18 | 1.386(2) | C17-H12 | 0.95 |
| C18-C19 | 1.389(2) | C18-H13 | 0.95 |
| C19-C20 | 1.386(2) | C19-H14 | 0.95 |
| C20-H15 | 0.95 | C21-C22 | 1.3959(19) |
| C21-C26 | 1.4023(19) | C21-P1 | 1.8028(14) |
| C22-C23 | 1.391(2) | C22-H16 | 0.95 |
| C23-C24 | 1.388(2) | C23-H17 | 0.95 |
| C24-C25 | 1.392(2) | C24-H18 | 0.95 |
| C25-C26 | 1.385(2) | C25-H19 | 0.95 |
| C26-H20 | 0.95 | | |

Table S- 120: Bond angles (°) for **[PPh4][DNT**].

| | | | |
|---|---|---|---|
| N2-C1-N5 | 117.42(13) | N2-C1-N1 | 120.60(13) |
| N5-C1-N1 | 121.98(13) | N3-C2-N5 | 117.24(13) |
| N3-C2-N4 | 121.23(13) | N5-C2-N4 | 121.52(13) |
| O4-N1-O3 | 124.43(14) | O4-N1-C1 | 117.94(13) |
| O3-N1-C1 | 117.63(13) | C1-N2-N3 | 103.89(12) |
| C2-N3-N2 | 104.01(12) | O1-N4-O2 | 124.61(14) |
| O1-N4-C2 | 117.88(13) | O2-N4-C2 | 117.51(13) |
| C2-N5-C1 | 97.43(12) | C4-C3-C8 | 120.52(13) |
| C4-C3-P1 | 120.54(11) | C8-C3-P1 | 118.67(11) |
| C5-C4-C3 | 119.29(14) | C5-C4-H5 | 120.4 |
| C3-C4-H5 | 120.4 | C6-C5-C4 | 119.92(15) |
| C6-C5-H4 | 120.0 | C4-C5-H4 | 120.0 |
| C5-C6-C7 | 121.01(14) | C5-C6-H3 | 119.5 |
| C7-C6-H3 | 119.5 | C6-C7-C8 | 119.65(15) |
| C6-C7-H2 | 120.2 | C8-C7-H2 | 120.2 |
| C7-C8-C3 | 119.60(14) | C7-C8-H1 | 120.2 |
| C3-C8-H1 | 120.2 | C14-C9-C10 | 120.48(13) |
| C14-C9-P1 | 121.37(11) | C10-C9-P1 | 118.06(10) |
| C11-C10-C9 | 119.04(13) | C11-C10-H6 | 120.5 |
| C9-C10-H6 | 120.5 | C12-C11-C10 | 120.32(14) |
| C12-C11-H7 | 119.8 | C10-C11-H7 | 119.8 |
| C13-C12-C11 | 120.45(14) | C13-C12-H8 | 119.8 |
| C11-C12-H8 | 119.8 | C12-C13-C14 | 120.41(14) |
| C12-C13-H9 | 119.8 | C14-C13-H9 | 119.8 |
| C13-C14-C9 | 119.26(14) | C13-C14-H10 | 120.4 |
| C9-C14-H10 | 120.4 | C16-C15-C20 | 119.68(13) |
| C16-C15-P1 | 119.27(11) | C20-C15-P1 | 121.05(11) |
| C17-C16-C15 | 119.98(13) | C17-C16-H11 | 120.0 |
| C15-C16-H11 | 120.0 | C18-C17-C16 | 119.98(14) |
| C18-C17-H12 | 120.0 | C16-C17-H12 | 120.0 |
| C17-C18-C19 | 120.39(14) | C17-C18-H13 | 119.8 |
| C19-C18-H13 | 119.8 | C20-C19-C18 | 120.26(14) |
| C20-C19-H14 | 119.9 | C18-C19-H14 | 119.9 |
| C19-C20-C15 | 119.70(14) | C19-C20-H15 | 120.2 |
| C15-C20-H15 | 120.2 | C22-C21-C26 | 120.16(13) |
| C22-C21-P1 | 122.39(11) | C26-C21-P1 | 117.34(10) |
| C23-C22-C21 | 119.46(13) | C23-C22-H16 | 120.3 |
| C21-C22-H16 | 120.3 | C24-C23-C22 | 120.39(13) |
| C24-C23-H17 | 119.8 | C22-C23-H17 | 119.8 |
| C23-C24-C25 | 120.07(14) | C23-C24-H18 | 120.0 |
| C25-C24-H18 | 120.0 | C26-C25-C24 | 120.23(14) |
| C26-C25-H19 | 119.9 | C24-C25-H19 | 119.9 |
| C25-C26-C21 | 119.66(13) | C25-C26-H20 | 120.2 |
| C21-C26-H20 | 120.2 | C3-P1-C15 | 108.78(7) |
| C3-P1-C9 | 108.00(6) | C15-P1-C9 | 110.48(6) |
| C3-P1-C21 | 109.99(6) | C15-P1-C21 | 111.25(6) |
| C9-P1-C21 | 108.29(6) | | |

Table S- 121: Anisotropic atomic displacement parameters (Å$^2$) for **[PPh4][DNT**].

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0163(7) | 0.0181(7) | 0.0190(7) | -0.0007(5) | 0.0002(5) | -0.0008(5) |
| C2 | 0.0197(7) | 0.0164(7) | 0.0204(7) | -0.0005(5) | 0.0006(6) | -0.0012(5) |
| N1 | 0.0200(7) | 0.0278(7) | 0.0232(7) | 0.0015(5) | 0.0006(5) | 0.0002(5) |
| N2 | 0.0192(6) | 0.0247(7) | 0.0221(6) | 0.0000(5) | 0.0006(5) | 0.0003(5) |
| N3 | 0.0189(6) | 0.0255(7) | 0.0228(6) | 0.0012(5) | 0.0001(5) | 0.0012(5) |
| N4 | 0.0267(7) | 0.0199(6) | 0.0229(7) | 0.0022(5) | 0.0017(5) | -0.0007(5) |
| N5 | 0.0172(6) | 0.0204(6) | 0.0216(6) | -0.0002(5) | 0.0008(5) | 0.0001(5) |
| O1 | 0.0359(7) | 0.0427(8) | 0.0247(6) | 0.0059(5) | -0.0041(5) | 0.0087(6) |
| O2 | 0.0282(6) | 0.0354(7) | 0.0304(6) | 0.0057(5) | 0.0099(5) | -0.0047(5) |
| O3 | 0.0341(7) | 0.0488(8) | 0.0223(6) | 0.0047(5) | 0.0083(5) | 0.0106(6) |
| O4 | 0.0177(6) | 0.0591(9) | 0.0340(7) | 0.0155(6) | 0.0012(5) | 0.0061(6) |
| C3 | 0.0130(6) | 0.0134(6) | 0.0201(7) | 0.0003(5) | 0.0025(5) | -0.0003(5) |
| C4 | 0.0205(7) | 0.0176(7) | 0.0207(7) | 0.0013(5) | 0.0004(6) | 0.0002(5) |
| C5 | 0.0218(8) | 0.0220(8) | 0.0314(9) | 0.0060(6) | -0.0042(6) | 0.0025(6) |
| C6 | 0.0178(7) | 0.0218(8) | 0.0431(10) | 0.0046(7) | 0.0068(7) | 0.0041(6) |
| C7 | 0.0243(8) | 0.0228(8) | 0.0310(9) | -0.0004(6) | 0.0121(7) | 0.0032(6) |
| C8 | 0.0201(7) | 0.0198(7) | 0.0212(7) | 0.0000(6) | 0.0048(6) | 0.0010(6) |
| C9 | 0.0191(7) | 0.0131(6) | 0.0133(6) | -0.0003(5) | 0.0026(5) | 0.0012(5) |
| C10 | 0.0197(7) | 0.0181(7) | 0.0152(7) | -0.0010(5) | 0.0019(5) | -0.0021(5) |
| C11 | 0.0289(8) | 0.0175(7) | 0.0166(7) | -0.0009(5) | 0.0052(6) | -0.0049(6) |
| C12 | 0.0356(9) | 0.0184(7) | 0.0137(7) | 0.0017(5) | 0.0016(6) | 0.0008(6) |
| C13 | 0.0253(8) | 0.0219(7) | 0.0165(7) | -0.0008(6) | -0.0046(6) | 0.0034(6) |
| C14 | 0.0187(7) | 0.0170(7) | 0.0173(7) | -0.0020(5) | 0.0007(5) | -0.0003(5) |
| C15 | 0.0174(7) | 0.0162(7) | 0.0114(6) | 0.0004(5) | 0.0014(5) | -0.0027(5) |
| C16 | 0.0190(7) | 0.0182(7) | 0.0133(6) | 0.0008(5) | 0.0017(5) | 0.0007(5) |
| C17 | 0.0287(8) | 0.0153(7) | 0.0171(7) | 0.0002(5) | 0.0010(6) | -0.0039(6) |
| C18 | 0.0231(8) | 0.0230(8) | 0.0211(7) | 0.0007(6) | 0.0005(6) | -0.0101(6) |
| C19 | 0.0176(7) | 0.0263(8) | 0.0222(7) | 0.0012(6) | 0.0018(6) | -0.0037(6) |
| C20 | 0.0181(7) | 0.0181(7) | 0.0188(7) | 0.0005(5) | 0.0017(5) | -0.0008(5) |
| C21 | 0.0169(7) | 0.0144(6) | 0.0123(6) | 0.0003(5) | 0.0000(5) | 0.0016(5) |
| C22 | 0.0201(7) | 0.0178(7) | 0.0167(7) | 0.0013(5) | 0.0033(5) | -0.0016(5) |
| C23 | 0.0234(8) | 0.0225(7) | 0.0165(7) | -0.0006(6) | 0.0060(6) | 0.0010(6) |
| C24 | 0.0283(8) | 0.0179(7) | 0.0173(7) | -0.0026(5) | 0.0034(6) | 0.0008(6) |
| C25 | 0.0226(8) | 0.0188(7) | 0.0188(7) | -0.0017(6) | -0.0001(6) | -0.0034(6) |
| C26 | 0.0164(7) | 0.0193(7) | 0.0157(7) | 0.0011(5) | 0.0018(5) | -0.0003(5) |
| P1 | 0.01298(17) | 0.01315(16) | 0.01276(16) | 0.00000(13) | 0.00129(12) | -0.00016(13) |

Table S- 122: Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å$^2$) for **[PPh4][DNT**].

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H5 | 0.1289 | 0.2926 | 0.5760 | 0.024 |
| H4 | -0.0453 | 0.3798 | 0.5690 | 0.031 |
| H3 | -0.1121 | 0.4370 | 0.7113 | 0.033 |
| H2 | -0.0126 | 0.4037 | 0.8622 | 0.031 |
| H1 | 0.1600 | 0.3152 | 0.8710 | 0.024 |
| H6 | 0.1359 | 0.1285 | 0.8211 | 0.021 |
| H7 | 0.1492 | 0.0316 | 0.9548 | 0.025 |
| H8 | 0.3298 | 0.0150 | 1.0503 | 0.027 |
| H9 | 0.4957 | 0.0997 | 1.0188 | 0.026 |
| H10 | 0.4857 | 0.1974 | 0.8861 | 0.021 |
| H11 | 0.3104 | 0.4282 | 0.7400 | 0.02 |
| H12 | 0.4633 | 0.5344 | 0.7503 | 0.025 |
| H13 | 0.6623 | 0.4893 | 0.7510 | 0.027 |
| H14 | 0.7102 | 0.3382 | 0.7445 | 0.026 |
| H15 | 0.5591 | 0.2308 | 0.7371 | 0.022 |
| H16 | 0.4672 | 0.2069 | 0.5834 | 0.022 |
| H17 | 0.4740 | 0.1013 | 0.4592 | 0.025 |
| H18 | 0.3194 | -0.0020 | 0.4301 | 0.025 |
| H19 | 0.1537 | 0.0027 | 0.5215 | 0.024 |
| H20 | 0.1467 | 0.1059 | 0.6475 | 0.021 |

# 2.19 Crystal Structure Report for [PNP][DNT]

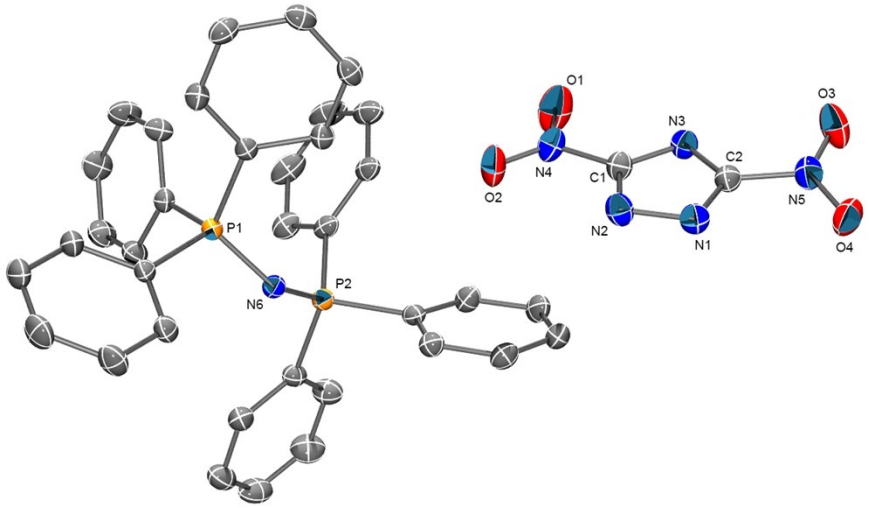


Figure S- 56: Molecular structure of **[PNP][DNT]**. Thermal ellipsoids are shown at the 50% probability levelHydrogen atoms were omitted for clarity.

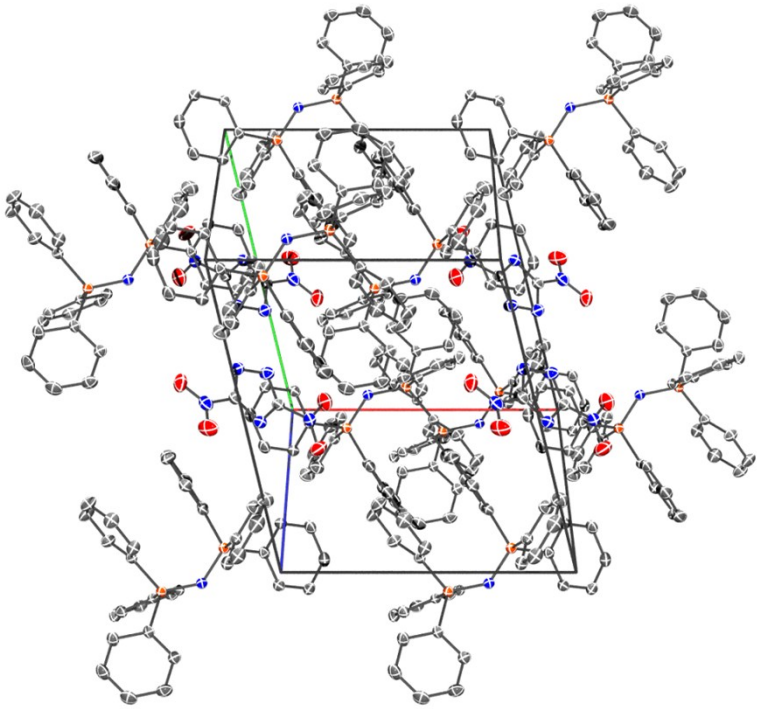

Figure S- 57: Projection of the packing of **[PNP][DNT]** perpendicular to the 001 plane. Hydrogen atoms were omitted for clarity.

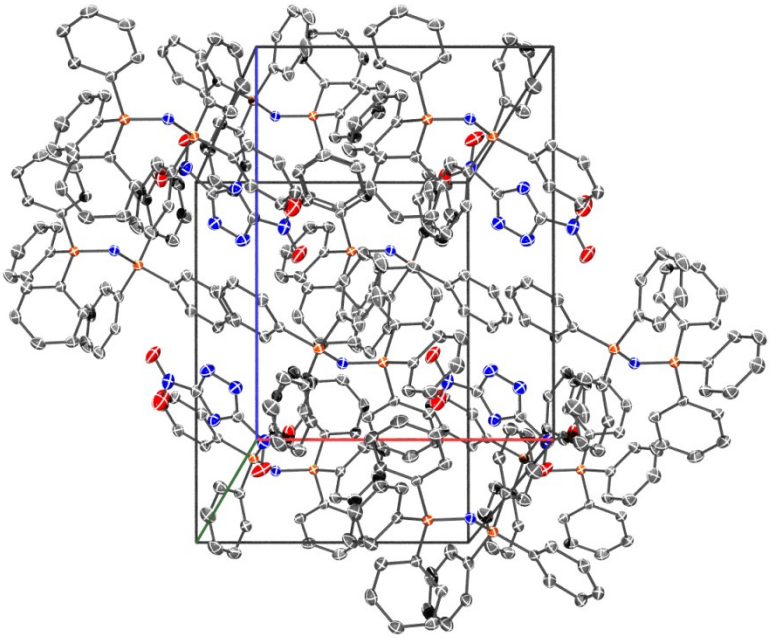

Figure S- 58: Projection of the packing of **[PNP][DNT]** perpendicular to the 010 plane. Hydrogen atoms were omitted for clarity.

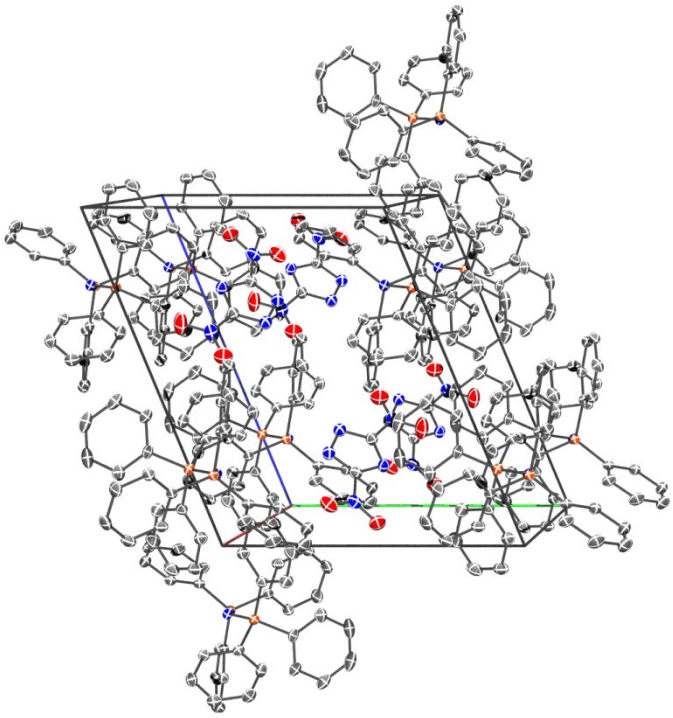

Figure S- 59: Projection of the packing of **[PNP][DNT]** perpendicular to the 100 plane. Hydrogen atoms were omitted for clarity.

Table S- 123: Sample and crystal data for **[PNP][DNT]**.

| | | |
|---|---|---|
| Identification code | PNPDNT | |
| Chemical formula | $C_{38}H_{30}N_6O_4P_2$ | |
| Formula weight | 696.62 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.140 x 0.180 x 0.220 mm | |
| Crystal habit | clear colourless prism | |
| Crystal system | triclinic | |
| Space group | P -1 | |
| Unit cell dimensions | a = 10.9099(7) Å | α = 112.6130(8)° |
| | b = 11.9031(8) Å | β = 90.0610(9)° |
| | c = 14.4603(10) Å | γ = 103.5780(9)° |
| Volume | 1676.28(19) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.380 $g/cm^3$ | |
| Absorption coefficient | 0.182 $mm^{-1}$ | |
| F(000) | 724 | |

Table S- 124: Data collection and structure refinement for **[PNP][DNT]**.

| | |
|---|---|
| Diffractometer | Bruker SMART APEX |
| Radiation source | fine-focus tube, MoKα |
| Theta range for data collection | 1.53 to 28.67° |
| Index ranges | -8<=h<=14, -15<=k<=15, -19<=l<=18 |
| Reflections collected | 10859 |
| Independent reflections | 7529 [R(int) = 0.0198] |
| Coverage of independent reflections | 87.1% |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.9750 and 0.9610 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXTL XT 2013/6 (Sheldrick, 2013) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXTL XLMP 2014/1 (Bruker AXS, 2013) |
| Function minimized | $\Sigma\, w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 7529 / 0 / 451 |
| Goodness-of-fit on $F^2$ | 1.025 |
| Final R indices | 5805 data; I>2σ(I) R1 = 0.0463, wR2 = 0.1150 |
| | all data R1 = 0.0635, wR2 = 0.1273 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0662P)^2+0.3671P]$ where $P=(F_o^2+2F_c^2)/3$ |
| Largest diff. peak and hole | 0.454 and -0.278 eÅ$^{-3}$ |
| R.M.S. deviation from mean | 0.058 eÅ$^{-3}$ |

Table S- 125: Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for **[PNP][DNT]**.U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| C1 | 0.07394(19) | 0.37659(18) | 0.69103(15) | 0.0254(4) |
| C2 | 0.94394(18) | 0.44309(18) | 0.77806(15) | 0.0240(4) |
| C3 | 0.54930(17) | 0.31309(17) | 0.39008(14) | 0.0186(4) |
| C4 | 0.67904(18) | 0.37103(18) | 0.41216(15) | 0.0235(4) |
| C5 | 0.72976(19) | 0.44236(18) | 0.51105(15) | 0.0266(4) |
| C6 | 0.6520(2) | 0.45749(18) | 0.58823(15) | 0.0260(4) |
| C7 | 0.52218(19) | 0.40392(18) | 0.56687(15) | 0.0247(4) |
| C8 | 0.47060(18) | 0.33201(17) | 0.46809(14) | 0.0205(4) |
| C9 | 0.54876(17) | 0.08009(17) | 0.21975(14) | 0.0201(4) |
| C10 | 0.50968(19) | 0.99040(19) | 0.12126(14) | 0.0261(4) |
| C11 | 0.5526(2) | 0.8824(2) | 0.08592(16) | 0.0318(5) |
| C12 | 0.6347(2) | 0.8625(2) | 0.14748(17) | 0.0337(5) |
| C13 | 0.6740(2) | 0.9503(2) | 0.24452(17) | 0.0338(5) |
| C14 | 0.63134(19) | 0.05844(19) | 0.28094(15) | 0.0261(4) |
| C15 | 0.54321(17) | 0.30383(17) | 0.18794(13) | 0.0193(4) |
| C16 | 0.47063(19) | 0.37510(18) | 0.16719(14) | 0.0233(4) |
| C17 | 0.5204(2) | 0.4506(2) | 0.11590(16) | 0.0308(5) |
| C18 | 0.6408(2) | 0.4547(2) | 0.08557(17) | 0.0344(5) |
| C19 | 0.7129(2) | 0.3833(2) | 0.10461(16) | 0.0322(5) |

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| C20 | 0.66445(19) | 0.3075(2) | 0.15573(15) | 0.0270(4) |
| C21 | 0.27924(17) | 0.97231(18) | 0.30737(15) | 0.0222(4) |
| C22 | 0.30675(19) | 0.85871(19) | 0.24983(17) | 0.0293(5) |
| C23 | 0.3562(2) | 0.7951(2) | 0.2976(2) | 0.0384(6) |
| C24 | 0.3767(2) | 0.8437(2) | 0.4012(2) | 0.0409(6) |
| C25 | 0.34950(19) | 0.9557(2) | 0.45865(18) | 0.0329(5) |
| C26 | 0.30133(18) | 0.02092(19) | 0.41273(15) | 0.0249(4) |
| C27 | 0.15141(18) | 0.96446(18) | 0.12688(14) | 0.0221(4) |
| C28 | 0.18225(19) | 0.9961(2) | 0.04534(15) | 0.0261(4) |
| C29 | 0.1212(2) | 0.9180(2) | 0.94961(16) | 0.0333(5) |
| C30 | 0.0302(2) | 0.8092(2) | 0.93584(17) | 0.0372(5) |
| C31 | 0.9981(2) | 0.7781(2) | 0.01710(18) | 0.0380(5) |
| C32 | 0.0578(2) | 0.8544(2) | 0.11242(16) | 0.0314(5) |
| C33 | 0.10477(17) | 0.12406(18) | 0.32572(14) | 0.0202(4) |
| C34 | 0.08232(18) | 0.23847(18) | 0.33571(14) | 0.0224(4) |
| C35 | 0.98966(18) | 0.28286(19) | 0.39363(15) | 0.0259(4) |
| C36 | 0.92040(19) | 0.2140(2) | 0.44369(15) | 0.0272(4) |
| C37 | 0.93994(19) | 0.0989(2) | 0.43193(16) | 0.0287(5) |
| C38 | 0.03039(18) | 0.05285(19) | 0.37246(15) | 0.0256(4) |
| N1 | 0.96594(17) | 0.51115(16) | 0.72238(13) | 0.0292(4) |
| N2 | 0.05519(17) | 0.46608(16) | 0.66335(13) | 0.0302(4) |
| N3 | 0.00801(16) | 0.35644(16) | 0.76297(13) | 0.0272(4) |
| N4 | 0.85466(17) | 0.46497(17) | 0.85265(14) | 0.0316(4) |
| N5 | 0.16231(17) | 0.30310(17) | 0.64344(15) | 0.0326(4) |
| N6 | 0.33309(14) | 0.18096(14) | 0.24908(12) | 0.0199(3) |
| O1 | 0.85488(18) | 0.41770(17) | 0.91407(13) | 0.0487(5) |
| O2 | 0.78299(15) | 0.52994(16) | 0.85036(13) | 0.0424(4) |
| O3 | 0.17244(18) | 0.21875(18) | 0.66908(16) | 0.0577(5) |
| O4 | 0.22110(16) | 0.32838(17) | 0.57930(13) | 0.0470(4) |
| P1 | 0.48354(4) | 0.21555(4) | 0.26231(3) | 0.01743(12) |
| P2 | 0.22558(4) | 0.06609(4) | 0.25143(4) | 0.01855(12) |

Table S- 126: Bond lengths (Å) for **[PNP][DNT]**.

| | | | |
|---|---|---|---|
| C1-N2 | 1.329(3) | C1-N3 | 1.330(3) |
| C1-N5 | 1.450(3) | C2-N3 | 1.329(3) |
| C2-N1 | 1.332(3) | C2-N4 | 1.444(3) |
| C3-C4 | 1.397(3) | C3-C8 | 1.399(3) |
| C3-P1 | 1.7979(18) | C4-C5 | 1.384(3) |
| C4-H4 | 0.95 | C5-C6 | 1.384(3) |
| C5-H5 | 0.95 | C6-C7 | 1.390(3) |
| C6-H6 | 0.95 | C7-C8 | 1.386(3) |
| C7-H7 | 0.95 | C8-H8 | 0.95 |
| C9-C14 | 1.394(3) | C9-C10 | 1.402(3) |
| C9-P1 | 1.8060(19) | C10-C11 | 1.382(3) |
| C10-H10 | 0.95 | C11-C12 | 1.383(3) |
| C11-H11 | 0.95 | C12-C13 | 1.381(3) |
| C12-H12 | 0.95 | C13-C14 | 1.382(3) |
| C13-H13 | 0.95 | C14-H14 | 0.95 |
| C15-C16 | 1.395(3) | C15-C20 | 1.399(3) |
| C15-P1 | 1.7982(18) | C16-C17 | 1.392(3) |
| C16-H16 | 0.95 | C17-C18 | 1.382(3) |
| C17-H17 | 0.95 | C18-C19 | 1.382(3) |
| C18-H18 | 0.95 | C19-C20 | 1.389(3) |
| C19-H19 | 0.95 | C20-H20 | 0.95 |
| C21-C22 | 1.392(3) | C21-C26 | 1.404(3) |
| C21-P2 | 1.8008(19) | C22-C23 | 1.390(3) |
| C22-H22 | 0.95 | C23-C24 | 1.379(4) |
| C23-H23 | 0.95 | C24-C25 | 1.375(3) |
| C24-H24 | 0.95 | C25-C26 | 1.381(3) |
| C25-H25 | 0.95 | C26-H26 | 0.95 |
| C27-C28 | 1.388(3) | C27-C32 | 1.401(3) |
| C27-P2 | 1.7955(19) | C28-C29 | 1.394(3) |
| C28-H28 | 0.95 | C29-C30 | 1.378(3) |
| C29-H29 | 0.95 | C30-C31 | 1.384(3) |
| C30-H30 | 0.95 | C31-C32 | 1.381(3) |
| C31-H31 | 0.95 | C32-H32 | 0.95 |
| C33-C34 | 1.393(3) | C33-C38 | 1.397(3) |
| C33-P2 | 1.797(2) | C34-C35 | 1.384(3) |
| C34-H34 | 0.95 | C35-C36 | 1.390(3) |
| C35-H35 | 0.95 | C36-C37 | 1.382(3) |
| C36-H36 | 0.95 | C37-C38 | 1.381(3) |
| C37-H37 | 0.95 | C38-H38 | 0.95 |
| N1-N2 | 1.364(2) | N4-O1 | 1.221(2) |
| N4-O2 | 1.230(2) | N5-O4 | 1.220(2) |
| N5-O3 | 1.223(2) | N6-P1 | 1.5881(16) |
| N6-P2 | 1.5903(16) | | |

Table S- 127: Bond angles (°) for **[PNP][DNT]**.

| | | | |
|---|---|---|---|
| N2-C1-N3 | 117.61(18) | N2-C1-N5 | 120.88(18) |
| N3-C1-N5 | 121.50(18) | N3-C2-N1 | 117.52(18) |
| N3-C2-N4 | 121.94(18) | N1-C2-N4 | 120.54(18) |
| C4-C3-C8 | 119.54(17) | C4-C3-P1 | 120.33(14) |
| C8-C3-P1 | 120.13(14) | C5-C4-C3 | 120.03(18) |
| C5-C4-H4 | 120.0 | C3-C4-H4 | 120.0 |
| C4-C5-C6 | 120.15(18) | C4-C5-H5 | 119.9 |
| C6-C5-H5 | 119.9 | C5-C6-C7 | 120.31(18) |
| C5-C6-H6 | 119.8 | C7-C6-H6 | 119.8 |
| C8-C7-C6 | 119.92(18) | C8-C7-H7 | 120.0 |
| C6-C7-H7 | 120.0 | C7-C8-C3 | 119.98(18) |
| C7-C8-H8 | 120.0 | C3-C8-H8 | 120.0 |
| C14-C9-C10 | 118.92(18) | C14-C9-P1 | 123.33(15) |
| C10-C9-P1 | 117.70(14) | C11-C10-C9 | 120.25(18) |
| C11-C10-H10 | 119.9 | C9-C10-H10 | 119.9 |
| C10-C11-C12 | 120.1(2) | C10-C11-H11 | 119.9 |
| C12-C11-H11 | 119.9 | C13-C12-C11 | 120.1(2) |
| C13-C12-H12 | 119.9 | C11-C12-H12 | 119.9 |
| C12-C13-C14 | 120.35(19) | C12-C13-H13 | 119.8 |
| C14-C13-H13 | 119.8 | C13-C14-C9 | 120.25(19) |
| C13-C14-H14 | 119.9 | C9-C14-H14 | 119.9 |
| C16-C15-C20 | 119.73(17) | C16-C15-P1 | 119.50(14) |
| C20-C15-P1 | 120.66(15) | C17-C16-C15 | 119.60(19) |
| C17-C16-H16 | 120.2 | C15-C16-H16 | 120.2 |
| C18-C17-C16 | 120.1(2) | C18-C17-H17 | 119.9 |
| C16-C17-H17 | 119.9 | C19-C18-C17 | 120.73(19) |
| C19-C18-H18 | 119.6 | C17-C18-H18 | 119.6 |
| C18-C19-C20 | 119.8(2) | C18-C19-H19 | 120.1 |
| C20-C19-H19 | 120.1 | C19-C20-C15 | 120.04(19) |
| C19-C20-H20 | 120.0 | C15-C20-H20 | 120.0 |
| C22-C21-C26 | 119.61(18) | C22-C21-P2 | 122.33(16) |
| C26-C21-P2 | 117.94(15) | C23-C22-C21 | 119.5(2) |
| C23-C22-H22 | 120.3 | C21-C22-H22 | 120.3 |
| C24-C23-C22 | 120.2(2) | C24-C23-H23 | 119.9 |
| C22-C23-H23 | 119.9 | C25-C24-C23 | 120.7(2) |
| C25-C24-H24 | 119.7 | C23-C24-H24 | 119.7 |
| C24-C25-C26 | 120.0(2) | C24-C25-H25 | 120.0 |
| C26-C25-H25 | 120.0 | C25-C26-C21 | 120.0(2) |
| C25-C26-H26 | 120.0 | C21-C26-H26 | 120.0 |
| C28-C27-C32 | 119.61(18) | C28-C27-P2 | 120.77(15) |
| C32-C27-P2 | 119.58(15) | C27-C28-C29 | 120.06(19) |
| C27-C28-H28 | 120.0 | C29-C28-H28 | 120.0 |
| C30-C29-C28 | 120.0(2) | C30-C29-H29 | 120.0 |
| C28-C29-H29 | 120.0 | C29-C30-C31 | 120.2(2) |
| C29-C30-H30 | 119.9 | C31-C30-H30 | 119.9 |
| C32-C31-C30 | 120.6(2) | C32-C31-H31 | 119.7 |
| C30-C31-H31 | 119.7 | C31-C32-C27 | 119.6(2) |
| C31-C32-H32 | 120.2 | C27-C32-H32 | 120.2 |
| C34-C33-C38 | 119.34(18) | C34-C33-P2 | 120.71(14) |

| | | | |
|---|---|---|---|
| C38-C33-P2 | 119.94(15) | C35-C34-C33 | 120.34(18) |
| C35-C34-H34 | 119.8 | C33-C34-H34 | 119.8 |
| C34-C35-C36 | 119.75(19) | C34-C35-H35 | 120.1 |
| C36-C35-H35 | 120.1 | C37-C36-C35 | 120.11(19) |
| C37-C36-H36 | 119.9 | C35-C36-H36 | 119.9 |
| C38-C37-C36 | 120.35(19) | C38-C37-H37 | 119.8 |
| C36-C37-H37 | 119.8 | C37-C38-C33 | 119.99(19) |
| C37-C38-H38 | 120.0 | C33-C38-H38 | 120.0 |
| C2-N1-N2 | 103.77(16) | C1-N2-N1 | 103.76(16) |
| C2-N3-C1 | 97.34(16) | O1-N4-O2 | 124.03(19) |
| O1-N4-C2 | 117.92(19) | O2-N4-C2 | 118.05(18) |
| O4-N5-O3 | 123.9(2) | O4-N5-C1 | 117.84(18) |
| O3-N5-C1 | 118.20(18) | P1-N6-P2 | 133.74(10) |
| N6-P1-C3 | 112.90(8) | N6-P1-C15 | 108.84(8) |
| C3-P1-C15 | 106.55(8) | N6-P1-C9 | 113.77(8) |
| C3-P1-C9 | 107.97(9) | C15-P1-C9 | 106.37(9) |
| N6-P2-C27 | 110.84(9) | N6-P2-C33 | 109.69(9) |
| C27-P2-C33 | 107.51(9) | N6-P2-C21 | 114.52(8) |
| C27-P2-C21 | 108.41(9) | C33-P2-C21 | 105.53(9) |

Table S- 128: Anisotropic atomic displacement parameters (Å$^2$) for **[PNP][DNT]**.The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0241(10) | 0.0232(10) | 0.0290(11) | 0.0110(8) | 0.0054(8) | 0.0049(8) |
| C2 | 0.0224(10) | 0.0227(10) | 0.0242(10) | 0.0078(8) | 0.0022(8) | 0.0033(8) |
| C3 | 0.0201(9) | 0.0171(9) | 0.0194(9) | 0.0076(7) | 0.0024(7) | 0.0058(7) |
| C4 | 0.0225(10) | 0.0226(10) | 0.0249(10) | 0.0089(8) | 0.0049(8) | 0.0054(8) |
| C5 | 0.0203(10) | 0.0219(10) | 0.0318(11) | 0.0051(9) | -0.0026(8) | 0.0041(8) |
| C6 | 0.0346(11) | 0.0202(10) | 0.0202(10) | 0.0041(8) | -0.0022(8) | 0.0083(8) |
| C7 | 0.0324(11) | 0.0221(10) | 0.0217(10) | 0.0087(8) | 0.0066(8) | 0.0104(8) |
| C8 | 0.0215(10) | 0.0191(9) | 0.0223(9) | 0.0093(8) | 0.0043(7) | 0.0056(7) |
| C9 | 0.0197(9) | 0.0202(9) | 0.0212(9) | 0.0090(8) | 0.0049(7) | 0.0052(7) |
| C10 | 0.0289(11) | 0.0301(11) | 0.0190(10) | 0.0072(8) | 0.0013(8) | 0.0111(9) |
| C11 | 0.0378(12) | 0.0308(11) | 0.0217(10) | 0.0037(9) | 0.0020(9) | 0.0110(9) |
| C12 | 0.0417(13) | 0.0265(11) | 0.0349(12) | 0.0082(9) | 0.0056(10) | 0.0189(10) |
| C13 | 0.0393(13) | 0.0326(12) | 0.0344(12) | 0.0127(10) | -0.0029(10) | 0.0193(10) |
| C14 | 0.0311(11) | 0.0244(10) | 0.0223(10) | 0.0075(8) | -0.0021(8) | 0.0092(8) |
| C15 | 0.0183(9) | 0.0223(9) | 0.0158(9) | 0.0065(7) | 0.0029(7) | 0.0043(7) |
| C16 | 0.0263(10) | 0.0243(10) | 0.0205(10) | 0.0089(8) | 0.0054(8) | 0.0088(8) |
| C17 | 0.0418(13) | 0.0309(11) | 0.0282(11) | 0.0182(9) | 0.0084(9) | 0.0133(9) |
| C18 | 0.0402(13) | 0.0363(12) | 0.0319(12) | 0.0216(10) | 0.0099(10) | 0.0053(10) |
| C19 | 0.0255(11) | 0.0440(13) | 0.0298(11) | 0.0199(10) | 0.0080(9) | 0.0047(9) |
| C20 | 0.0226(10) | 0.0377(12) | 0.0254(10) | 0.0170(9) | 0.0059(8) | 0.0085(9) |
| C21 | 0.0173(9) | 0.0224(10) | 0.0307(11) | 0.0162(8) | 0.0013(8) | 0.0021(7) |
| C22 | 0.0243(11) | 0.0248(10) | 0.0368(12) | 0.0122(9) | 0.0002(9) | 0.0028(8) |
| C23 | 0.0287(12) | 0.0236(11) | 0.0636(17) | 0.0178(11) | -0.0022(11) | 0.0073(9) |

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C24 | 0.0302(12) | 0.0383(13) | 0.0644(17) | 0.0347(13) | -0.0086(11) | 0.0025(10) |
| C25 | 0.0243(11) | 0.0417(13) | 0.0390(13) | 0.0267(11) | -0.0022(9) | 0.0016(9) |
| C26 | 0.0179(10) | 0.0300(11) | 0.0308(11) | 0.0183(9) | 0.0024(8) | 0.0025(8) |
| C27 | 0.0224(10) | 0.0220(9) | 0.0206(9) | 0.0068(8) | 0.0001(7) | 0.0063(7) |
| C28 | 0.0242(10) | 0.0299(11) | 0.0259(10) | 0.0118(9) | 0.0022(8) | 0.0087(8) |
| C29 | 0.0397(13) | 0.0392(13) | 0.0234(11) | 0.0105(10) | 0.0031(9) | 0.0179(10) |
| C30 | 0.0410(13) | 0.0349(12) | 0.0267(11) | 0.0000(10) | -0.0087(10) | 0.0138(10) |
| C31 | 0.0395(13) | 0.0273(12) | 0.0363(13) | 0.0054(10) | -0.0072(10) | 0.0008(10) |
| C32 | 0.0323(12) | 0.0295(11) | 0.0297(11) | 0.0120(9) | -0.0031(9) | 0.0022(9) |
| C33 | 0.0172(9) | 0.0235(10) | 0.0197(9) | 0.0096(8) | -0.0001(7) | 0.0033(7) |
| C34 | 0.0212(10) | 0.0221(10) | 0.0245(10) | 0.0105(8) | 0.0020(8) | 0.0042(8) |
| C35 | 0.0232(10) | 0.0238(10) | 0.0316(11) | 0.0106(9) | 0.0012(8) | 0.0083(8) |
| C36 | 0.0203(10) | 0.0348(11) | 0.0266(11) | 0.0117(9) | 0.0036(8) | 0.0079(8) |
| C37 | 0.0215(10) | 0.0370(12) | 0.0332(11) | 0.0211(10) | 0.0074(8) | 0.0056(9) |
| C38 | 0.0231(10) | 0.0254(10) | 0.0335(11) | 0.0170(9) | 0.0051(8) | 0.0066(8) |
| N1 | 0.0313(10) | 0.0277(9) | 0.0308(10) | 0.0129(8) | 0.0049(7) | 0.0094(7) |
| N2 | 0.0366(10) | 0.0278(9) | 0.0298(10) | 0.0139(8) | 0.0092(8) | 0.0102(8) |
| N3 | 0.0273(9) | 0.0262(9) | 0.0307(9) | 0.0144(8) | 0.0059(7) | 0.0064(7) |
| N4 | 0.0284(10) | 0.0279(9) | 0.0312(10) | 0.0066(8) | 0.0058(8) | 0.0024(8) |
| N5 | 0.0262(10) | 0.0289(10) | 0.0429(11) | 0.0145(9) | 0.0083(8) | 0.0071(8) |
| N6 | 0.0191(8) | 0.0211(8) | 0.0225(8) | 0.0115(7) | 0.0028(6) | 0.0058(6) |
| O1 | 0.0650(12) | 0.0477(10) | 0.0418(10) | 0.0246(9) | 0.0278(9) | 0.0177(9) |
| O2 | 0.0308(9) | 0.0437(10) | 0.0474(10) | 0.0085(8) | 0.0081(7) | 0.0164(7) |
| O3 | 0.0602(12) | 0.0511(12) | 0.0878(15) | 0.0435(12) | 0.0318(11) | 0.0344(10) |
| O4 | 0.0389(10) | 0.0582(11) | 0.0497(11) | 0.0248(9) | 0.0246(8) | 0.0172(8) |
| P1 | 0.0173(2) | 0.0186(2) | 0.0169(2) | 0.00732(19) | 0.00221(18) | 0.00481(18) |
| P2 | 0.0181(2) | 0.0189(2) | 0.0195(2) | 0.00898(19) | 0.00148(18) | 0.00404(18) |

Table S- 129: Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for **[PNP][DNT]**.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H4 | 0.7325 | 0.3615 | 0.3593 | 0.028 |
| H5 | 0.8181 | 0.4810 | 0.5260 | 0.032 |
| H6 | 0.6876 | 0.5047 | 0.6561 | 0.031 |
| H7 | 0.4689 | 0.4166 | 0.6199 | 0.03 |
| H8 | 0.3818 | 0.2956 | 0.4534 | 0.025 |
| H10 | 0.4535 | 0.0039 | 0.0787 | 0.031 |
| H11 | 0.5256 | -0.1782 | 0.0192 | 0.038 |
| H12 | 0.6641 | -0.2118 | 0.1230 | 0.04 |
| H13 | 0.7306 | -0.0636 | 0.2865 | 0.041 |
| H14 | 0.6584 | 0.1182 | 0.3479 | 0.031 |
| H16 | 0.3878 | 0.3721 | 0.1879 | 0.028 |
| H17 | 0.4714 | 0.4994 | 0.1017 | 0.037 |
| H18 | 0.6745 | 0.5071 | 0.0512 | 0.041 |
| H19 | 0.7952 | 0.3860 | 0.0828 | 0.039 |
| H20 | 0.7137 | 0.2582 | 0.1688 | 0.032 |

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H22 | 0.2919 | -0.1751 | 0.1785 | 0.035 |
| H23 | 0.3759 | -0.2821 | 0.2587 | 0.046 |
| H24 | 0.4099 | -0.2007 | 0.4332 | 0.049 |
| H25 | 0.3639 | -0.0118 | 0.5300 | 0.039 |
| H26 | 0.2832 | 0.0986 | 0.4524 | 0.03 |
| H28 | 0.2450 | 0.0710 | 0.0548 | 0.031 |
| H29 | 0.1422 | -0.0603 | -0.1061 | 0.04 |
| H30 | -0.0105 | -0.2446 | -0.1296 | 0.045 |
| H31 | -0.0656 | -0.2964 | 0.0072 | 0.046 |
| H32 | 0.0357 | -0.1677 | 0.1679 | 0.038 |
| H34 | 0.1309 | 0.2863 | 0.3026 | 0.027 |
| H35 | -0.0266 | 0.3601 | 0.3992 | 0.031 |
| H36 | -0.1405 | 0.2461 | 0.4860 | 0.033 |
| H37 | -0.1091 | 0.0512 | 0.4649 | 0.034 |
| H38 | 0.0420 | -0.0272 | 0.3633 | 0.031 |

# 2.20 Crystal Structure Report for [TMA][DNT]

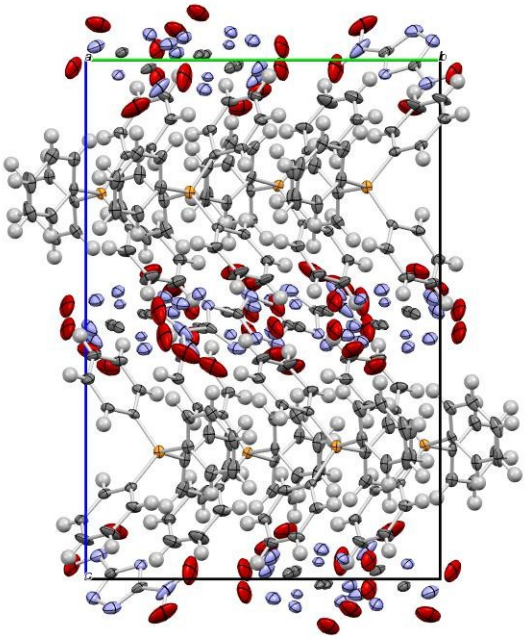

Figure S- 60: Projection of the packing of [TMA][DNT] along the a axis. Hydrogen atoms were omitted for clarity.

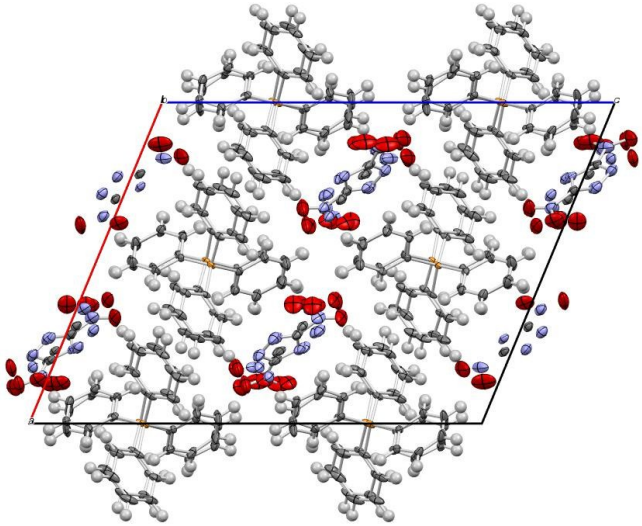

Figure S- 61: Projection of the packing of [TMA][DNT] along the b axis. Hydrogen atoms were omitted for clarity.

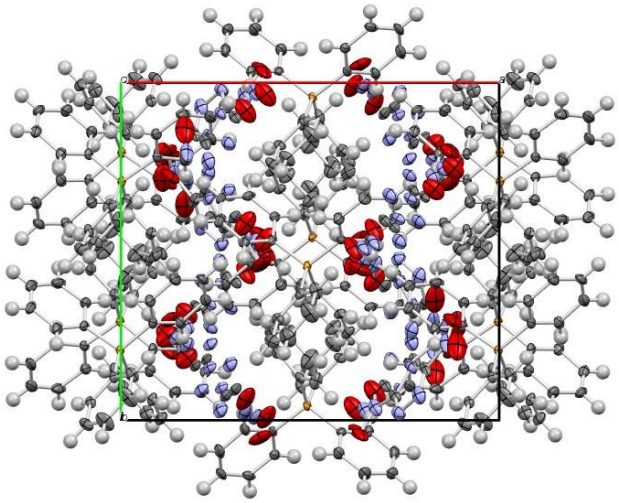

Figure S- 62: Projection of the packing of [TMA][DNT] along the c axis. Hydrogen atoms were omitted for clarity.

Table S- 130. Sample and crystal data for [TMA][DNT].

| | | |
|---|---|---|
| Identification code | TMADNT | |
| Chemical formula | $C_6H_{12}N_6O_4$ | |
| Formula weight | 232.22 g/mol | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.122 x 0.217 x 0.398 mm | |
| Crystal habit | clear colourless prism | |
| Crystal system | monoclinic | |
| Space group | P 1 21/c 1 | |
| Unit cell dimensions | a = 6.1515(3) Å | α = 90° |
| | b = 17.1906(10) Å | β = 92.6300(10)° |
| | c = 9.8599(5) Å | γ = 90° |
| Volume | 1041.57(10) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.481 $g/cm^3$ | |
| Absorption coefficient | 0.124 $mm^{-1}$ | |
| F(000) | 488 | |

Table S- 131. Data collection and structure refinement for TMADNT.

| | |
|---|---|
| Diffractometer | Bruker APEX DUO |
| Radiation source | fine-focus tube, MoKα |
| Theta range for data collection | 2.37 to 30.47° |
| Reflections collected | 3159 |
| Independent reflections | 3159 [R(int) = 0.0146] |
| Coverage of independent reflections | 99.6% |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.9850 and 0.9520 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXTL XT 2014/4 (Bruker AXS, 2014) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXTL XL 2014/6 (Bruker AXS, 2014) |
| Function minimized | $\Sigma\, w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 3159 / 28 / 184 |
| Goodness-of-fit on $F^2$ | 1.096 |
| Final R indices | 2867 data; I>2σ(I) R1 = 0.0406, wR2 = 0.1086 |
| | all data R1 = 0.0455, wR2 = 0.1120 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0572P)^2+0.2829P]$ where $P=(F_o^2+2F_c^2)/3$ |
| Largest diff. peak and hole | 0.425 and -0.249 eÅ$^{-3}$ |
| R.M.S. deviation from mean | 0.055 eÅ$^{-3}$ |

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for TMADNT.

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| C3 | 0.2023(4) | 0.42712(9) | 0.86891(18) | 0.0415(4) |
| C4 | 0.2689(3) | 0.30501(10) | 0.75384(14) | 0.0308(3) |
| C5 | 0.4957(3) | 0.34277(11) | 0.95365(18) | 0.0353(4) |
| C6 | 0.1193(3) | 0.30403(11) | 0.97743(19) | 0.0378(4) |
| N6 | 0.27214(17) | 0.34569(6) | 0.88835(10) | 0.0169(2) |
| C1 | 0.7680(2) | 0.39433(7) | 0.42610(12) | 0.0152(2) |
| C2 | 0.74165(19) | 0.46874(8) | 0.58067(12) | 0.0157(2) |
| N1 | 0.7414(2) | 0.39849(7) | 0.63943(11) | 0.0212(2) |
| N2 | 0.7584(2) | 0.34801(6) | 0.53445(11) | 0.0212(2) |
| N3 | 0.75917(16) | 0.47107(6) | 0.44636(11) | 0.01488(19) |
| N4 | 0.7886(2) | 0.36165(7) | 0.29179(12) | 0.0193(2) |
| N5 | 0.72257(18) | 0.53863(7) | 0.66087(12) | 0.0205(2) |
| O1 | 0.83042(19) | 0.40703(7) | 0.19958(11) | 0.0273(2) |
| O2 | 0.7646(2) | 0.29171(6) | 0.27647(12) | 0.0338(3) |
| O3 | 0.73521(17) | 0.60172(6) | 0.60315(11) | 0.0266(2) |
| O4 | 0.6933(2) | 0.53090(8) | 0.78278(13) | 0.0323(3) |
| C1' | 0.774(5) | 0.4323(11) | 0.4591(19) | 0.0152(2) |
| C2' | 0.740(5) | 0.5084(12) | 0.6096(17) | 0.0157(2) |

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| N1' | 0.745(5) | 0.5510(11) | 0.4956(19) | 0.0212(2) |
| N2' | 0.766(5) | 0.4997(12) | 0.395(2) | 0.0212(2) |
| N3' | 0.759(4) | 0.4324(13) | 0.5966(19) | 0.01488(19) |
| N4' | 0.797(5) | 0.3630(11) | 0.379(2) | 0.0193(2) |
| N5' | 0.726(6) | 0.5466(12) | 0.740(2) | 0.0205(2) |
| O1' | 0.832(5) | 0.3018(12) | 0.451(2) | 0.0273(2) |
| O2' | 0.810(8) | 0.376(2) | 0.257(2) | 0.0338(3) |
| O3' | 0.707(5) | 0.5023(13) | 0.836(2) | 0.0266(2) |
| O4' | 0.699(5) | 0.6167(12) | 0.740(2) | 0.0323(3) |

Table S- 132: Bond lengths (Å) for TMADNT

| | | | |
|---|---|---|---|
| C3-N6 | 1.4741(18) | C3-H3A | 0.98 |
| C3-H3B | 0.98 | C3-H3C | 0.98 |
| C4-N6 | 1.4986(16) | C4-H4A | 0.98 |
| C4-H4B | 0.98 | C4-H4C | 0.98 |
| C5-N6 | 1.4923(18) | C5-H5A | 0.98 |
| C5-H5B | 0.98 | C5-H5C | 0.98 |
| C6-N6 | 1.4979(18) | C6-H6A | 0.98 |
| C6-H6B | 0.98 | C6-H6C | 0.98 |
| C1-N3 | 1.3356(15) | C1-N2 | 1.3360(15) |
| C1-N4 | 1.4495(17) | C1-C2 | 2.0019(17) |
| C2-N3 | 1.3341(15) | C2-N1 | 1.3395(16) |
| C2-N5 | 1.4460(16) | N1-N2 | 1.3584(15) |
| N4-O2 | 1.2198(16) | N4-O1 | 1.2341(15) |
| N5-O3 | 1.2290(16) | N5-O4 | 1.2307(18) |
| C1'-N2' | 1.319(17) | C1'-N3' | 1.363(17) |
| C1'-N4' | 1.440(16) | C1'-C2' | 1.997(15) |
| C2'-N3' | 1.318(17) | C2'-N1' | 1.343(17) |
| C2'-N5' | 1.452(16) | N1'-N2' | 1.338(17) |
| N4'-O2' | 1.225(18) | N4'-O1' | 1.282(17) |
| N5'-O4' | 1.218(17) | N5'-O3' | 1.223(17) |

Table 5. Bond angles (°) for TMADNT.

| | | | |
|---|---|---|---|
| N6-C3-H3A | 109.5 | N6-C3-H3B | 109.5 |
| H3A-C3-H3B | 109.5 | N6-C3-H3C | 109.5 |
| H3A-C3-H3C | 109.5 | H3B-C3-H3C | 109.5 |
| N6-C4-H4A | 109.5 | N6-C4-H4B | 109.5 |
| H4A-C4-H4B | 109.5 | N6-C4-H4C | 109.5 |
| H4A-C4-H4C | 109.5 | H4B-C4-H4C | 109.5 |
| N6-C5-H5A | 109.5 | N6-C5-H5B | 109.5 |
| H5A-C5-H5B | 109.5 | N6-C5-H5C | 109.5 |
| H5A-C5-H5C | 109.5 | H5B-C5-H5C | 109.5 |
| N6-C6-H6A | 109.5 | N6-C6-H6B | 109.5 |
| H6A-C6-H6B | 109.5 | N6-C6-H6C | 109.5 |
| H6A-C6-H6C | 109.5 | H6B-C6-H6C | 109.5 |
| C3-N6-C5 | 110.20(12) | C3-N6-C6 | 110.08(14) |
| C5-N6-C6 | 108.75(12) | C3-N6-C4 | 109.63(11) |
| C5-N6-C4 | 109.93(11) | C6-N6-C4 | 108.21(12) |
| N3-C1-N2 | 117.75(12) | N3-C1-N4 | 121.69(11) |
| N2-C1-N4 | 120.56(11) | N3-C1-C2 | 41.39(7) |
| N2-C1-C2 | 76.35(8) | N4-C1-C2 | 163.09(10) |
| N3-C2-N1 | 117.26(12) | N3-C2-N5 | 122.02(12) |
| N1-C2-N5 | 120.72(11) | N3-C2-C1 | 41.45(7) |
| N1-C2-C1 | 75.81(8) | N5-C2-C1 | 163.46(10) |
| C2-N1-N2 | 104.17(10) | C1-N2-N1 | 103.66(10) |
| C2-N3-C1 | 97.16(11) | O2-N4-O1 | 124.06(13) |
| O2-N4-C1 | 118.69(11) | O1-N4-C1 | 117.25(11) |
| O3-N5-O4 | 124.24(13) | O3-N5-C2 | 118.13(11) |
| O4-N5-C2 | 117.62(12) | N2'-C1'-N3' | 118.2(14) |
| N2'-C1'-N4' | 117.8(15) | N3'-C1'-N4' | 124.1(17) |
| N2'-C1'-C2' | 77.2(10) | N3'-C1'-C2' | 41.0(8) |
| N4'-C1'-C2' | 165.1(15) | N3'-C2'-N1' | 116.9(14) |
| N3'-C2'-N5' | 122.9(16) | N1'-C2'-N5' | 120.1(16) |
| N3'-C2'-C1' | 42.7(8) | N1'-C2'-C1' | 74.2(10) |
| N5'-C2'-C1' | 165.5(16) | N2'-N1'-C2' | 105.6(15) |
| C1'-N2'-N1' | 103.1(15) | C2'-N3'-C1' | 96.2(13) |
| O2'-N4'-O1' | 132.(2) | O2'-N4'-C1' | 114.(2) |
| O1'-N4'-C1' | 113.2(18) | O4'-N5'-O3' | 127.(2) |
| O4'-N5'-C2' | 117.3(19) | O3'-N5'-C2' | 114.6(19) |

**Table S- 133**: Anisotropic atomic displacement parameters (Å$^2$) for TMADNT.
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C3 | 0.0595(11) | 0.0193(6) | 0.0433(8) | 0.0026(6) | -0.0233(8) | 0.0053(7) |
| C4 | 0.0309(7) | 0.0421(8) | 0.0195(6) | -0.0069(5) | 0.0018(5) | -0.0012(7) |
| C5 | 0.0239(7) | 0.0485(9) | 0.0328(8) | -0.0043(7) | -0.0073(6) | 0.0049(7) |
| C6 | 0.0393(9) | 0.0401(9) | 0.0351(8) | 0.0046(7) | 0.0154(7) | -0.0091(7) |
| N6 | 0.0162(4) | 0.0192(5) | 0.0151(4) | 0.0016(3) | -0.0002(4) | 0.0004(4) |
| C1 | 0.0130(5) | 0.0155(5) | 0.0170(5) | 0.0006(4) | 0.0008(4) | 0.0008(4) |
| C2 | 0.0119(5) | 0.0178(5) | 0.0174(5) | -0.0014(4) | -0.0002(4) | 0.0002(5) |
| N1 | 0.0241(6) | 0.0216(5) | 0.0179(5) | 0.0018(4) | 0.0020(4) | 0.0005(5) |
| N2 | 0.0267(6) | 0.0175(5) | 0.0194(5) | 0.0023(4) | 0.0018(4) | 0.0016(5) |
| N3 | 0.0117(4) | 0.0149(4) | 0.0179(4) | 0.0003(4) | -0.0008(4) | 0.0000(4) |
| N4 | 0.0192(5) | 0.0202(6) | 0.0184(5) | -0.0014(4) | 0.0002(5) | 0.0011(4) |
| N5 | 0.0129(4) | 0.0226(5) | 0.0257(5) | -0.0073(4) | -0.0016(4) | -0.0002(4) |
| O1 | 0.0362(6) | 0.0284(5) | 0.0177(4) | 0.0016(4) | 0.0046(4) | 0.0027(5) |
| O2 | 0.0482(7) | 0.0204(5) | 0.0329(5) | -0.0091(4) | 0.0028(5) | -0.0016(5) |
| O3 | 0.0209(5) | 0.0186(4) | 0.0400(6) | -0.0059(4) | -0.0021(4) | 0.0010(4) |
| O4 | 0.0316(6) | 0.0417(7) | 0.0239(5) | -0.0126(5) | 0.0027(5) | -0.0009(6) |
| C1' | 0.0130(5) | 0.0155(5) | 0.0170(5) | 0.0006(4) | 0.0008(4) | 0.0008(4) |
| C2' | 0.0119(5) | 0.0178(5) | 0.0174(5) | -0.0014(4) | -0.0002(4) | 0.0002(5) |
| N1' | 0.0241(6) | 0.0216(5) | 0.0179(5) | 0.0018(4) | 0.0020(4) | 0.0005(5) |
| N2' | 0.0267(6) | 0.0175(5) | 0.0194(5) | 0.0023(4) | 0.0018(4) | 0.0016(5) |
| N3' | 0.0117(4) | 0.0149(4) | 0.0179(4) | 0.0003(4) | -0.0008(4) | 0.0000(4) |
| N4' | 0.0192(5) | 0.0202(6) | 0.0184(5) | -0.0014(4) | 0.0002(5) | 0.0011(4) |
| N5' | 0.0129(4) | 0.0226(5) | 0.0257(5) | -0.0073(4) | -0.0016(4) | -0.0002(4) |
| O1' | 0.0362(6) | 0.0284(5) | 0.0177(4) | 0.0016(4) | 0.0046(4) | 0.0027(5) |
| O2' | 0.0482(7) | 0.0204(5) | 0.0329(5) | -0.0091(4) | 0.0028(5) | -0.0016(5) |
| O3' | 0.0209(5) | 0.0186(4) | 0.0400(6) | -0.0059(4) | -0.0021(4) | 0.0010(4) |
| O4' | 0.0316(6) | 0.0417(7) | 0.0239(5) | -0.0126(5) | 0.0027(5) | -0.0009(6) |

**Table S- 134**: Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å$^2$) for TMADNT.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H3A | 0.2097 | 0.4541 | 0.9566 | 0.062 |
| H3B | 0.0524 | 0.4283 | 0.8308 | 0.062 |
| H3C | 0.2984 | 0.4531 | 0.8065 | 0.062 |
| H4A | 0.3207 | 0.2515 | 0.7666 | 0.046 |
| H4B | 0.3638 | 0.3326 | 0.6928 | 0.046 |
| H4C | 0.1199 | 0.3043 | 0.7141 | 0.046 |
| H5A | 0.5374 | 0.2885 | 0.9703 | 0.053 |
| H5B | 0.4978 | 0.3710 | 1.0400 | 0.053 |
| H5C | 0.5987 | 0.3669 | 0.8935 | 0.053 |
| H6A | 0.1149 | 0.3310 | 1.0648 | 0.057 |
| H6B | 0.1699 | 0.2505 | 0.9923 | 0.057 |
| H6C | -0.0267 | 0.3033 | 0.9334 | 0.057 |

# 2.21 Crystal Structure Report for [TMA][DNT]·HDNT

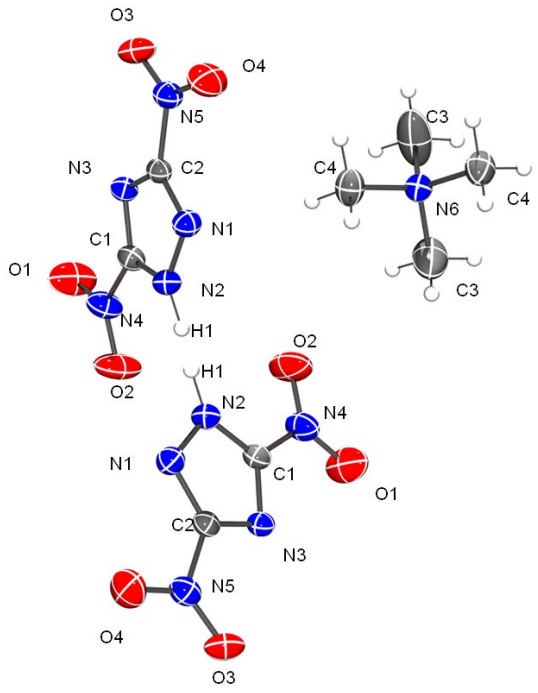


Figure S- 63: Molecular structure of **[TMA][DNT]·HDNT**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atom H1 has a site occupancy factor of 50%.

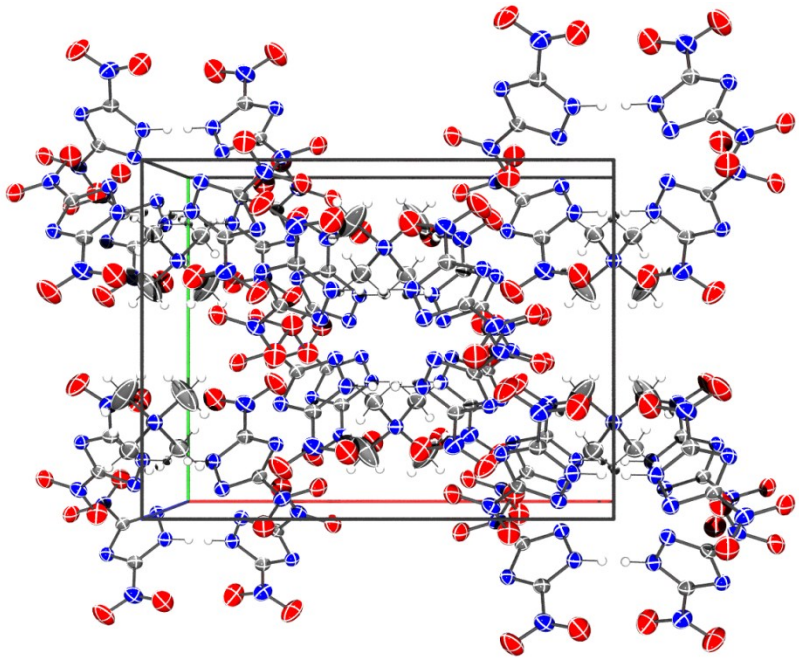

Figure S- 64: Projection of the packing of **[TMA][DNT]·HDNT** perpendicular to the 001 plane.

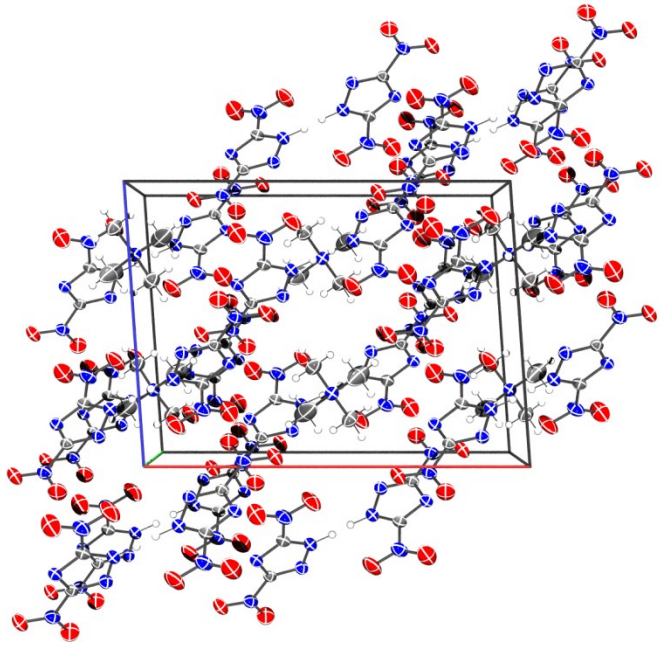

Figure S- 65: Projection of the packing of **[TMA][DNT]·HDNT** perpendicular to the 010 plane.

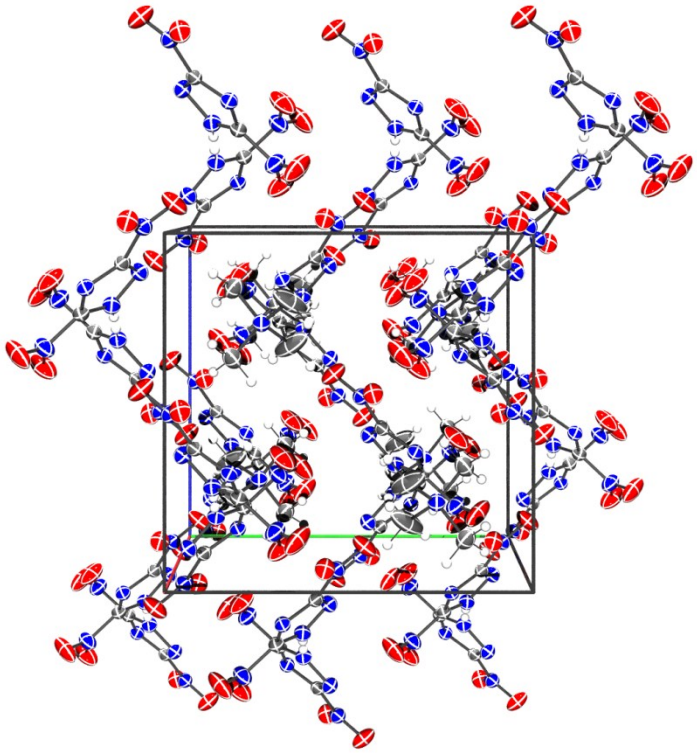

Figure S- 66: Projection of the packing of **[TMA][DNT]·HDNT** perpendicular to the 100 plane.

Table S- 135: Sample and crystal data for **[TMA][DNT]·HDNT**.

| | | |
|---|---|---|
| Identification code | TMADNT | |
| Chemical formula | $C_8H_7N_{11}O_8$ | |
| Formula weight | 391.30 | |
| Temperature | 130(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal size | 0.230 x 0.280 x 0.440 mm | |
| Crystal habit | clear colourless prism | |
| Crystal system | monoclinic | |
| Space group | C 1 2/c 1 | |
| Unit cell dimensions | a = 14.336(3) Å | α = 90° |
| | b = 10.931(2) Å | β = 93.978(3)° |
| | c = 10.644(2) Å | γ = 90° |
| Volume | 1664.0(6) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.562 $g/cm^3$ | |
| Absorption coefficient | 0.138 $mm^{-1}$ | |
| F(000) | 808 | |

Table S- 136: Data collection and structure refinement for **[TMA][DNT]·HDNT**.

| | |
|---|---|
| Diffractometer | Bruker SMART APEX |
| Radiation source | fine-focus tube, MoKα |
| Theta range for data collection | 2.35 to 28.58° |
| Index ranges | -19<=h<=13, -14<=k<=13, -13<=l<=14 |
| Reflections collected | 5163 |
| Independent reflections | 1961 [R(int) = 0.0224] |
| Coverage of independent reflections | 92.0% |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.9690 and 0.9420 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXTL XT 2013/6 (Sheldrick, 2013) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXTL XLMP 2014/1 (Bruker AXS, 2013) |
| Function minimized | $\Sigma\, w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 1961 / 0 / 125 |
| Goodness-of-fit on $F^2$ | 1.040 |
| Final R indices | 1646 data; I>2σ(I) R1 = 0.0418, wR2 = 0.1111 |
| | all data R1 = 0.0499, wR2 = 0.1192 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0670P)^2+0.7354P]$ where $P=(F_o^2+2F_c^2)/3$ |
| Largest diff. peak and hole | 0.254 and -0.307 eÅ$^{-3}$ |
| R.M.S. deviation from mean | 0.053 eÅ$^{-3}$ |

Table S- 137: Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for **[TMA][DNT]·HDNT.**U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| C1 | 0.34252(9) | 0.29195(11) | 0.71462(12) | 0.0263(3) |
| C2 | 0.29794(8) | 0.40615(11) | 0.57578(11) | 0.0239(3) |
| C3 | 0.57220(17) | 0.1587(3) | 0.3150(2) | 0.0821(8) |
| C4 | 0.45563(11) | 0.31434(14) | 0.34491(15) | 0.0398(4) |
| N1 | 0.38464(8) | 0.44292(10) | 0.60342(11) | 0.0285(3) |
| N2 | 0.41386(8) | 0.36538(10) | 0.69675(10) | 0.0280(3) |
| N3 | 0.26658(7) | 0.31256(9) | 0.64125(10) | 0.0258(3) |
| N4 | 0.34994(9) | 0.19539(11) | 0.80850(12) | 0.0385(3) |
| N5 | 0.23910(8) | 0.46537(10) | 0.47719(10) | 0.0310(3) |
| N6 | 0.5 | 0.23705(14) | 0.25 | 0.0293(3) |
| O1 | 0.28007(9) | 0.13506(12) | 0.82168(13) | 0.0618(4) |
| O2 | 0.42566(9) | 0.18172(13) | 0.86577(13) | 0.0589(4) |
| O3 | 0.15760(7) | 0.43273(9) | 0.46247(11) | 0.0392(3) |
| O4 | 0.27536(9) | 0.54403(11) | 0.41513(12) | 0.0509(3) |

Table S- 138: Bond lengths (Å) for **[TMA][DNT]·HDNT.**

| | | | |
|---|---|---|---|
| C1-N3 | 1.3145(16) | C1-N2 | 1.3241(17) |
| C1-N4 | 1.4524(17) | C2-N1 | 1.3199(17) |
| C2-N3 | 1.3334(16) | C2-N5 | 1.4524(16) |
| C3-N6 | 1.478(2) | C3-H3A | 0.98 |
| C3-H3B | 0.98 | C3-H3C | 0.98 |
| C4-N6 | 1.4928(17) | C4-H4A | 0.98 |
| C4-H4B | 0.98 | C4-H4C | 0.98 |
| N1-N2 | 1.3503(15) | N2-H1 | 0.9216 |
| N4-O1 | 1.2155(17) | N4-O2 | 1.2168(17) |
| N5-O3 | 1.2214(16) | N5-O4 | 1.2220(16) |
| N6-C3 | 1.478(2) | N6-C4 | 1.4927(17) |

Table S- 139: Bond angles (°) for **[TMA][DNT]·HDNT**.

| | | | |
|---|---|---|---|
| N3-C1-N2 | 115.27(11) | N3-C1-N4 | 123.47(12) |
| N2-C1-N4 | 121.26(11) | N1-C2-N3 | 117.62(11) |
| N1-C2-N5 | 121.06(11) | N3-C2-N5 | 121.31(11) |
| N6-C3-H3A | 109.5 | N6-C3-H3B | 109.5 |
| H3A-C3-H3B | 109.5 | N6-C3-H3C | 109.5 |
| H3A-C3-H3C | 109.5 | H3B-C3-H3C | 109.5 |
| N6-C4-H4A | 109.5 | N6-C4-H4B | 109.5 |
| H4A-C4-H4B | 109.5 | N6-C4-H4C | 109.5 |
| H4A-C4-H4C | 109.5 | H4B-C4-H4C | 109.5 |
| C2-N1-N2 | 102.24(10) | C1-N2-N1 | 106.44(10) |
| C1-N2-H1 | 131.2 | N1-N2-H1 | 122.2 |
| C1-N3-C2 | 98.43(10) | O1-N4-O2 | 126.11(13) |
| O1-N4-C1 | 116.88(12) | O2-N4-C1 | 117.01(12) |
| O3-N5-O4 | 125.11(12) | O3-N5-C2 | 117.71(11) |
| O4-N5-C2 | 117.18(12) | C3-N6-C3 | 109.1(3) |
| C3-N6-C4 | 109.13(11) | C3-N6-C4 | 109.18(11) |
| C3-N6-C4 | 109.18(11) | C3-N6-C4 | 109.13(11) |
| C4-N6-C4 | 111.06(16) | | |

Table S- 140: Anisotropic atomic displacement parameters (Å$^2$) for **[TMA][DNT]·HDNT**.The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0306(7) | 0.0245(6) | 0.0234(6) | -0.0009(5) | -0.0015(5) | -0.0007(5) |
| C2 | 0.0268(6) | 0.0232(6) | 0.0215(6) | -0.0020(4) | 0.0004(5) | 0.0026(5) |
| C3 | 0.0846(16) | 0.1018(17) | 0.0630(13) | 0.0458(13) | 0.0274(12) | 0.0554(14) |
| C4 | 0.0426(9) | 0.0360(7) | 0.0419(8) | -0.0086(6) | 0.0114(7) | -0.0041(6) |
| N1 | 0.0274(6) | 0.0282(5) | 0.0298(6) | 0.0031(4) | 0.0009(4) | 0.0002(4) |
| N2 | 0.0265(5) | 0.0291(5) | 0.0277(6) | 0.0005(4) | -0.0020(4) | 0.0006(4) |
| N3 | 0.0263(6) | 0.0259(5) | 0.0246(5) | -0.0010(4) | -0.0019(4) | -0.0019(4) |
| N4 | 0.0439(7) | 0.0367(6) | 0.0335(6) | 0.0097(5) | -0.0068(5) | -0.0056(5) |
| N5 | 0.0350(6) | 0.0298(6) | 0.0276(6) | 0.0010(4) | -0.0012(5) | 0.0054(5) |
| N6 | 0.0297(8) | 0.0281(7) | 0.0302(8) | 0 | 0.0029(6) | 0 |
| O1 | 0.0568(8) | 0.0579(8) | 0.0687(9) | 0.0342(7) | -0.0099(6) | -0.0219(6) |
| O2 | 0.0528(7) | 0.0659(8) | 0.0543(7) | 0.0289(6) | -0.0222(6) | -0.0082(6) |
| O3 | 0.0322(5) | 0.0390(6) | 0.0444(6) | -0.0011(4) | -0.0121(4) | 0.0047(4) |
| O4 | 0.0512(7) | 0.0552(7) | 0.0459(7) | 0.0256(6) | 0.0016(5) | 0.0020(6) |

Table S- 141: Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å$^2$) for **[TMA][DNT]·HDNT**.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| H3A | 0.6192 | 0.2102 | 0.3606 | 0.123 |
| H3B | 0.6023 | 0.1088 | 0.2529 | 0.123 |
| H3C | 0.5429 | 0.1050 | 0.3747 | 0.123 |
| H4A | 0.5029 | 0.3678 | 0.3871 | 0.06 |
| H4B | 0.4286 | 0.2616 | 0.4074 | 0.06 |
| H4C | 0.4062 | 0.3644 | 0.3026 | 0.06 |
| H1 | 0.4744 | 0.3656 | 0.7320 | 0.034 |

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