Supporting Information

Melt-cast Materials: Combining the Advantages of Highly Nitrated Azoles and Open-chain Nitramines

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1. IR and Raman spectroscopy

1.1. Discussion

The IR spectrum of 1-(3-nitro-1*H*-1,2,4-triazol-5-on-4-yl)-2-nitrazapropane (**1**) shows a broad valance stretching mode of the N–H bond in the range of 3162–3096 cm^{-1}. For the two times alkylated **2** the N–H vibration mode disappeared. The C–H vibration bands of compounds **1** and **2** are observed in a range from 3060–2856 cm^{-1} (Raman) and 3062–2852 cm^{-1} (IR). For both NTO derivatives the C=O valence vibration appears as very sharp and intensive band in a range of 1738–1717 cm^{-1} in the IR spectra. The vibrational frequencies for the asymmetric stretching mode of the C-bonded nitro group are observed at 1554–1540 cm^{-1}. The symmetric stretching modes are located at lower energy (1354–1340 cm^{-1}). The same trend is observed for the nitramine nitro groups showing the ν_{as} stretching modes at 1586 and 1578 cm^{-1} in the Raman spectra and the ν_{s} stretching modes in a range of 1306–1260 cm^{-1} (IR). For compound **2** an additional vibration mode of the nitramine nitro group is observed due to the different chemical surroundings of the two nitramine moieties.

The C–H valence vibrations of the 1,2,4-triazole derivatives **3**–**5** are located in the range of 3080–2795 cm^{-1}. The asymmetric and symmetric stretching modes of the nitramine nitro groups are observed at 1644–1552 cm^{-1} and 1300–1237 cm^{-1}, respectively. According to Mel'nikov[1], the intensive bands at 1440 cm^{-1} and 1380 cm^{-1} of compound **3** respective at 1403 cm^{-1} for **4** and 1492 cm^{-1} for **5** in the Raman spectrum are caused by coupled stretching and bending modes of the ONC respective NCN valence angles of the nitro group and of the fragment of the triazole ring. For the nitro group introduced in 5-position of **3**, a shift to lower frequencies is observed. Furthermore, the characteristic asymmetric and symmetric IR-intensive stretching modes of the *C*-bonded nitro groups are located in a range of 1540–1496 cm^{-1} and 1334–1306 cm^{-1}, whereas for **3** a splitting of these vibrations into two bands is observed due to a different surrounding of the nitro groups in 3- and 5-position. Additionally, the N–H valence vibrations of **4** are seen at 3428 cm^{-1}.

The dinitroimidazole based compounds **6** and **7** show the same characteristic vibrations of the C–H, nitramine and C-bonded nitro groups as the 1,2,4-triazole derivatives in similar ranges. In addition to the aliphatic C–H vibration modes, aromatic C–H valence vibrations are observed for **6** and **7** at 3146–3126 cm^{-1}.

The aromatic C–H vibrations of nitramines **8–10** are seen in a range from 3174–3122 cm^{-1}. The C–H valence vibrations of the 3,5-dinitropyrazole substituted nitramine are shifted to higher wavenumbers compared to the 3,4-dinitropyrazole derivatives. The aliphatic C–H valence vibrations of the nitramine group of **8–12** are observed from 3073–2954 cm^{-1}, whereas the vibrations of the methyl group are located at lower wavenumbers. The asymmetric and symmetric nitramine N–NO_2 stretching modes are at 1648–1558 cm^{-1} and 1318–1232 cm^{-1}. Furthermore, the characteristic asymmetric and symmetric IR-intensive stretching modes of the *C*-bonded nitro groups are located in a range of 1544–1480 cm^{-1} and 1409–1318 cm^{-1}.

Additionally, a C_{ar}–Cl vibration at 1054 cm^{-1} respective N–H valence vibrations at 3489-3383 cm^{-1} could be assigned for nitramines **11** and **12**.

1.2. Spectroscopic data

1-(3-Nitro-1*H*-1,2,4-triazol-5-on-4-yl)-2-nitrazapropane (1)

IR $\tilde{\nu}/cm^{-1}$: 3162 (w), 3094 (w), 3062 (w), 2960 (w), 2928 (vw), 2852 (vw), 2794 (vw), 1770 (vw), 1732 (s), 1716 (vs), 1690 (w), 1584 (vw), 1540 (vs), 1454 (m), 1414 (w), 1380 (w), 1340 (m), 1292 (m), 1278 (w), 1260 (m), 1184 (w), 1110 (vw), 1056 (w), 1026 (w), 934 (w), 860 (vw), 840 (w), 800 (w), 766 (w),736 (w), 710 (w), 662 (w), 632 (vw), 610 (w), 736 (w), 710 (w), 662 (w), 632 (vw), 610 (w). Raman $\tilde{\nu}/cm^{-1}$: 3061 (14), 3012 (55), 2959 (32), 2910 (7), 2890 (6), 2856 (4), 1717 (5), 1578 (59), 1547 (39), 1469 (20), 1450 (29), 1413 (41), 1397 (56), 1341 (100), 1292 (10), 1273 (9), 1188 (29), 1108 (74), 1057 (12), 1026 (9), 936 (14), 862 (75), 842 (24), 801 (63), 739 (5), 716 (5), 663 (8), 608 (29), 591 (6), 478 (18),450 (10), 426 (21), 416 (26), 409 (22), 329 (6), 253 (15), 197 (13), 131 (5), 109 (17).

2,4-Bis((methyl(nitro)amino)methyl)-3-nitro-1,2,4-triazol-5-one (2)

IR $\tilde{\nu}/cm^{-1}$: 3042 (vw), 3018 (vw), 3008 (vw), 2978 (vw), 2966 (vw), 2942 (vw), 1738 (vs), 1554 (s), 1540 (s), 1470 (m), 1452 (m), 1438 (w), 1430 (w), 1414 (m), 1386 (m), 1354 (w), 1334 (w), 1306 (s), 1292 (s), 1262 (m), 1218 (w), 1176 (w), 1126 (w), 1112 (w), 1088 (w), 1018 (m), 960 (vw), 896 (w), 864 (vw), 854 (vw), 816 (vw), 784 (m), 768 (w), 762 (w), 748 (w), 730 (w), 712 (w), 682 (w), 648 (vw), 632 (w), 610 (w). Raman $\tilde{\nu}/cm^{-1}$: 3044 (25), 3019 (26), 2978 (59), 2923 (12), 2902 (12), 2849 (6), 1753 (3), 1739 (10), 1586 (100), 1550 (49), 1496 (7), 1454 (97), 1429 (18), 1414 (23), 1390 (85), 1380 (53), 1357 (44), 1317 (68), 1289 (44), 1271 (22), 1245 (31), 1219 (57), 1176 (10), 1128 (62), 1114 (18), 1088 (14), 1033 (7), 1023 (9), 986 (29), 960 (16),899 (17), 864 (35), 855 (70), 818 (43), 786 (8), 772 (2), 749 (5), 732 (5), 713 (3), 682 (5), 652 (12), 632 (6), 614 (20), 610 (19), 598 (15), 502 (12), 429 (19), 413 (23), 387 (8), 356 (4), 350 (4), 305 (10), 267 (12), 248 (2).

1-(3,5-Dinitro-1,2,4-triazol-1-yl)-2-nitrazapropane (3)

IR $\tilde{\nu}/cm^{-1}$: 3062 (vw), 3036 (w), 2988 (vw), 2970 (vw), 2942 (vw), 2912 (vw), 2882 (vw), 1582 (vs), 1574 (vs), 1540 (s), 1516 (vs), 1476 (m), 1462 (m), 1438 (w), 1426 (m), 1412 (w), 1400 (w), 1382 (w), 1360 (w), 1334 (m), 1318 (s), 1300 (s), 1282 (vs), 1216 (m), 1188 (w), 1124 (w), 1042 (m), 1022 (w), 976 (w), 878 (w),862 (m), 830 (m), 764 (w), 736 (w), 690 (m), 646 (w), 614 (w). Raman $\tilde{\nu}/cm^{-1}$: 3065 (4), 3037 (9), 2989 (16), 2969 (10), 2949 (3), 2913 (3), 2899 (3), 1583 (7), 1574 (9), 1568 (12), 1541 (4), 1520 (5), 1478 (7), 1462 (11), 1440 (96), 1429 (100), 1413 (28), 1402 (20), 1383 (42), 1361 (5), 1342 (16), 1321 (22), 1301 (7), 1285 (9), 1218 (21), 1191 (3), 1125 (13), 1051 (3), 1041 (4), 1025 (13),978 (6), 878 (22), 864 (4), 830 (15), 770 (3), 760 (14), 736 (2), 691 (4), 644 (2), 617 (5), 601 (2), 521 (1), 485 (3), 420 (8), 379 (5), 357 (9), 335 (6), 305 (10), 289 (5), 206 (7), 185 (5), 164 (9), 116 (48), 88 (85).

1-(5-Amino-3-nitro-1,2,4-triazol-1-yl)-2-nitrazapropane (4)

IR $\tilde{\nu}$/cm^{-1}: 3428 (s), 3298 (w), 3224 (w), 3176 (m), 3040 (w), 2359 (w), 2332 (w), 1641 (s), 1569 (m), 1538 (m), 1517 (vs), 1455 (m), 1447 (m), 1436 (m), 1426 (m), 1401 (m), 1384 (m), 1341 (w), 1306 (s), 1299 (vs), 1262 (m), 1246 (m), 1225 (m), 1102 (w), 1091 (w), 1021 (m), 949 (w), 856 (m), 844 (m), 797 (w), 762 (w), 730 (w), 712 (w), 656 (w). Raman $\tilde{\nu}$/cm^{-1}: 3432 (1), 3241 (1), 3225 (1), 3175 (2), 3167 (1), 3025 (1), 2997 (13), 2925 (1), 2795 (1), 1647 (6), 1576 (18), 1550 (7), 1514 (50), 1440 (6), 1427 (19), 1403 (100), 1345 (8), 1307 (39), 1262 (4), 1231 (30), 1105 (22), 1028 (14), 953 (13), 856 (18), 800 (18), 767 (3), 710 (4), 661 (2), 652 (1), 631 (1), 612 (5), 588 (1), 478 (1), 452 (1), 425 (6), 392 (2), 359 (2), 303 (2), 267 (6), 216 (4).

5,5'-Bi(1-(2-nitrazapropan-1-yl)-3-nitro-1,2,4-triazole) (5)

IR $\tilde{\nu}$/cm^{-1}: 3048 (w), 2365 (vw), 2333 (vw), 1560 (s), 1552 (s), 1538 (vs), 1493 (w), 1473 (m), 1452 (m), 1412 (s), 1386 (m), 1360 (w), 1336 (w), 1312 (s), 1298 (vs), 1287 (vs), 1237 (vs), 1096 (w), 1050 (m), 1025 (s), 969 (w), 959 (w), 862 (vw), 836 (vs), 760 (m), 727 (w), 716 (m), 682 (w), 662 (w). Raman $\tilde{\nu}$/cm^{-1}: 3050 (3), 3002 (23), 2961 (7), 1621 (6), 1598 (96), 1560 (5), 1492 (64), 1453 (5), 1435 (13), 1420 (22). 1388 (30), 1359 (4), 1339 (4), 1315 (16), 1278 (8), 1242 (8), 1222 (3), 1177 (5), 1129 (9), 1031 (13), 991 (3), 972 (3), 864 (18), 774 (6), 745 (3), 602 (5), 418 (4), 281 (4).

1-(2,4-Dinitroimidazol-1-yl)-2-nitrazapropane (6)

IR $\tilde{\nu}$/cm^{-1}: 3146 (w), 3068 (vw), 3004 (vw), 2948 (vw), 1542 (vs), 1514 (m), 1494 (s), 1464 (m), 1430 (m), 1408 (w), 1396 (w), 1378 (w), 1354 (m), 1334 (vs), 1302 (s), 1270 (m), 1256 (s), 1178 (w), 1128 (m), 1028 (m), 994 (w), 956 (w), 880 (vw), 862 (w), 850 (m), 836 (w), 820 (m), 766 (w), 750 (w), 724 (w), 680 (m), 648 (vw), 622 (vw), 610 (w), 680 (m), 648 (vw), 622 (vw), 610 (w). Raman $\tilde{\nu}$/cm^{-1}: 3148 (4), 3069 (3), 3041 (1), 3005 (6), 2963 (3), 2896 (1), 1565 (3), 1548 (20), 1522 (17), 1514 (24), 1468 (3), 1433 (100), 1410 (33), 1386 (19), 1355 (21), 1338 (17), 1309 (8), 1296 (13), 1273 (24), 1180 (4), 1134 (7), 1109 (2), 1033 (2), 1015 (2), 996 (14), 957 (3), 863 (4), 854 (8),838 (2), 820 (4), 757 (2), 752 (2), 726 (4), 612 (4).

1-(4,5-Dinitroimidazol-1-yl)-2-nitrazapropane (7)

IR $\tilde{\nu}$/cm^{-1}: 3126 (m), 3052 (w), 3006 (vw), 2960 (vw), 1562 (w), 1528 (vs), 1518 (vs), 1494 (vs), 1466 (m), 1454 (m), 1426 (m), 1388 (w), 1356 (m), 1342 (s), 1314 (s), 1286 (s), 1252 (s), 1216 (m), 1164 (m), 1128 (w), 1032 (m), 1018 (w), 962 (w), 872 (vw), 856 (w), 846 (m), 814 (m), 766 (w), 754 (m), 714 (w), 696 (m), 638 (w), 622 (vw), 612 (w). Raman $\tilde{\nu}$/cm^{-1}: 3126 (20), 3053 (12), 3038 (6), 3005 (25), 2959 (13), 2897 (5), 1565 (45), 1544 (36), 1521 (31), 1498 (11), 1468 (4), 1457 (6), 1428 (16), 1413 (6), 1390 (51), 1371 (85), 1360 (62), 1344 (100), 1318 (16), 1289 (29), 1255 (5), 1221 (2), 1165 (5), 1130 (19), 1035 (6), 1018 (4), 966 (5), 874 (4), 857 (56), 819 (11),764 (13), 757 (22), 715 (13), 698 (4), 649 (4), 613 (10), 501 (8), 459 (3), 448 (5), 402 (6), 363 (3), 342 (5), 300 (5), 231 (7), 205 (10), 198 (8), 149 (3), 113 (24).

1-(3,5-Dinitropyrazol-1-yl)-2-nitrazapropane (8)

IR $\tilde{\nu}$/cm^{-1}: 3174 (w), 3152 (w), 3066 (w), 3020 (w), 2954 (w), 2868 (w), 1564 (w), 1536 (m), 1514 (m), 1462 (w), 1430 (w), 1384 (w), 1344 (m), 1288 (m), 1240 (w), 1186 (w), 1110 (w), 1090 (w), 1050 (w), 1022 (w), 1000 (w), 972 (w), 852 (w), 834 (w), 764 (w), 742 (w), 684 (w), 658 (w), 636 (w), 624 (w). Raman $\tilde{\nu}$/cm^{-1}: 3175 (4), 3152 (4), 3069 (4), 3055 (4), 3021 (14), 3010 (10), 2954 (8), 2927 (3), 1567 (7), 1555 (8), 1542 (5), 1532 (5), 1516 (10), 1487 (6), 1467 (16), 1433 (29), 1409 (100), 1386 (30), 1355 (13), 1335 (7), 1320 (6), 1307 (6), 1286 (10), 1243 (10), 1186 (3), 1116 (3), 1052 (1), 1026 (1), 1003 (11), 977 (2), 971 (1), 875 (10), 863 (12), 818 (9), 760 (4), 747 (3), 739 (2), 685 (2), 641 (1), 608 (5), 574 (1), 531 (1), 496 (2), 485 (1), 434 (3), 402 (2), 384 (2), 352 (4), 343 (4), 298 (8), 272 (3).

1-(3,4-Dinitropyrazol-1-yl)-2-nitrazapropane (9)

IR $\tilde{\nu}$/cm^{-1}: 3147 (w), 3122 (m), 3053 (w), 3008 (vw), 2959 (vw), 1544 (s), 1523 (vs), 1465 (m), 1448 (m), 1425 (w), 1388 (w), 1364 (m), 1324 (m), 1292 (m), 1275 (s), 1253 (m), 1186 (w), 1136 (m), 1119 (m), 1075 (m), 1017 (m), 1003 (m), 959 (w), 878 (w), 861 (m), 808 (m), 763 (w), 748 (m), 679 (w), 665 (w). Raman $\tilde{\nu}$/cm^{-1}: 3148 (9), 3132 (14), 3123 (20), 3056 (20), 3007 (42), 2957 (29), 2928 (9), 2887 (8), 1609 (6), 1567 (29), 1559 (31), 1543 (36), 1523 (86), 1465 (82), 1417 (96), 1389 (26), 1363 (75), 1353 (100), 1322 (65), 1280 (30), 1258 (14), 1160 (12), 1140 (10), 1119 (13), 1004 (61), 960 (18), 863 (90), 855 (76), 810 (12), 762 (19), 753 (14), 743 (16), 681 (6), 666 (8), 609 (29), 593 (11), 498 (16), 492 (17), 452 (13), 436 (12), 424 (12), 395 (23), 382 (21), 329 (20), 309 (15), 275 (9), 204 (45).

1-(3,4,4'-Trinitro-1,3'-bipyrazol-2'-yl)-2-nitrazapropane (10)

IR $\tilde{\nu}$/cm^{-1}: 3144 (w), 3053 (w), 3008 (w), 1599 (m), 1568 (m), 1528 (m), 1512 (m), 1501 (m), 1466 (m), 1451 (w), 1438 (w), 1416 (w), 1402 (m), 1365 (m), 1337 (m), 1315 (m), 1292 (m), 1248 (m), 1226 (w), 1185 (w), 1121 (w), 1041 (w), 1027 (w), 1012 (w), 945 (w), 877 (w), 869 (w), 856 (w), 826 (m), 807 (m), 762 (m), 747 (w), 697 (w), 664 (w). Raman $\tilde{\nu}$/cm^{-1}: 3143 (23), 3054 (9), 3035 (4), 3008 (22), 2951 (9), 2892 (3), 2855 (2), 2836 (2), 1599 (83), 1572 (13), 1552 (37), 1535 (39), 1518 (29), 1500 (52), 1478 (14), 1464 (19), 1454 (22), 1433 (34), 1415 (57), 1403 (100), 1380 (16), 1364 (45), 1338 (62), 1315 (25), 1291 (10), 1252 (16), 1227 (12), 1194 (15), 1126 (5), 1118 (9),1043 (13), 1030 (2), 1013 (5), 952 (24), 942 (34), 869 (4), 858 (41), 827 (4), 807 (3), 764 (19), 755 (7), 748 (5), 700 (4), 662 (5), 638 (4), 631 (3), 617 (5), 606 (7), 579 (6), 476 (3), 461 (4), 450 (3), 442 (3), 383 (3), 370 (4), 353 (5), 313 (5),294 (10), 278 (11), 241 (3).

1-(5-Chloro-3,4-dinitropyrazol-1-yl)-2-nitrazapropane (11)

IR $\tilde{\nu}$/cm^{-1}: 3055 (vw), 2998 (vw), 2965 (vw), 1562 (m), 1533 (vs), 1498 (s), 1461 (m), 1452 (m), 1444 (m), 1426 (m), 1406 (m), 1384 (w), 1359 (m), 1339 (s), 1334 (m), 1292 (m), 1266 (s), 1235 (s), 1168 (w), 1128 (w), 1044 (w), 1027 (m), 961 (w), 888

(w), 852 (w), 814 (m), 774 (w), 762 (m), 752 (m), 710 (w), 681 (w). Raman $\tilde{\nu}$/cm^{-1}: 3056 (14), 3023 (7), 2998 (30), 2967 (20), 2892 (6), 2867 (4), 2857(4), 1567 (21), 1544 (14), 1522 (14), 1501 (59), 1476 (18), 1461 (26), 1445 (100), 1430 (29), 1397 (22), 1366 (51), 1339 (83), 1293 (6), 1258 (24), 1170 (5), 1129 (15), 1044 (14), 1033 (8), 959 (7), 888 (7), 853 (40), 815 (9), 774 (20), 755 (11), 711 (2), 682 (2), 639 (4), 610 (11), 539 (7), 523 (4), 448 (11), 423 (5), 387 (9), 369 (15), 344 (18), 311 (12), 271(7), 223 (9), 199 (12), 171 (19), 126 (41), 105 (89), 82 (80).

1-(4-Amino-3,5-dinitropyrazol-1-yl)-2-nitrazapropane (12)

IR $\tilde{\nu}$/cm^{-1}: 3489 (w), 3383 (w), 3079 (vw), 2982 (vw), 2361 (vw), 2337 (vw), 1648 (m), 1612 (vw), 1581 (vw), 1547 (vw), 1516 (m), 1480 (s), 1429 (m), 1405 (w), 1385 (w), 1359 (w), 1318 (s), 1298 (vs), 1245 (vs), 1223 (m), 1152 (w), 1075 (w), 1025 (m), 974 (w), 889 (w), 849 (w), 827 (m), 790 (m), 758 (m), 748 (w), 705 (w), 665 (w), 649 (m), 614 (w). Raman $\tilde{\nu}$/cm^{-1}: 3373 (2), 2982 (5), 1654 (13), 1642 (9), 1572 (5), 1481 (3), 1433 (6), 1407 (11), 1378 (84), 1344 (51), 1325 (18), 1225 (9), 851 (7), 830 (17), 794 (9), 651 (5), 601 (3), 350 (7).

2. HMBC spectrum of 1-(3,4,4'-trinitro-1,3'-bipyrazol-2'-yl)-2-nitraza-propane (10)

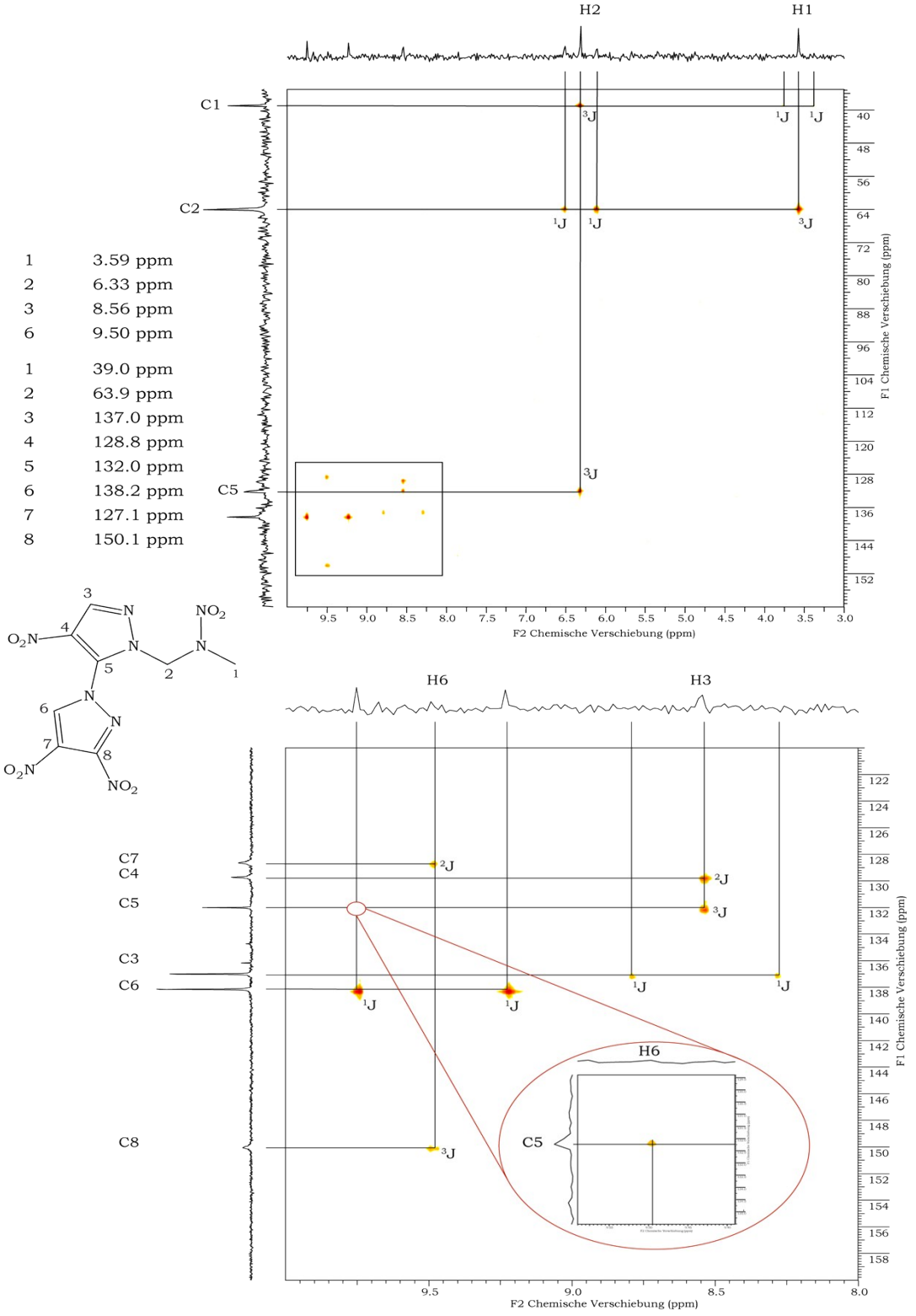

Figure S1: HMBC spectrum of 1-(3,4,4'-trinitro-1,3'-bipyrazol-2'-yl)-2-nitrazapropane (**10**), (T = 25 °C; conc = 5.6 x 10^{-3} mmol/mL; 1024 x 1024 matrix; pulse delay = 1 s; repetition time = 1.9 s) (above), enlarged detail of HMBC spectrum (below).

3. Crystal structures

3.1. 1-(3-Nitro-1*H*-1,2,4-triazol-5-on-4-yl)-2-nitrazapropane (1)

1-(3-Nitro-1*H*-1,2,4-triazol-5-on-4-yl)-2-nitrazapropane (**1**) crystallizes from acetone and dichloromethane in the monoclinic space group $P2_1$ with two formula units per unit cell and a crystal density of 1.721 g cm^{-3} at 173 K.

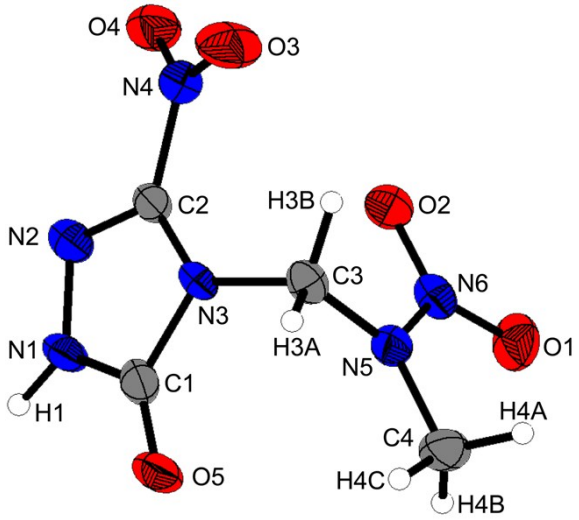

Figure S2: Molecular structure of 1-(3-nitro-1*H*-1,2,4-triazol-5-on-4-yl)-2-nitrazapropane (**1**). Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths [Å]: N5–N6 1.340(2), N1–N2 1.370(2), C1–O5 1.214(3), C2–N4 1.457(3), C1–N1 1.358(3), C1–N3 1.400(3), C2–N2 1.293(3), C2–N3 1.351(3), C3–N3 1.462(3), C3–N5 1.449(3), C4–N5 1.458(3). Selected bond angles [°]: N6–N5–C3 117.05(19), N6–N5–C4 118.3(2), C3–N5–C4 123.8(2), O3–N4–O4 126.2(2), O3–N4–C2 116.9(2), O4–N4–C2 116.9(2), C2–N3–C1 105.71(19), C2–N3–C3 130.66(19), C1–N3–C3 120.4(2), C2–N2–N1 102.37(19), C1–N1–N2 113.7(2), O1–N6–O2 124.8(2), O1–N6–N5 118.6(2), O2–N6–N5 116.6(2), N5–C3–N3 111.5(2), N2–C2–N3 115.00(19), N2–C2–N4 120.2(2), N3–C2–N4 124.6(2), O5–C1–N1 131.3(2), O5–C1–N3 125.4(2), N1–C1–N3 103.2(2).

Table S1: Interactions within the crystal structure of 1-(3-nitro-1*H*-1,2,4-triazol-5-on-4-yl)-2-nitrazapropane (**1**).

D−H···A	D−H [Å]	H···A [Å]	D···A [Å]	∠DHA [°]	Comment
N1−H1···O5	0.930	1.841	2.755	166.87	inter
C4−H4A···O3	0.996	2.531	3.318	138.77	inter
C3−H3B···O1	0.996	2.545	3.279	130.39	inter
C3−H3A···N2	1.003	2.621	3.535	151.43	inter
C4−H4C···O2	0.987	2.600	3.282	126.25	inter
dipolar interactions ΣvdW radii (N−O) < 3.07 Å[18]					
N4–O2 2.935 Å^{intra} N6–O2 2.970 Å^{inter}					
dipolar interactions ΣvdW radii (C−O) < 3.22 Å[18]					
C2−O2 2.869 Å^{intra}					

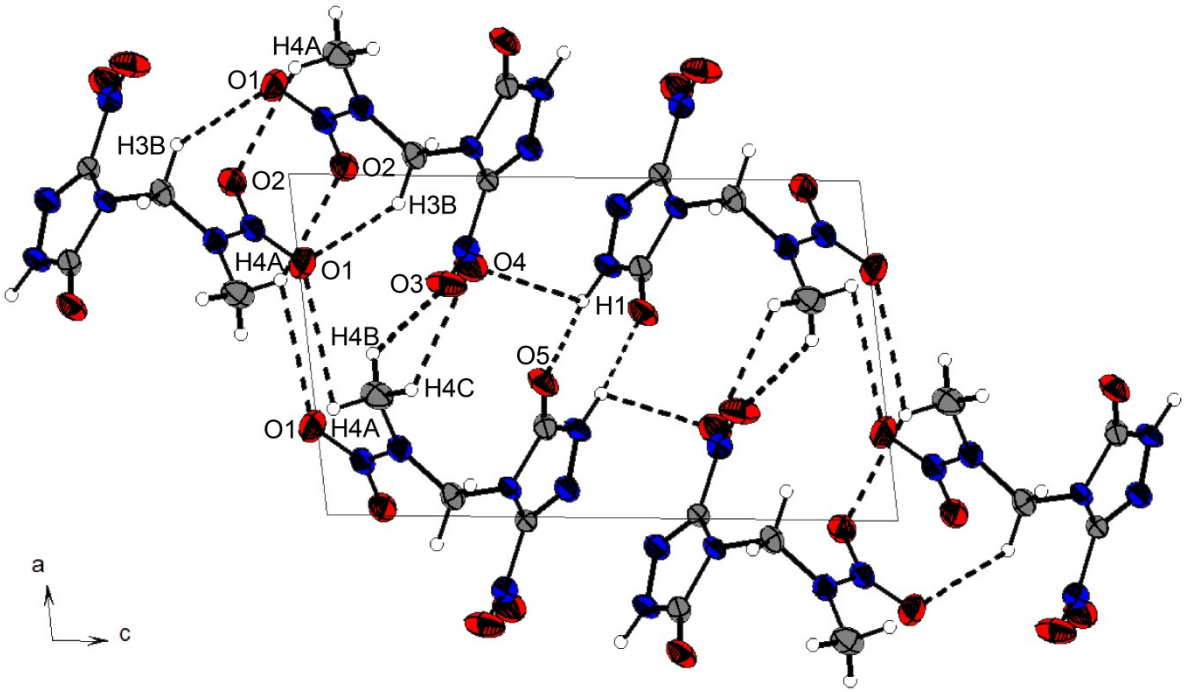

Figure S3: Crystal structure of **1** along *b* axis; intermolecular classical N–H···O hydrogen bonds are shown black dotted and non-classical hydrogen bonds are shown grey dotted.

3.2. 2,4-Bis(2-nitrazaprop-1-yl)-3-nitro-1,2,4-triazol-5-one (2)

Single crystals from 2,4-bis(2-nitrazaprop-1-yl)-3-nitro-1,2,4-triazol-5-one (**2**) suitable for single crystal X-ray structure analysis were obtained by crystallization from 2N nitric acid. It crystallizes as HNO_3-adduct in the monoclinic space group $P2_1$ with two formula units per unit cell and a crystal density of 1.721 g cm^{-3} at 173 K.

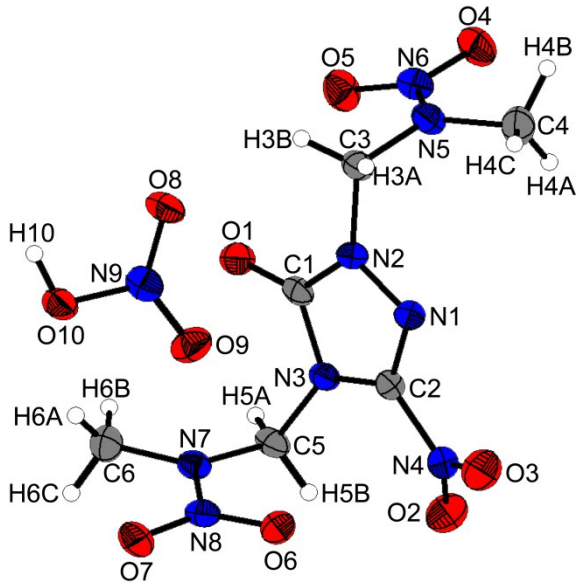

Figure S4: Molecular structure of 2,4-bis(2-nitrazaprop-1-yl)-3-nitro-1,2,4-triazol-5-one (**2**) as nitric acid adduct. Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths [Å]: N5–N6 1.346(3), N7–N8 1.344(3), N1–N2 1.376(2), C1–O1 1.230(3), C2–N4 1.458(3), C1–N2 1.363(3), C1–N3 1.391(3), C2–N1 1.282(3), C2–N3 1.366(3), C3–N2 1.464(3), C5–N3 1.473(3), C3–N5 1.440(3), C5–N7 1.444(3), C4–N5 1.459(3), C6–N7 1.458(3), N9–O10 1.357(2), N9–O8 1.211(2), N9–O9 1.217(2), N4–O2 1.213(3), N4–O3 1.224(3), N6–O4 1.234(2), N6–O5 1.236(2), N8–O6 1.245(2),

N8–O7 1.227(2). Selected bond angles [°]: C2–N1–N2 103.16(19), C2–N3–C1 105.40(18), C2–N3–C5 130.85(19), C1–N3–C5 121.8(2), N8–N7–C5 117.5(2), N8–N7–C6 118.0(2), C5–N7–C6 124.3(2), N6–N5–C3 117.5(2), N6–N5–C4 117.5(2), C3–N5–C4 123.0(2), C1–N2–N1 112.61(16), C1–N2–C3 128.5(2), N1–N2–C3 118.83(19), O7–N8–O6 124.4(2), O7–N8–N7 118.1(2), O6–N8–N7 117.49(19), O4–N6–O5 124.5(2), O4–N6–N5 117.4(2), O5–N6–N5 118.10(19), O9–N9–O8 127.16(18), O9–N9–O10 114.74(16), O8–N9–O10 118.09(17), N5–C3–N2 112.6(2), O2–N4–O3 126.4(2), O2–N4–C2 117.2(2), O3–N4–C2 116.4(2), N7–C5–N3 112.63(19), O1–C1–N2 130.8(2), O1–C1–N3 125.2(2), N2–C1–N3 104.00(19), N1–C2–N3 114.8(2), N1–C2–N4 120.1(2), N3–C2–N4 124.6(2).

Table S2: Interactions within the crystal structure of 2,4-*bis*(2-nitrazaprop-1-yl)-3-nitro-1,2,4-triazol-5-one · HNO_3 (**2** · HNO_3).

D–H···A	D–H [Å]	H···A [Å]	D···A [Å]	∠DHA [°]	Comment
C5–H5B···O2	0.971	2.367	3.013	123.42	intra
O10–H10···O1	0.870	1.747	2.616	176.35	inter
C3–H3B···O5	1.004	2.364	3.320	158.83	inter
C5–H5B···O7	0.971	2.440	3.175	132.20	inter
C6–H6A···O8	0.878	2.491	3.368	176.66	inter
C4–H4A···O7	0.940	2.534	3.137	122.13	inter
C4–H4B···O4	0.910	2.635	3.349	135.91	inter

dipolar interactions ΣvdW radii (N−O) < 3.07 Å[18]
N4–O6 2.776 Å^{intra} N8–O8 2.850 Å^{inter} N7–O8 2.939 Å^{inter}

dipolar interactions ΣvdW radii (C−O) < 3.22 Å[18]
C2–O6 2.864 Å^{intra} C1–O8 2.891 Å^{inter} C2–O3 3.075 Å^{inter}

3.3. 1-(3,5-Dinitro-1,2,4-triazol-1-yl)-2-nitrazapropane (3)

1-(3,5-Dinitro-1,2,4-triazol-1-yl)-2-nitrazapropane (**3**) crystallizes from acetone and dichloromethane in the monoclinic space group *Cc* with four formula units per unit cell and a crystal density of 1.778 g cm^{-3} at 173 K.

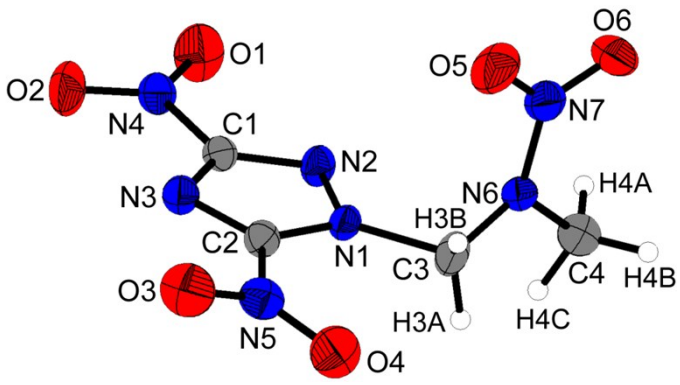

Figure S5: Molecular structure of 1-(3,5-dinitro-1,2,4-triazol-1-yl)-2-nitrazapropane (**3**). Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths [Å]: N6–N7 1.353(3), N1–N2 1.349(3), C2–N5 1.451(3), C1–N4 1.460(3), C2–N3 1.312(3), C2–N1 1.348(4), C1–N3 1.333(3), C1–N2 1.322(3), C3–N6 1.431(4), C3–N1 1.494(3), C4–N6 1.447(4). Selected bond angles [°]: C1–N2–N1 100.8(2), N7–N6–C3 117.2(3), N7–N6–C4 118.1(3), C3–N6–C4 123.0(3), C2–N3–C1 99.9(3), C2–N1–N2 108.6(2), C2–N1–C3 130.2(3), N2–N1–C3 121.1(2), O2–N4–O1 125.5(3), O2–N4–C1 117.0(3), O1–N4–C1 117.5(3), O4–N5–O3 127.2(3), O4–N5–C2 116.2(3), O3–N5–C2 116.6(3), O5–N7–O6 125.5(3), O5–N7–N6 117.1(3), O6–N7–N6 117.4(3), N2–C1–N3 118.3(2), N2–C1–N4 120.8(3), N3–C1–N4 120.8(3), N6–C3–N1 111.0(3), N3–C2–N1 112.4(3), N3–C2–N5 123.4(3), N1–C2–N5 124.2(2).

Table S3: Selected Interactions within the crystal structure of 1-(3,5-dinitro-1,2,4-triazol-1-yl)-2-nitrazapropane (**3**).

D−H···A	D−H [Å]	H···A [Å]	D···A [Å]	∠DHA [°]	Comment
C3−H4C···N3	0.957	2.562	3.357	140.63	inter
C4−H4A···O4	0.937	2.476	3.192	133.34	inter
C4−H4B···O5	0.989	2.590	3.414	140.77	inter
C3−H3A···N3	0.946	2.508	3.442	169.34	inter
C4−H4C···O2	0.957	2.602	3.493	155.18	inter
dipolar interactions ΣvdW radii (N···O) < 3.07 Å[18]					
N5···O5 2.924 Å^{inter} N5···O1 2.950 Å^{inter}					
dipolar interactions ΣvdW radii (C···O) < 3.22 Å[18]					
C3···O4 2.806 Å^{intra} C2···O1 2.862 Å^{inter} C4···O3 3.036 Å^{inter}					
dipolar interactions ΣvdW radii (O···O) < 3.04 Å[18]					
O3–O5 2.925 Å^{inter}					

3.4. 1-(5-Amino-3-nitro-1,2,4-trazol-1-yl)-2-nitrazapropane (4)

Suitable single crystals for X-ray analysis were obtained from diffusion crystallization from acetone / dichloromethane. 1-(5-Amino-3-nitro-1,2,4-triazol-1-yl)-2-nitrazapropane (**4**) crystallizes in the triclinic space group *P*-1 with two formula units per unit cell and a density of 1.682 g cm^{-3} at 173 K.

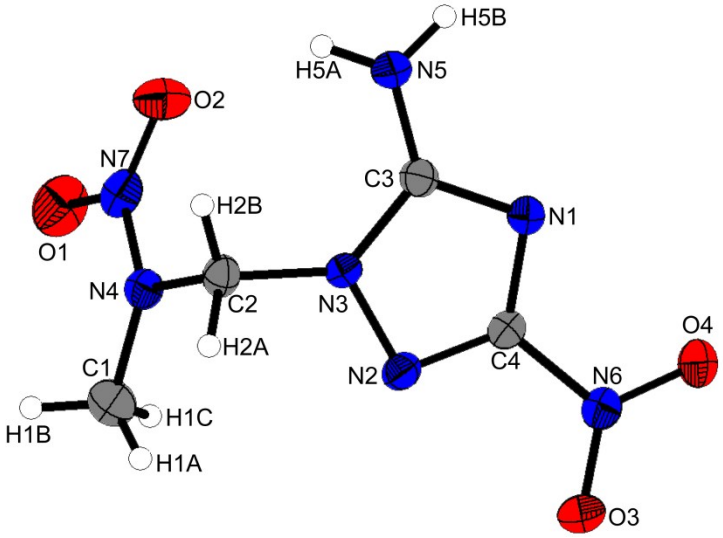

Figure S6: Molecular structure of 1-(5-amino-3-nitro-1,2,4-tiazol-1-yl)-2-nitrazapropane (**4**). Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths [Å]: O4−N6 1.235(2), O2−N7 1.233(2), O3−N6 1.222(2), O1−N7 1.231(2), N1−C3 1.344(2), N1−C4 1.346(2), N2−C4 1.305(2), N2−N3 1.373(2), N5−C3 1.336(2), N6−C4 1.455(2), N4−N7 1.348(2), N4−C2 1.448(2), N4−C1 1.460(2), N3−C3 1.365(2), N3−C2 1.4550(19). Selected bond angles [°]:C3−N1−C4 101.37(12), C4−N2−N3 100.17(11), O3−N6−O4 124.87(13), O3−N6−C4 118.01(13), O4−N6−C4 117.11(12), N7−N4−C2 117.68(13), N7−N4−C1 117.82(14), C2−N4−C1 122.90(14), C3−N3−N2 110.47(12), C3−N3−C2 129.88(13), N2−N3−C2 119.58(12), O1−N7−O2 124.61(14), O1−N7−N4 117.58(14), O2−N7−N4 117.80(13), N5−C3−N1 126.02(14), N5−C3−N3 124.75(15), N1−C3−N3 109.03(13), N4−C2−N3 113.08(13), N2−C4−N1 118.96(13), N2−C4−N6 120.03(13), N1−C4−N6 120.98(13).

Table S4: Selected non-classical hydrogen bonds within the crystal structure of **4**.

D−H···A	D−H [Å]	H···A [Å]	D···A [Å]	∠DHA [°]	Comment
N5−H5A···O2	0.84(2)	2.39(2)	3.046(2)	135.2(17)	intra
C2−H2B···O3	0.96(2)	2.39(2)	3.208(2)	141.8(13)	inter
N5−H5B···N1	0.86(2)	2.18(2)	3.025(2)	167.2(19)	inter
C1−H1B···O3	0.93(3)	2.47(3)	3.238(2)	139.9(25)	inter
C2−H2A···O4	1.00(2)	2.47(2)	3.395(2)	154.4(14)	inter
N5−H5A···O4	0.84(2)	2.49(2)	3.221(2)	145.6(18)	inter
C1−H1A···O2	0.93(3)	2.539(3)	3.454(2)	170.7(21)	inter

3.5. 5,5'-Bi(1-(2-nitrazapropyl-1-yl)-3-nitro-1,2,4-triazole) (5)

5,5'-Bi(1-(2-nitrazapropane-1-yl)-3-nitro-1,2,4-triazole) (**5**) crystallizes in the monoclinic space group *C*2/*c* with four formula units per unit cell and a crystal density of 1.689 g cm^{-3} at 173 K. Its molecular structure is shown in Figure S7 and its interactions are summarized in Table S5.

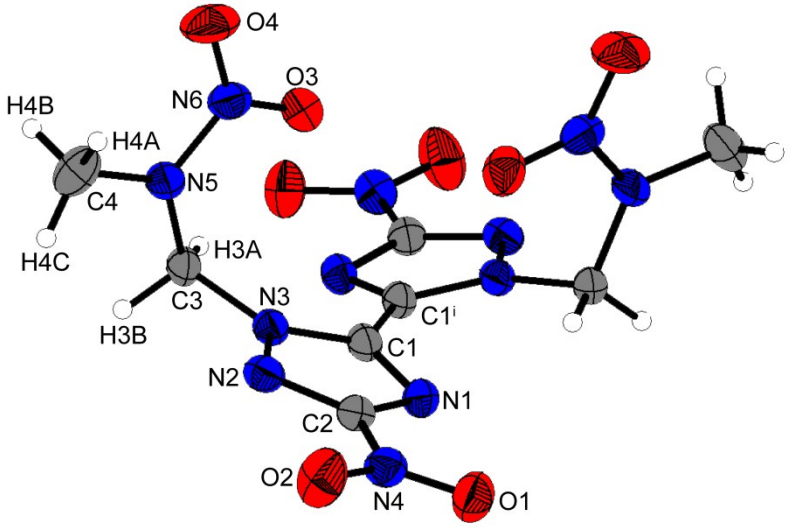

Figure S7: Molecular structure of 5,5'-Bi(1-(2-nitrazapropan-1-yl)-3-nitro-1,2,4-triazole) (**5**). Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths [Å]: O1−N4 1.218(2), O2−N4 1.224(2), O3−N6 1.227(2), O4−N6 1.236(2), N1−C1 1.332(3), N1−C2 1.344(2), N2−C2 1.316(2), N2−N3 1.352(2), N3−C1 1.355(2), N3−C3 1.474(2), N4−C2 1.457(3), N5−N6 1.351(2), N5−C3 1.436(3), N5−C4 1.454(3), C1−C1^{i} 1.462(4). Selected bond angles [°]: C1−N1−C2 100.89(16), C2−N2−N3 101.05(15), N2−N3−C1 109.78(16), N2−N3−C3 119.06(16), C1−N3−C3 131.05(17), O1−N4−O2 124.92(18), O1−N4−C2 117.30(17), O2−N4−C2 117.76(18), N6−N5−C3 116.69(17), N6−N5−C4 119.15(19), C3−N5−C4 123.84(19), O3−N6−O4 125.01(19), O3−N6−N5 117.98(18), O4−N6−N5 117.01(19), N1 C1 N3 110.44(17), N1 C1 C1 125.1(2), N3 C1 C1 124.4(2), N2 C2 N1 117.83(18), N2 C2 N4 120.59(17), N1− C2 N4 121.51(18), N5 C3 N3 111.27(16).

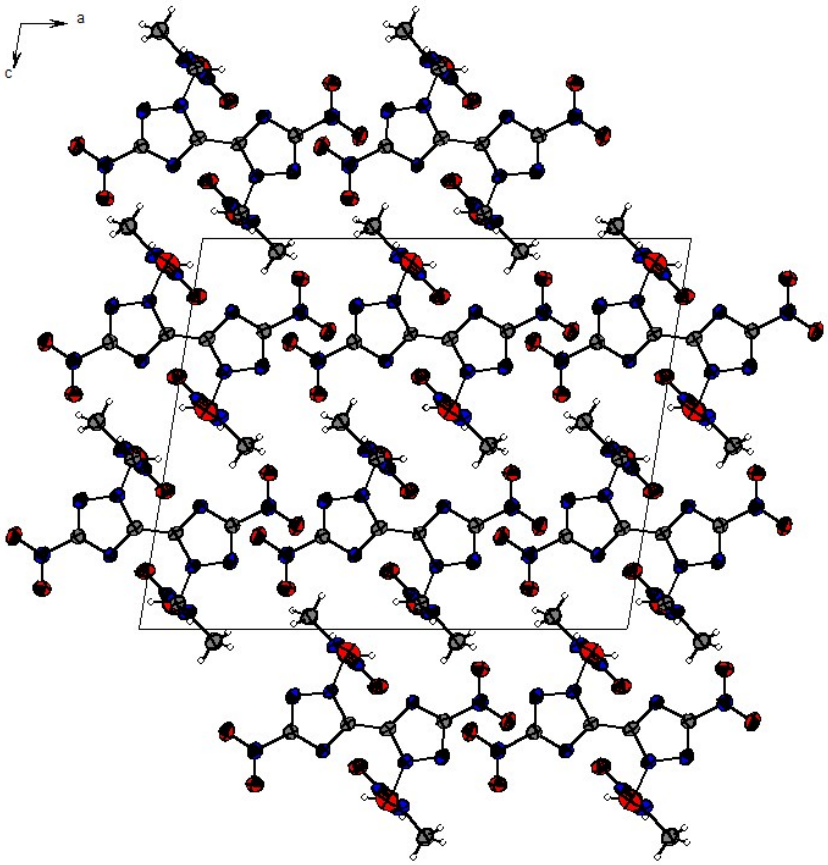

Figure S8: Crystal structure of **5** along the *b* axis.

Table S5: Selected interactions within the crystal structure of **5**.

D−H···A	D−H [Å]	H···A [Å]	D···A [Å]	∠DHA [°]	Comment
C3−H3A···N1^{i}	0.95(2)	2.37(2)	3.097(3)	133.8(16)	intra
C4−H4C···O1	0.98(3)	2.52(3)	3.385(4)	146.8(25)	inter
C3−H3B···O1	0.98(2)	2.54(2)	3.473(3)	159.8(16)	inter
C4−H4B···O1	0.95(3)	2.88(3)	3.525(4)	126.6(19)	inter
C4−H4A···O3	0.89(3)	2.59(3)	3.315(3)	139.5(23)	inter
dipolar interactions ΣvdW radii (C···O) < 3.22 Å[2]					
C1^{i}···O3 3.082(2) Å^{intra} C3···O4 2.920(2) Å^{inter}					
dipolar interactions ΣvdW radii (N···O) < 3.07 Å[2]					
N3···O3 2.935(2) Å^{intra} N3···O4 2.955(2) Å^{inter}					
dipolar interactions ΣvdW radii (N···C) < 3.25 Å[2]					
N1^{i}···C3 3.097(3) Å^{intra}					

3.6. 1-(2,4-Dinitroimidazol-1-yl)-2-nitrazapropane (6)

1-(2,4-Dinitroimidazol-1-yl)-2-nitrazapropane (**6**) crystallizes in the monoclinic space group $P2_1/c$ with four formula units per unit and a crystal density of 1.735 g cm^{-3} at 173 K. The molecular structure is depicted in Figure S9 and selected interactions within the crystal structure are summarized in Table S6.

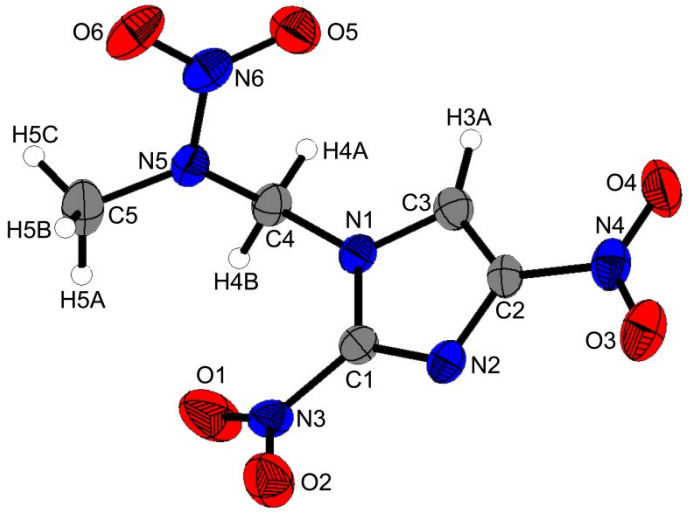

Figure S9: Molecular structure of 1-(2,4-dinitroimidazol-1-yl)-2-nitrazapropane (**6**). Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths [Å]: N5−N6 1.359(2), C1−N3 1.465(2), C2−N4 1.443(2), C4−N1 1.485(2), C4−N5 1.430(2), C5−N5 1.460(2), C1−N1 1.364(2), C1−N2 1.298(2), C3−N1 1.360(2), C2−N2 1.356(2), C3−C2 1.363(2). Selected bond angles [°]:C3−N1−C1 105.27(13), C3−N1−C4 124.33(14), C1−N1−C4 130.17(14), N6−N5−C4 116.68(14), N6−N5−C5 117.21(15), C4−N5−C5 124.85(17), C1−N2−C2 102.42(13), O5−N6−O6 125.05(16), O5−N6−N5 117.79(15), O6−N6−N5 117.15(15), O3−N4−O4 125.06(15), O3−N4−C2 118.20(15), O4−N4−C2 116.73(15), O1−N3−O2 126.59(16), O1−N3−C1 116.99(15), O2−N3−C1 116.32(14), N5−C4−N1 111.62(14), N2−C2−C3 112.89(14), N2−C2−N4 120.48(14), C3−C2−N4 126.63(15), N1−C3−C2 104.87(15), N2−C1−N1 114.54(15), N2−C1−N3 122.36(15), N1−C1−N3 123.09(14).

Table S6: Selected interactions within the crystal structure of **6**.

D−H···A	D−H [Å]	H···A [Å]	D···A [Å]	∠DHA [°]	Comment
C5−H5A···O1	1.010	2.426	3.113	124.61	intra
C3−H3···O3	0.969	2.579	3.241	125.58	inter
dipolar interactions ΣvdW radii (N···O) < 3.07 Å[2]					
N6···O2 2.886 Å	N5···O2 2.901 Å	N6···O6 3.028 Å			
dipolar interactions ΣvdW radii (C···O) < 3.22 Å[2]					
C1···O6 2.946 Å	C4···O4 3.032 Å	C4···O2 3.168 Å			
dipolar interactions ΣvdW radii (O···O) < 3.04 Å[2]					
O2···O4 2.905 Å	O5···O1 2.980 Å				

3.7. 1-(4,5-Dinitroimidazol-1-yl)-2-nitrazapropane (7)

Suitable single crystals for X-ray analysis were obtained from diffusion crystallization from acetone / dichloromethane. 1-(4,5-Dinitroimidazol-1-yl)-2-nitrazapropane (**7**) crystallizes in the monoclinic space group *Cc* with four formula units per unit cell and a crystal density of 1.767 g cm^{-3} at 173 K.

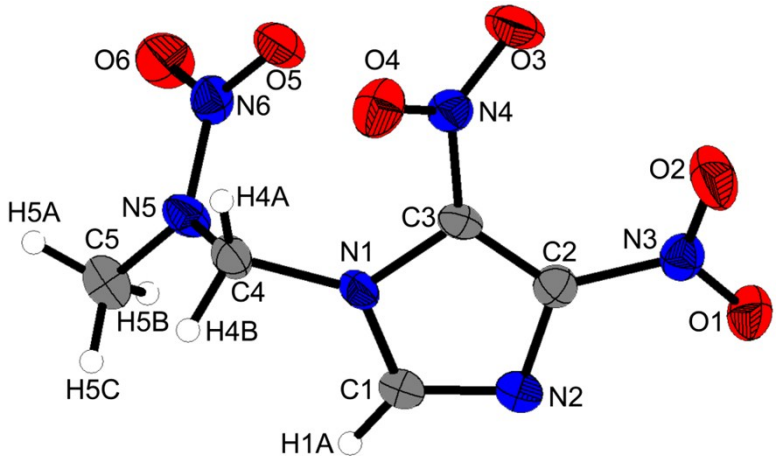

Figure S10: Molecular structure of 1-(4,5-dinitroimidazol-1-yl)-2-nitrazapropane (**7**). Thermal ellipsoids are shown at the 50 % probability level. Selected bond lengths [Å]: N5−N6 1.361(3), C2−N3 1.447(4), C3−N4 1.431(4), C4−N1 1.468(4), C4−N5 1.430(4), C5−N5 1.458(4), C1−N2 1.309(4), C1−N1 1.349(4), C2−N2 1.355(4), C3−N1 1.390(4), C2−C3 1.362(4). Selected bon angles [°]: O1−N3−O2 124.7(4), O1−N3−C2 117.7(4), O2−N3−C2 117.6(3), O6−N6−O5 126.3(4), O6−N6−N5 116.8(3), O5−N6−N5 116.9(3), N6−N5−C4 116.4(3), N6−N5−C5 117.6(3), C4−N5−C5 125.6(4), C1−N1−C3 104.8(3), C1−N1−C4 124.5(3), C3−N1−C4 129.7(3), C1−N2−C2 103.9(4), N5−C4−N1 112.1(4), C2−C3−N1 105.5(3), C2−C3−N4 133.5(4), N1−C3−N4 120.9(3), O4−N4−O3 125.7(4), O4−N4−C3 116.9(3), O3−N4−C3 117.4(4), N2−C2−C3 111.6(4), N2−C2−N3 119.9(3), C3−C2−N3 128.6(4), N2−C1−N1 114.2(4).

Table S7: Selected interactions within the crystal structure of **7**.

D−H···A	D−H [Å]	H···A [Å]	D···A [Å]	∠DHA [°]	Comment
C4−H4A···O4	0.950	2.339	2.986	124.90	intra
C4−H4B···O5	0.967	2.456	3.398	164.76	inter
C5−H5C···O6	0.975	2.534	3.355	141.73	inter
C5−H5B···N2	1.003	2.589	3.446	143.41	inter
C1−H1A···O1	0.906	2.605	3.482	163.09	inter
C1−H1A···O2	0.906	2.657	3.356	134.66	inter
C4−H4A···O6	0.950	2.691	3.457	138.05	inter
dipolar interactions ΣvdW radii (N···O) < 3.07 Å[2]					
N4···O6 2.963 Å	N6···O1 2.992 Å	N5···O4 3.005 Å	N4···O2^{intra} 3.042 Å		
N4···O5^{intra} 2.705 Å					
dipolar interactions ΣvdW radii (C···O) < 3.22 Å[2]					
C4···O4 3.039 Å	C5···O4 3.154 Å	C3···O1 3.188 Å	C2···O1 3.204 Å		
dipolar interactions ΣvdW radii (O···O) < 3.04 Å[2]					
O6···O4 2.831 Å					

3.8. 1-(3,5-Dinitropyrazol-1-yl)-2-nitrazapropane (8)

1-(3,5-Dinitropyrazol-1-yl)-2-nitrazapropane (**8**) crystallizes from acetone / dichloromethane in the triclinic space group *P*-1 with four formula units per unit cell and a crystal density of 1.680 g cm^{-3} at 173 K. The asymmetric unit, depicted in Figure S11, consists of two formula units.

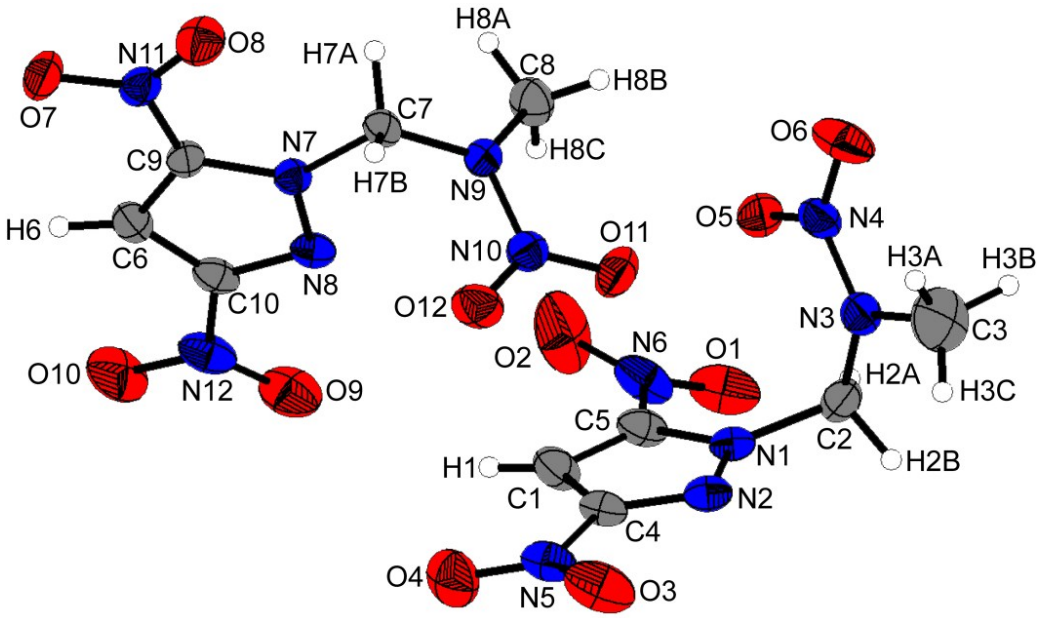

Figure S11: Asymmetric unit of 1-(3,5-dinitropyrazol-1-yl)-2-nitrazapropane (**8**). Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths [Å]: O8−N11 1.2224(15), O9−N12 1.2254(17), N9−N10 1.3563(16), N9−C7 1.4154(17), N9−C8 1.4499(19), O7−N11 1.2222(14), O6−N4 1.2249(15), O5−N4 1.2302(15), O12−N10 1.2273(15), N2−C4 1.3183(18), N2−N1 1.3404(15), N11−C9 1.4338(18), O11−N10 1.2248(14), N8−C10 1.3299(17), N8−N7 1.3351(15), N1−C5 1.3574(18), N1−C2 1.4654(18), N7−C9 1.3545(16), N7−C7 1.4863(17), O4−N6 1.2274(17), N3−N4 1.3459(16), N3−C2 1.4319(19), N3−C3 1.450(2), O3−N6 1.2190(17), N12−O10 1.2197(16), N12−C10 1.4465(18), O1−N5 1.2256(18), O2−N5 1.2152(18), N5−C5 1.4414(19), N6−C4 1.4419(19), C10−C6 1.377(2), C1−C5 1.352(2), C1−C4 1.386(2), C9−C6 1.362(2). Selected bond angles [°]: N10−N9−C7 117.78(11), N10−N9−C8 118.61(12), C7−N9−C8 122.88(13), C4−N2−N1 103.81(11), O7−N11−O8 124.85(13), O7−N11−C9 116.21(12), O8−N11−C9 118.94(11), C10−N8−N7 103.43(11), N2−N1−C5 110.43(11), N2−N1−C2 117.93(11), C5−N1−C2 130.55(12), N8−N7−C9 110.72(11), N8−N7−C7 119.96(11), C9−N7−C7 129.31(11), O11−N10−O12 125.08(12), O11−N10−N9 116.43(12), O12−N10−N9 118.49(11), N4−N3−C2 116.19(12), N4−N3−C3 119.19(15), C2−N3−C3 123.17(15), O10−N12−O9 124.94(13), O10−N−12C10 116.87(14), O9−N12−C10 118.19(13), O2−N5−O1 125.31(14), O2−N5−C5 115.89(15), O1−N5−C5 118.79(14), O3−N6−O4 124.78(14), O3−N6−C4 118.82(13), O4−N6−C4 116.40(13), N9−C7−N7 111.40(11), O6−N4−O5 124.74(13), O6−N4−N3 117.71(12), O5−N4−N3 117.55(11), N8−C10−C6 114.77(12), N8−C10−N12 118.85(13), C6−C10−N12 126.37(13), C5−C1−C4 102.10(14), N7−C9−C6 109.43(13), N7−C9−N11 122.66(12), C6−C9−N11 127.87(13), N3−C2−N1 111.76(12), C9−C6−C10 101.65(13), N2−C4−C1 114.33(13), N2−C4−N6 119.32(13), C1−C4−N6 126.34(14), C1−C5−N1 109.31(13), C1−C5−N5 127.44(14), N1−C5−N5 123.13(13).

Table S8: Interactions within the crystal structure of **8**.

D−H···A	D−H [Å]	H···A [Å]	D···A [Å]	∠DHA [°]	Comment
C2−H2B···O7	0.994	2.234	3.194	161.91	inter
C2−H2A···O1	0.992	2.273	2.970	126.31	intra
C7−H7A···O6	0.964	2.322	3.133	141.37	inter
C6−H6···O2	0.916	2.410	3.111	133.33	inter
C7−H7B···O6	0.942	2.667	3.572	161.43	inter
dipolar interactions ΣvdW radii (N···O) < 3.07 Å[2]					
N6···O9 2.913 Å					
dipolar interactions ΣvdW radii (C···O) < 3.22 Å[2]					
C9···O5 2.906 Å	C4···O9 3.033 Å		C9···O3 3.033 Å		C8···O7 3.060 Å
C4···O11 3.061 Å	C2···O4 3.112 Å				

3.9. 1-(3,4-Dinitropyrazol-1-yl)-2-nitrazapropane (9)

Suitable single crystals for X-ray analysis were obtained by slow evaporation of an aqueous ethanol solution. 1-(3,4-Dinitropyrazol-1-yl)-2-nitrazapropane (**9**) crystallizes in the monoclinic space group $P2_1/c$ with eight formula units per unit cell and a crystal density of 1.703 g cm^{-3} at 173 K. The asymmetric unit, depicted in Figure S12, consists of two molecules of **9**.

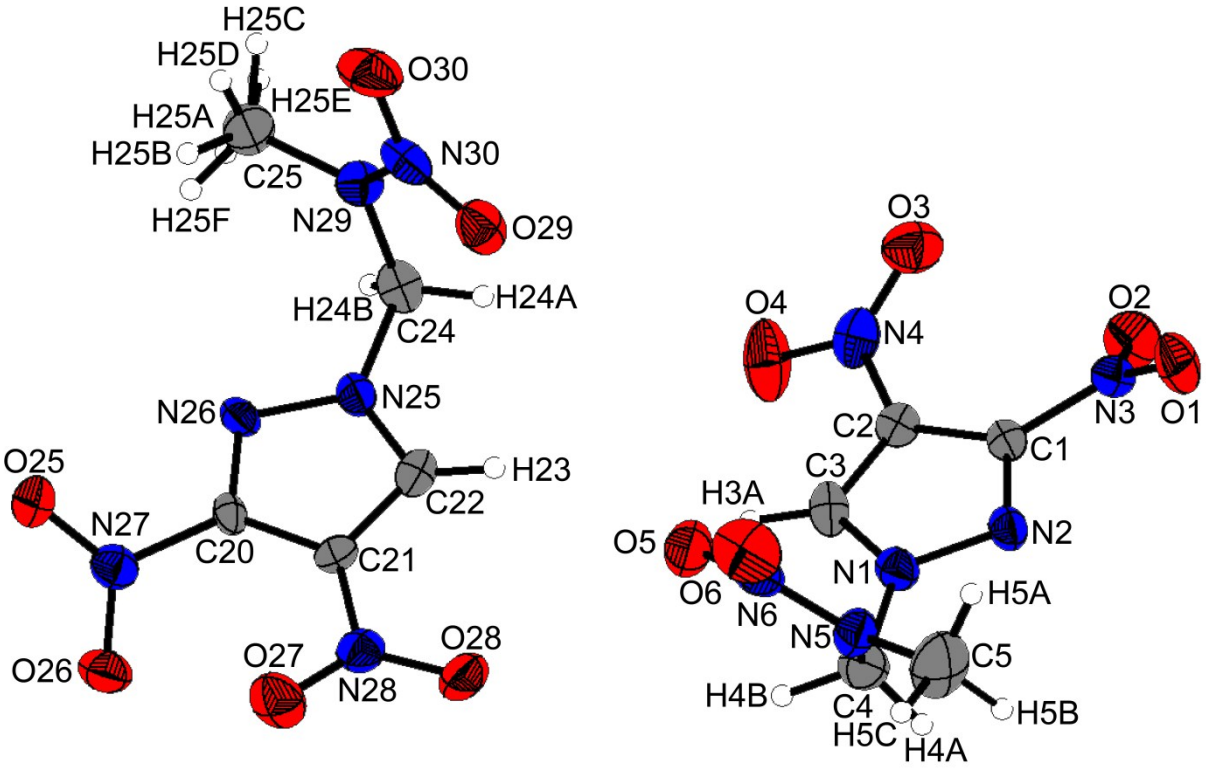

Figure S12: Asymmetric unit of 1-(3,4-dinitropyrazol-1-yl)-2-nitrazapropane (**9**). Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths [Å]: O1−N3 1.224(2), O2−N3 1.224(2), O3−N4 1.225(2), O4−N4 1.223(2), O5−N6 1.234(3), O6−N6 1.232(2), N1−C3 1.333(3), N1−N2 1.358(3), N1−C4 1.472(3), N2−C1 1.312(3), N3−C1 1.447(3), N4−C2 1.445(3), N5−N6 1.348(3), N5−C4 1.427(3), N5−C5 1.444(3), C1−C2 1.398(3), C2−C3 1.365(4), O28−N28 1.229(3), O27−N28 1.228(2), O26−N27 1.220(2), O25−N27 1.224(2), O29−N30 1.219(3), O30−N30 1.235(3), N25−C22 1.329(3), N25−N26 1.361(2), N25−C24 1.476(3), C22−C21 1.365(3), N28−C21 1.434(3), N27−C20 1.462(3), N29−N30 1.376(3), N29−C24 1.427(3), N29−C25 1.461(3), C21−C20 1.391(3), C20−N26 1.315(3). Selected bond angles [°]: C3−N1−N2 113.1(2), C3−N1−C4 127.7(3), N2−N1−C4 119.1(2), C1−N2−N1 103.5(2), O1−N3−O2 125.0(2), O1−N3−C1 117.0(2), O2−N3−C1 118.0(2), O4−N4−O3 125.4(3), O4−N4−C2 116.8(3), O3−N4−C2 117.9(2), N6−N5−C4 116.9(3), N6−N5−C5 119.2(2), C4−N5−C5 123.7(3), O6−N6−O5 125.0(3), O6−N6−N5 117.5(3), O5−N6−N5 117.5(2), N2−C1−C2 112.3(2), N2−C1−N3 118.9(2), C2−C1−N3 128.8(3), C3−C2−C1 104.8(3), C3−C2−N4 124.2(3), C1−C2−N4 130.9(3), N1−C3−C2 106.3(3), N5−C4−N1 112.2(2), C22−N25−N26 113.7(2), C22−N25−C24 127.9(2), N26−N25−C24 118.4(2), N25−C22−C21 105.9(3), O27−N28−O28 124.9(3), O27−N28−C21 117.6(2), O28−N28−C21 117.5(2), O26−N27−O25 125.0(2), O26−N27−C20 118.4(2), O25−N27−C20 116.6(2), N30−N29−C24 115.7(2), N30−N29−C25 118.6(2), C24−N29−C25 122.1(2), O29−N30−O30 126.5(2), O29−N30−N29 117.7(2), O30−N30−N29 115.7(3), C22−C21−C20 105.0(3), C22−C21−N28 125.1(3), C20−C21−N28 129.6(3), N26−C20−C21 112.6(2), N26−C20−N27 117.7(2), C21−C20−N27 129.6(3), C20−N26−N25 102.8(2), N29−C24−N25 113.4(2).

Table S9: Interactions within the crystal structure of **9**.

D−H···A	D−H [Å]	H···A [Å]	D···A [Å]	∠DHA [°]	Comment
C4−H4B···O2	0.940	2.279	3.155	154.74	inter
C4−H4A···O25	1.073	2.428	3.371	145.99	inter
C24−H24A···O26	0.919	2.444	3.359	173.63	inter
C23−H23···O5	0.909	2.473	3.270	146.50	inter
C24−H24B···O1	0.975	2.478	3.385	154.51	inter
C3−H3A···O29	0.943	2.587	3.444	151.33	inter
dipolar interactions ΣvdW radii (N···O) < 3.07 Å[2]					
N30···O27 2.817 Å		N3···O4 2.849 Å		N27···O28 2.893 Å	
dipolar interactions ΣvdW radii (C···O) < 3.22 Å[2]					
C21···O28 3.040 Å		C24···O29 3.086 Å		C3···O6 3.113 Å	

3.10. 1-(3,4,4'-Trinitro-1,3'-bipyrazol-2'-yl)-2-nitrazapropane (10)

1-(3,4,4'-Trinitro-1,3'bipyrazol-2'-yl)-2-nitrazapropane (**10**) crystallizes from dichloromethane in the triclinic space group *P*-1 with two formula units per unit cell and a crystal density of 1.731 g cm^{-3} at 173 K.

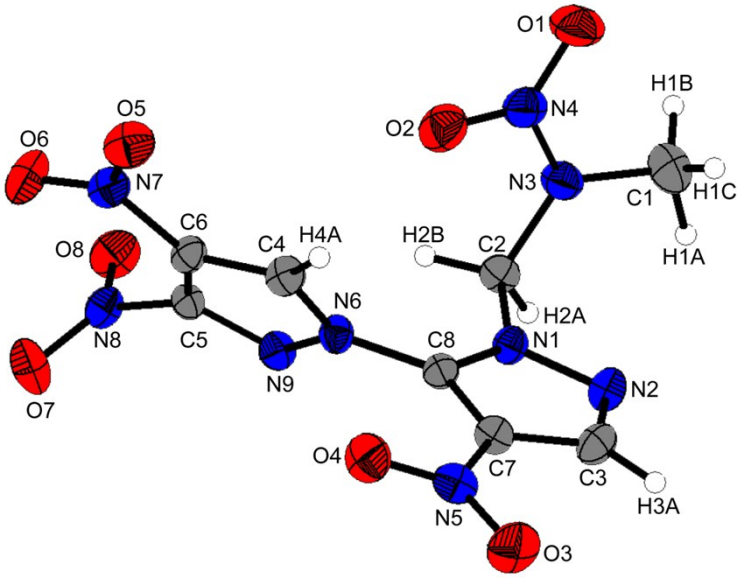

Figure S13: Molecular structure of 1-(3,4,4'-trinitro-1,3'-bipyrazol-2'-yl)-2-nitrazapropane (**10**). Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths [Å]: N3−N4 1.358(2), N1−N2 1.367(2), N6−N9 1.379(2), C5−N8 1.450(2), C6−N7 1.440(2), C7−N5 1.432(2), C8−N6 1.409(2), C3−N2 1.324(2), C8−N1 1.342(2), C4−N6 1.350(2), C5−N9 1.316(2), C2−N1 1.472(2), C2−N3 1.430(2), C1−N3 1.461(3), C3−C7 1.393(3), C7−C8 1.369(2), C4−C6 1.364(3), C5−C6 1.398(3). Selected bond angles [°]: O5−N7−O6 125.65(16), O5−N7−C6 116.62(16), O6−N7−C6 117.73(16), O3−N5−O4 124.59(16), O3−N5−C7 116.97(16), O4−N5−C7 118.43(16), C8−N1−N2 111.98(14), C8−N1−C2 130.79(16), N2−N1−C2 117.09(15), C4−N6−N9 112.95(15), C4−N6−C8 128.24(15), N9−N6−C8 118.61(14), C3−N2−N1 104.82(15), O7−N8−O8 125.87(16), O7−N8−C5 117.46(15), O8−N8−C5 116.66(16), O2−N4−O1 125.72(18), O2−N4−N3 117.65(17), O1−N4−N3 116.63(17), C5−N9−N6 103.05(15), N4−N3−C2 116.77(16), N4−N3−C1 118.29(18), C2−N3−C1 123.86(19), C4−C6−C5 105.73(15), C4−C6−N7 126.03(17), C5−C6−N7 127.99(16), N1− C8−C7 106.30(15), N1−C8−N6 121.31(15), C7−C8−N6 132.39(16), C8−C7−C3 106.07(17), C8−C7−N5 128.23(17), C3−C7−N5 125.70(17), N3−C2−N1 111.65(15), N6−C4−C6 105.73(17), N9−C5−C6 112.53(16), N9−C5−N8 117.72(16), C6−C5−N8 129.69(16), N2−C3−C7 110.83(17).

Table S10: Interactions within the crystal structure of **10**.

D−H···A	D−H [Å]	H···A [Å]	D···A [Å]	∠DHA [°]	Comment
C4−H4···O1	0.953	2.159	3.021	149.81	inter
C2−H2B···N9	0.978	2.463	3.135	125.56	intra
C2−H2A···N9	0.975	2.514	3.279	135.24	inter
C2−H2B···O6	0.978	2.526	3.255	131.26	inter
C1−H1A···O3	0.997	2.621	3.430	138.30	inter
C3−H3A···N2	0.957	2.702	3.416	131.95	inter
dipolar interactions ΣvdW radii (N···O) < 3.07 Å[2] N7–O8 2.921 Å					
dipolar interactions ΣvdW radii (C···O) < 3.22 Å[2] C6–O8 3.114 Å					
dipolar interactions ΣvdW radii (O···O) < 3.04 Å[2] O5–O5 2.871 Å O2–O8 2.893 Å					

3.11. 1-(5-Chloro-3,4-dinitropyrazol-1-yl)-2-nitrazapropane (11)

Suitable single crystals for X-ray analysis were obtained by slow evaporation of acetonitrile. 1-(5-Chloro-3,4-dinitropyrazol-1-yl)-2-nitrazapropane (**11**) crystallizes in the monoclinic space group $P2_1/c$ with four formula units per unit cell and a crystal density of 1.799 g cm^{-3} at 173 K.

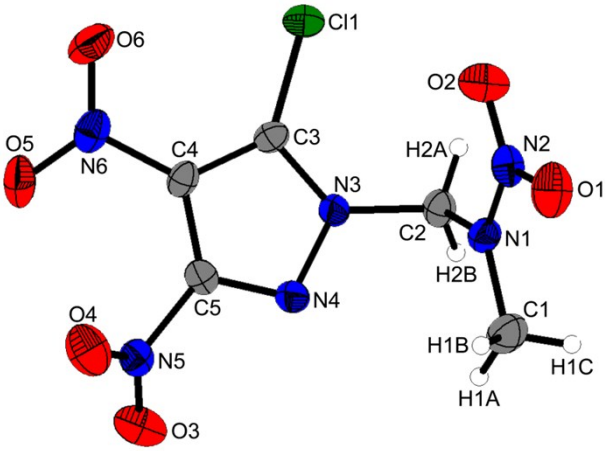

Figure S14: Molecular structure of 1-(5-chloro-3,4-dinitropyrazol-1-yl)-2-nitrazapropane (**11**). Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths [Å]: C3−Cl 1.688(2), N1−N2 1.347(2), N3−N4 1.358(2), C4−N6 1.435(3), C5−N5 1.480(3), C5−N4 1.310(3), C3−N3 1.353(3), C2−N3 1.474(3), C2−N1 1.443(3), C1−N1 1.455(3), C3−C4 1.383(3), C4−C5 1.398(3). Selected bond angles [°]: C5−N4−N3 104.03(15), O4−N5−O3 127.2(2), O4−N5−C5 116.19(18), O3−N5−C5 116.54(18), O1−N2−O2 124.93(19), O1−N2−N1 117.34(18), O2−N2−N1 117.73(18), C3−N3−N4 112.65(16), C3−N3−C2 129.99(18), N4−N3−C2 117.06(16), N3−C3−C4 105.95(17), N3−C3−Cl 122.64(16), C4−C3−Cl 131.39(16), N2−N1−C2 118.46(18), N2−N1−C1 118.27(18), C2−N1−C1 123.3(2), O6−N6−O5 124.60(18), O6−N6−C4 118.65(19), O5−N6−C4 116.75(19), N1−C2−N3 111.68(17), C3−C4−C5 104.40(17), C3−C4−N6 126.64(19), C5−C4−N6 128.7(2), N4−C5−C4 112.97(18), N4−C5−N5 117.50(17), C4−C5−N5 129.30(18).

Table S11: Selected interactions within the crystal structure of **11**.

D–H···A	D–H [Å]	H···A [Å]	D···A [Å]	∠DHA [°]	Comment
C1–H1C···O6	0.911	2.461	3.266	147.32	inter
C2–H2B···O2	0.957	2.550	3.431	153.00	inter
C2–H2A···O5	0.931	2.607	3.062	110.63	inter
C2–H2A···O1	0.931	2.635	3.263	125.33	inter

dipolar interactions ΣvdW radii (N···O) < 3.07 Å[2] N6–O3 2.886 Å
dipolar interactions ΣvdW radii (C···O) < 3.22 Å[2] C2–O5 3.062 Å
dipolar interactions ΣvdW radii (O···O) < 3.04 Å[2] O6–O3 2.850 Å

3.12. 1-(4-Amino-3,5-dinitropyrazol-1-yl)-2-nitrazapropane (12)

Suitable crystals for X-ray analysis were obtained by diffusion crystallization from acetonitrile / dichloromethane. 1-(4-Amino-3,5-dinitropyrazol-1-yl)-2-nitrazapropane (**12**) crystallizes in the monoclinic space group $P2_1/c$ with four formula units per unit and a crystal density of 1.820 g cm^{-3} at 173 K.

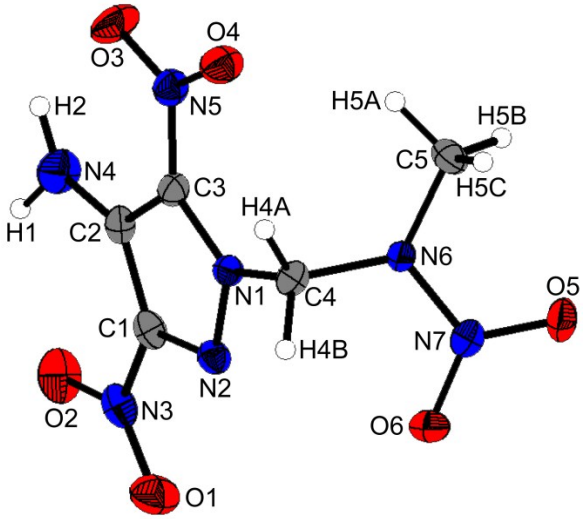

Figure S15: Molecular structure of 1-(4-amino-3,5-dinitropyrazol-1-yl)-2-nitrazapropane (**12**). Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths [Å]: O1–N3 1.225(2), O2–N3 1.237(2), O3–N5 1.243(2), O4–N5 1.227(2), O5–N7 1.231(2), O6–N7 1.233(2), N1–N2 1.326(2), N1–C3 1.376(2), N1–C4 1.483(2), N2–C1 1.333(2), N3–C1 1.429(2), N4–C2 1.347(2), N5–C3 1.404(2), N6–N7 1.359(2), N6–C4 1.442(2), N6–C5 1.462(2), C1–C2 1.407(2), C2–C3 1.395(2). Selected bond angles [°]: N2–N1–C3 110.64(14), N2–N1–C4 117.62(15), C3–N1–C4 131.67(16), N1–N2–C1 105.32(16), O1–N3–O2 124.35(19), O1–N3–C1 119.01(17), O2–N3–C1 116.63(18), O4–N5–O3 123.12(17), O4–N5–C3 120.60(16), O3–N5–C3 116.27(16), N7–N6–C4 117.32(15), N7–N6–C5 116.34(15), C4–N6–C5 122.95(16), O5–N7–O6 124.39(17), O5–N7–N6 117.11(16), O6–N7–N6 118.50(15), N2–C1–C2 113.96(18), N2–C1–N3 119.60(19), C2–C1–N3 126.43(18), N4–C2–C3 129.6(2), N4–C2–C1 129.3(2), C3–C2–C1 101.12(16), N1–C3–C2 108.95(17), N1–C3–N5 125.09(16), C2–C3–N5 125.95(17), N6–C4–N1 113.39(15).

Table S12: Selected interactions within the crystal structure of **12**.

D–H···A	D–H [Å]	H···A [Å]	D···A [Å]	∠DHA [°]	Interaction
C5–H5A···O4	0.981(2)	2.3212(16)	3.174(3)	144.94(13)	intra
N4–H2···O3	0.8954(7)	2.1781(16)	2.7687(18)	122.93(6)	intra
N4–H1···O2	0.8763(7)	2.2521(17)	2.8219(18)	122.54(6)	intra
C4–H4A···O4	0.9902(7)	2.3817(15)	2.9061(17)	112.34(6)	intra
C4–H4B···O6	0.9904(6)	2.2531(17)	2.6276(18)	100.94(5)	intra
C4–H4A···O6	0.9902(7)	2.4025(17)	3.3827(18)	170.31(6)	inter
N4–H1···O3	0.8763(7)	2.4858(14)	3.0075(16)	118.79(5)	inter
N4–H1···O2	0.8763(7)	2.5768(17)	3.1444(18)	123.13(6)	inter
C4–H4B···O5	0.9904(6)	2.6017(14)	3.5332(16)	156.74(5)	inter

C5–H5B···N2	0.980(2)	2.5903(16)	3.479(3)	150.99(13)	inter
C5–H5C···O6	0.980(2)	2.5719(14)	3.293(2)	130.43(12)	inter
C4–H4B···O5	0.9904(6)	2.5871(15)	3.2073(15)	120.66(5)	inter
dipolar interactions ΣvdW radii (N···O) < 3.07 Å[2]					
N4···O3 2.7687(18) Å^{intra}		N4···O2 2.8219(18) Å^{intra}			
dipolar interactions ΣvdW radii (C···O) < 3.22 Å[2]					
C4···O4 2.9061(17) Å^{intra}		C3···O1 3.0179(17) Å			

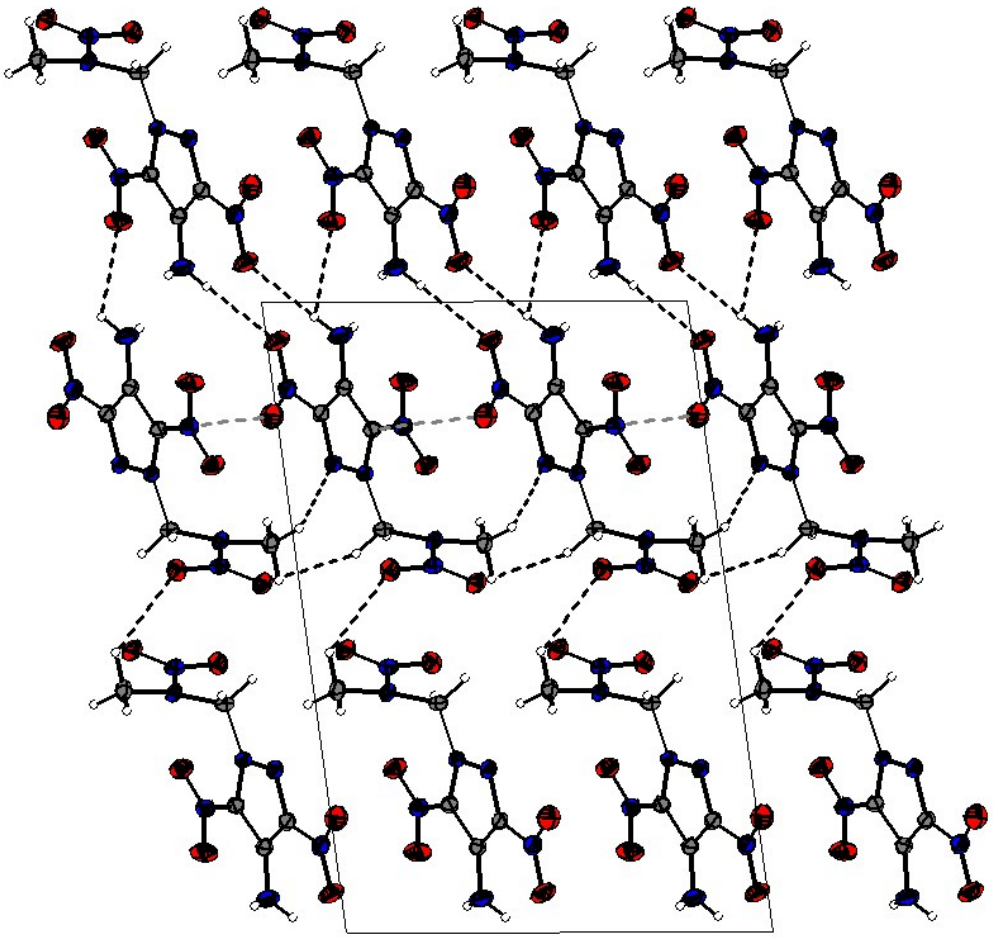

Figure S16: Unit cell of nitramine **12** along the *b* axis; non-classical hydrogen bonds are shown black dotted and dipolar C···O interactions are shown grey dotted.

4. Overview of selected crystallographic data

Table S13: Overview of selected crystallographic data of compounds **1**–**4**.

Compound	**1**	**2**	**3**	**4**
Molecular formula	$C_4H_6N_6O_5$	$C_6H_{10}N_8O_7 \cdot HNO_3$	$C_4H_5N_7O_6$	$C_4H_7N_7O_4$
Molecular weight [g mol^{-1}]	218.13	369.24	247.13	217.14
Color, habit	colorless block	colorless block	colorless block	colorless plate
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1$	$P2_1$	Cc	P-1
a [Å]	6.7610(6)	10.828(2)	15.831(4)	6.3027(8)
b [Å]	5.5064(6)	5.5849(11)	7.0572(7)	6.8628(8)
c [Å]	11.3925(10)	12.363(3)	11.133(3)	10.6253(14)
α [°]	90	90	90	72.876(11)
β [°]	97.072(9)	107.59(3)	132.07(4)	87.968(11)
γ [°]	90	90	90	77.540(11)
V [Å^3]	420.90(7)	712.6(2)	923.3(11)	428.68(10)
Z	2	2	4	2
ρ_{calcd} [g cm^{-3}]	1.721	1.721	1.778	1.682
μ [mm^{-1}]	0.157	0.162	0.165	0.148
F(000)	224	380	504	224
λ MoK_α [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	173	173	173	173
Θ min/max [°]	4.42/26.30	4.15/26.37	4.81/28.95	4.33/25.99
Data set h; k; l	−4: 8; −6: 6; −14: 13	−13: 11; −6: 6; −15: 12	−21: 20; −9: 5; −12: 14	−7: 7; −8: 8; −13: 13
Measured reflexes	2241	3846	1895	4326
Independent reflexes	1644	2832	1260	1671
Reflexes ($F_0 > 4\sigma(F_0)$)	1177	2094	957	1330
Parameters	160	270	174	164
R_1/R_1 (1 > 2 σ)	0.0567/0.0344	0.0529/0.0349	0.0472/0.0306	0.0466/0.0332
wR_2/wR_2 (1 > 2 σ)	0.0527/0.0488	0.0611/0.0577	0.0547/0.0515	0.0839/0.0755
GOF	0.840	0.865	0.895	1.073
Resd. dens. [e/Å^3]	+0.17/−0.13	+0.18/−0.16	+0.14/−0.16	+0.05/−0.28
CCDC	1439321	1439320	1439317	1439314

Table S14: Overview of selected crystallographic data of compounds **5**–**8**.

Compound	**5**	**6**	**7**	**8**
Molecular formula	$C_8H_{10}N_{12}O_8$	$C_5H_6N_6O_6$	$C_5H_6N_6O_6$	$C_5H_6N_6O_6$
Molecular weight [g mol^{-1}]	402.28	246.14	246.14	246.14
Color, habit	colorless plate	colorless block	colorless block	colorless block
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	*C*2/*c*	*P*2$_1$/*c*	*Cc*	*P*-1
a [Å]	17.5192(17)	11.4913(12)	5.7787(8)	8.2316(5)
b [Å]	6.4082(6)	6.9525(5)	20.764(3)	9.5937(5)
c [Å]	14.2000(14)	12.8652(11)	7.7190(11)	12.7855(7)
α [°]	90	90	90	93.595(4)
β [°]	99.184(9)	113.537(10)	92.393(12)	102.892(5)
γ [°]	90	90	90	96.844(4)
V [Å^3]	1573.7(3)	942.33(14)	925.4(4)	973.06(9)
Z	4	4	4	4
ρ_{calcd} [g cm^{-3}]	1.698	1.735	1.767	1.680
μ [mm^{-1}]	0.151	0.159	0.162	0.154
F(000)	824	504	504	504
λ MoK$_α$ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	173	173	173	173
Θ min/max [°]	4.34/25.57	4.24/26.37	4.43/27.49	4.23/26.37
Data set h; k; l	−17: 21; −7: 5; −16: 17	−14: 11; −8: 8; −12: 16	−7: 7; −26: 14; −10: 8	−10: 10; −11: 11; −15: 15
Measured reflexes	3779	4194	2573	10170
Independent reflexes	1472	1920	1820	3961
Reflexes ($F_0 > 4σ(F_0)$)	1102	1157	1216	2844
Parameters	147	178	167	356
R_1/R_1 (1 > 2 σ)	0.0627/0.0858	0.0635/0.0322	0.0653/0.0388	0.0480/0.0316
wR_2/wR_2 (1 > 2 σ)	0.1022/0.0895	0.0680/0.0630	0.0834/0.0782	0.0797/0.0755
GOF	1.043	0.835	0.861	0.943
Resd. dens. [e/Å^3]	+0.25/−0.19	+0.17/−0.21	+0.19/−0.30	+0.22/−0.20
CCDC	1439315	1439319	1439318	1439310

Table S15: Overview of selected crystallographic data of compounds **9**–**12**.

Compound	**9**	**10**	**11**	**12**
Molecular formula	$C_5H_6N_6O_6$	$C_8H_7N_9O_8$	$C_5H_5ClN_6O_6$	$C_5H_7N_7O_6$
Molecular weight [g mol^{-1}]	246.14	357.20	280.58	261.15
Color, habit	colorless plate	colorless block	colorless bar	yellow block
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	*P*2$_1$/*c*	*P*-1	*P*2$_1$/*c*	*P*2$_1$/*c*
a [Å]	17.1342(16)	8.5617(9)	5.6441(6)	15.9508(16)
b [Å]	9.3680(8)	9.3986(9)	12.0820(12)	5.6426(7)
c [Å]	12.5388(12)	9.7876(10)	15.3446(15)	10.6832(11)
α [°]	90	113.277(9)	90	90
β [°]	107.400(10)	106.073(9)	98.068(10)	97.579(9)
γ [°]	90	92.266(8)	90	90
V [Å^3]	1920.5(3)	685.23(12)	1036.02(18)	953.13(18)
Z	8	2	4	4
ρ_{calcd} [g cm^{-3}]	1.703	1.731	1.799	1.820
μ [mm^{-1}]	0.156	0.155	0.406	0.165
F(000)	1008	364	568	536
λ MoK$_α$ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	173	173	173	173
Θ min/max [°]	4.18/25.35	4.35/26.37	4.21/26.37	4.21/25.00
Data set h; k; l	−20: 15; −11: 10; −15: 14	−10: 10; −5: 11; −12: 11	−7: 7; −15: 15; −19: 19	−18: 18; −4: 6; −11: 12
Measured reflexes	9206	3705	10410	3330
Independent reflexes	3495	2777	2100	1684
Reflexes ($F_0 > 4σ(F_0)$)	1592	1700	1327	1368
Parameters	332	254	183	143
R_1/R_1 (1 > 2 σ)	0.1104/0.0375	0.0680/0.0356	0.0647/0.0335	0.0535/0.0404
wR_2/wR_2 (1 > 2 σ)	0.0575/0.0492	0.0696/0.0640	0.0723/0.0669	0.1026/0.0910
GOF	0.728	0.822	0.849	1.111
Resd. dens. [e/Å^3]	+0.17/−0.20	+0.20/−0.18	+0.27/−0.20	+0.20/−0.28
CCDC	1439311	1439312	1439314	1439316

5. References

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