Supporting Information

# Trinitroethyl – A Functionality Leading to Energetic Compounds with High Nitro Content

Haixiang Gao, Jean'ne M. Shreeve

**S1. Crystallographic Data and Structure Refinement Parameters of 9**.



**Table S1.** Crystal data and structure refinement for **9**.

| | | | |
|---|---|---|---|
| Identification code | | **9** | |
| Empirical formula | | $C_4H_3N_7O_{12}$ | |
| CCDC number | 969795 | | |
| Formula weight | | 341.13 | |
| Temperature | | 150(2) K | |
| Wavelength | | 0.71073 Å | |
| Crystal system | | Orthorhombic | |
| Space group | | Pbca | |
| Unit cell dimensions | | a = 12.523(2) Å | α= 90°. |
| | | b = 11.3630(19) Å | β= 90°. |
| | | c = 16.558(3) Å | γ = 90°. |
| Volume | | 2356.2(7) $Å^3$ | |
| Z | | 8 | |
| Density (-123°C) | | 1.923 $Mg/m^3$ | |
| Density (20°C) | | 1.879 $Mg/m^3$ | |
| Absorption coefficient | | 0.195 $mm^{-1}$ | |
| F(000) | | 1376 | |
| Crystal size | | 0.22 x 0.10 x 0.02 $mm^3$ | |
| Theta range for data collection | | 2.46 to 26.44°. | |
| Index ranges | | -15<=h<=15, -14<=k<=14, -20<=l<=20 | |
| Reflections collected | | 19773 | |
| Independent reflections | | 2409 [$R_{int}$ = 0.0547] | |
| Completeness to theta = 26.44° | | 99.2 % | |
| Absorption correction | | Semi-empirical from equivalents | |
| Max. and min. transmission | | 0.9961 and 0.9583 | |
| Refinement method | | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | | 2409 / 0 / 208 | |
| Goodness-of-fit on $F^2$ | | 1.029 | |
| Final R indices [I>2sigma(I)] | | $R_1$ = 0.0319, $wR_2$ = 0.0725 | |
| R indices (all data) | | $R_1$ = 0.0527, $wR_2$ = 0.0826 | |
| Largest diff. peak and hole | | 0.226 and -0.302 e.$Å^{-3}$ | |

**Table S2.** Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **9**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 9181(1) | 5745(1) | 7224(1) | 17(1) |
| C(2) | 8839(2) | 6879(1) | 6810(1) | 22(1) |
| N(3) | 8152(1) | 6516(1) | 6143(1) | 21(1) |
| C(4) | 7831(1) | 7268(1) | 5651(1) | 20(1) |
| C(5) | 7104(1) | 6852(1) | 4982(1) | 17(1) |
| N(6) | 10011(1) | 5047(1) | 6749(1) | 24(1) |
| O(7) | 10192(1) | 5376(1) | 6068(1) | 36(1) |
| O(8) | 10415(1) | 4224(1) | 7107(1) | 35(1) |
| N(9) | 8204(1) | 4971(1) | 7345(1) | 21(1) |
| O(10) | 7498(1) | 5429(1) | 7735(1) | 33(1) |
| O(11) | 8187(1) | 4011(1) | 7023(1) | 30(1) |
| N(12) | 9699(1) | 5960(1) | 8036(1) | 21(1) |
| O(13) | 10382(1) | 6728(1) | 8029(1) | 29(1) |
| O(14) | 9433(1) | 5354(1) | 8602(1) | 33(1) |
| N(15) | 7024(1) | 5515(1) | 4986(1) | 19(1) |
| O(16) | 6459(1) | 5104(1) | 5508(1) | 29(1) |
| O(17) | 7570(1) | 4991(1) | 4500(1) | 28(1) |
| N(18) | 5982(1) | 7357(1) | 5050(1) | 21(1) |
| O(19) | 5923(1) | 8279(1) | 5415(1) | 31(1) |
| O(20) | 5266(1) | 6823(1) | 4720(1) | 34(1) |
| N(21) | 7529(1) | 7221(1) | 4154(1) | 23(1) |
| O(22) | 8480(1) | 7416(1) | 4132(1) | 34(1) |
| O(23) | 6898(1) | 7273(1) | 3600(1) | 38(1) |

**Table S3.** Bond lengths [Å] and angles [°] for **9**.

| | | | |
|---|---|---|---|
| C(1)-N(12) | 1.513(2) | C(1)-N(9) | 1.520(2) |
| C(1)-C(2) | 1.520(2) | C(1)-N(6) | 1.525(2) |
| C(2)-N(3) | 1.459(2) | C(2)-H(2A) | 0.9900 |
| C(2)-H(2B) | 0.9900 | N(3)-C(4) | 1.248(2) |
| C(4)-C(5) | 1.509(2) | C(4)-H(4) | 0.9500 |
| C(5)-N(15) | 1.522(2) | C(5)-N(18) | 1.522(2) |
| C(5)-N(21) | 1.531(2) | N(6)-O(7) | 1.2094(19) |
| N(6)-O(8) | 1.2176(19) | N(9)-O(11) | 1.2137(18) |
| N(9)-O(10) | 1.2140(18) | N(12)-O(14) | 1.2098(18) |
| N(12)-O(13) | 1.2224(18) | N(15)-O(16) | 1.2112(18) |
| N(15)-O(17) | 1.2112(18) | N(18)-O(19) | 1.2114(18) |
| N(18)-O(20) | 1.2126(18) | N(21)-O(23) | 1.211(2) |
| N(21)-O(22) | 1.212(2) | | |
| | | | |
| N(12)-C(1)-N(9) | 108.77(12) | N(12)-C(1)-C(2) | 112.60(12) |
| N(9)-C(1)-C(2) | 108.85(13) | N(12)-C(1)-N(6) | 104.48(12) |
| N(9)-C(1)-N(6) | 108.36(12) | C(2)-C(1)-N(6) | 113.58(13) |
| N(3)-C(2)-C(1) | 105.53(12) | N(3)-C(2)-H(2A) | 110.6 |
| C(1)-C(2)-H(2A) | 110.6 | N(3)-C(2)-H(2B) | 110.6 |
| C(1)-C(2)-H(2B) | 110.6 | H(2A)-C(2)-H(2B) | 108.8 |
| C(4)-N(3)-C(2) | 119.44(14) | N(3)-C(4)-C(5) | 117.33(15) |
| N(3)-C(4)-H(4) | 121.3 | C(5)-C(4)-H(4) | 121.3 |
| C(4)-C(5)-N(15) | 110.46(13) | C(4)-C(5)-N(18) | 112.61(13) |
| N(15)-C(5)-N(18) | 108.44(13) | C(4)-C(5)-N(21) | 111.18(13) |
| N(15)-C(5)-N(21) | 107.43(12) | N(18)-C(5)-N(21) | 106.49(12) |
| O(7)-N(6)-O(8) | 127.83(15) | O(7)-N(6)-C(1) | 116.65(14) |
| O(8)-N(6)-C(1) | 115.53(14) | O(11)-N(9)-O(10) | 127.33(14) |
| O(11)-N(9)-C(1) | 118.50(13) | O(10)-N(9)-C(1) | 114.09(13) |
| O(14)-N(12)-O(13) | 127.33(14) | O(14)-N(12)-C(1) | 118.57(13) |
| O(13)-N(12)-C(1) | 114.05(13) | O(16)-N(15)-O(17) | 127.86(14) |
| O(16)-N(15)-C(5) | 115.18(13) | O(17)-N(15)-C(5) | 116.84(13) |
| O(19)-N(18)-O(20) | 127.82(15) | O(19)-N(18)-C(5) | 114.76(14) |
| O(20)-N(18)-C(5) | 117.38(13) | O(23)-N(21)-O(22) | 127.60(15) |
| O(23)-N(21)-C(5) | 117.66(15) | O(22)-N(21)-C(5) | 114.74(14) |

**Table S4.** Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **9**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 18(1) | 16(1) | 18(1) | -3(1) | 0(1) | -2(1) |
| C(2) | 27(1) | 15(1) | 22(1) | 0(1) | -5(1) | -1(1) |
| N(3) | 27(1) | 17(1) | 20(1) | 0(1) | -4(1) | -1(1) |
| C(4) | 22(1) | 14(1) | 22(1) | -2(1) | -1(1) | -1(1) |
| C(5) | 20(1) | 12(1) | 20(1) | 0(1) | 1(1) | 1(1) |
| N(6) | 22(1) | 18(1) | 31(1) | -5(1) | 4(1) | -4(1) |
| O(7) | 40(1) | 37(1) | 31(1) | -5(1) | 16(1) | -6(1) |
| O(8) | 31(1) | 22(1) | 53(1) | -3(1) | -3(1) | 8(1) |
| N(9) | 21(1) | 22(1) | 19(1) | 2(1) | -3(1) | -4(1) |
| O(10) | 23(1) | 42(1) | 35(1) | -5(1) | 7(1) | -1(1) |
| O(11) | 38(1) | 21(1) | 32(1) | -2(1) | -1(1) | -10(1) |
| N(12) | 21(1) | 19(1) | 23(1) | -2(1) | -3(1) | 2(1) |
| O(13) | 30(1) | 23(1) | 34(1) | -1(1) | -9(1) | -8(1) |
| O(14) | 37(1) | 39(1) | 24(1) | 10(1) | -5(1) | -6(1) |
| N(15) | 20(1) | 14(1) | 24(1) | -1(1) | -5(1) | 0(1) |
| O(16) | 32(1) | 18(1) | 37(1) | 4(1) | 7(1) | -5(1) |
| O(17) | 32(1) | 20(1) | 32(1) | -8(1) | 2(1) | 5(1) |
| N(18) | 23(1) | 18(1) | 22(1) | 1(1) | 1(1) | 4(1) |
| O(19) | 38(1) | 20(1) | 35(1) | -6(1) | 3(1) | 8(1) |
| O(20) | 23(1) | 34(1) | 46(1) | -8(1) | -9(1) | 1(1) |
| N(21) | 32(1) | 16(1) | 22(1) | 0(1) | 2(1) | -2(1) |
| O(22) | 29(1) | 39(1) | 36(1) | 2(1) | 10(1) | -3(1) |
| O(23) | 48(1) | 45(1) | 22(1) | 7(1) | -7(1) | -8(1) |

**Table S5.** Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for **9**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2A) | 8444 | 7391 | 7191 | 26 |
| H(2B) | 9469 | 7314 | 6607 | 26 |
| H(4) | 8035 | 8071 | 5694 | 23 |

**Table S6.** Torsion angles [°] for **9**.

| | |
|---|---|
| N(12)-C(1)-C(2)-N(3) | -167.44(13) |
| N(9)-C(1)-C(2)-N(3) | -46.75(16) |
| N(6)-C(1)-C(2)-N(3) | 74.06(17) |
| C(1)-C(2)-N(3)-C(4) | -173.52(15) |
| C(2)-N(3)-C(4)-C(5) | -178.74(14) |
| N(3)-C(4)-C(5)-N(15) | -7.6(2) |
| N(3)-C(4)-C(5)-N(18) | 113.84(17) |
| N(3)-C(4)-C(5)-N(21) | -126.75(16) |
| N(12)-C(1)-N(6)-O(7) | -132.61(14) |
| N(9)-C(1)-N(6)-O(7) | 111.55(16) |
| C(2)-C(1)-N(6)-O(7) | -9.5(2) |
| N(12)-C(1)-N(6)-O(8) | 47.08(17) |
| N(9)-C(1)-N(6)-O(8) | -68.76(17) |
| C(2)-C(1)-N(6)-O(8) | 170.15(14) |
| N(12)-C(1)-N(9)-O(11) | -117.85(15) |
| C(2)-C(1)-N(9)-O(11) | 119.13(15) |
| N(6)-C(1)-N(9)-O(11) | -4.84(19) |
| N(12)-C(1)-N(9)-O(10) | 65.28(17) |
| C(2)-C(1)-N(9)-O(10) | -57.74(17) |
| N(6)-C(1)-N(9)-O(10) | 178.30(13) |
| N(9)-C(1)-N(12)-O(14) | 13.88(19) |
| C(2)-C(1)-N(12)-O(14) | 134.61(16) |
| N(6)-C(1)-N(12)-O(14) | -101.68(16) |
| N(9)-C(1)-N(12)-O(13) | -168.31(13) |
| C(2)-C(1)-N(12)-O(13) | -47.57(19) |
| N(6)-C(1)-N(12)-O(13) | 76.13(15) |
| C(4)-C(5)-N(15)-O(16) | 76.49(17) |
| N(18)-C(5)-N(15)-O(16) | -47.36(17) |
| N(21)-C(5)-N(15)-O(16) | -162.08(14) |
| C(4)-C(5)-N(15)-O(17) | -99.81(16) |
| N(18)-C(5)-N(15)-O(17) | 136.34(14) |
| N(21)-C(5)-N(15)-O(17) | 21.62(19) |
| C(4)-C(5)-N(18)-O(19) | 24.68(19) |
| N(15)-C(5)-N(18)-O(19) | 147.24(13) |
| N(21)-C(5)-N(18)-O(19) | -97.42(15) |
| C(4)-C(5)-N(18)-O(20) | -157.35(14) |
| N(15)-C(5)-N(18)-O(20) | -34.80(19) |
| N(21)-C(5)-N(18)-O(20) | 80.54(16) |
| C(4)-C(5)-N(21)-O(23) | -157.88(14) |
| N(15)-C(5)-N(21)-O(23) | 81.14(17) |
| N(18)-C(5)-N(21)-O(23) | -34.88(18) |
| C(4)-C(5)-N(21)-O(22) | 22.94(18) |
| N(15)-C(5)-N(21)-O(22) | -98.03(15) |
| N(18)-C(5)-N(21)-O(22) | 145.94(14) |