

Structures of Two Cyano Nitramines (I): 1-Benzylnitrocyanamide and (II): 1,4-Nitrocyanamidylbutane

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Abstract. (I) *N*-Cyano-*N*-nitrotolylamine, $C_8H_7N_3O_2$, $M_r = 177.16$, monoclinic, Cc , $a = 10.090$ (2), $b = 10.811$ (3), $c = 8.414$ (2) Å, $\beta = 112.68$ (2)°, $V = 846.7$ (2) Å³, $Z = 4$, $D_x = 1.390$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.10$ mm⁻¹, $F(000) = 368$, $T = 225$ K, final $R = 0.030$, $wR = 0.032$ for 757 observed reflections. (II) *N,N'*-Dicyano-*N,N'*-dinitro-1,4-butane-diamine, $C_6H_8N_6O_4$, $M_r = 228.2$, monoclinic, $P2_1/n$, $a = 9.154$ (2), $b = 6.066$ (2), $c = 9.092$ (3) Å, $\beta = 100.57$ (2)°, $V = 496.3$ (2) Å³, $Z = 2$, $D_x = 1.527$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.12$ mm⁻¹, $F(000) = 236$, $T = 225$ K, final $R = 0.047$, $wR = 0.062$ for 683 observed reflections. In (I) both the cyanamide and the benzyl moieties are planar to within ± 0.02 Å with a dihedral angle of 69.3° between the two planes. The closest intermolecular approaches involve the cyanide nitrogen and the two nitramine nitrogens (3.06 and 3.00 Å). Molecule (II) sits on a center of symmetry and the N–C–C–C–N chain is all-*trans* and planar (± 0.01 Å). The cyanamide groups are planar to within ± 0.04 Å and are approximately perpendicular to the chain (dihedral angle between the planes is 83.2°). In (II) the closest intermolecular approaches are between symmetry-related oxygen atoms (2.83 Å) and between the nitro group nitrogen and an oxygen atom (3.05 Å).

Experimental. Both materials were synthesized by Clifford Coon of Lawrence Livermore Laboratory, Livermore, California. Colorless crystals, $0.12 \times 0.55 \times 0.20$ mm for (I) and $0.04 \times 0.25 \times 0.80$ mm for (II). Automated Nicolet *R3m* diffractometer with incident-beam graphite monochromator; 25 centered reflections with $22^\circ \leq 2\theta \leq 30^\circ$ used for determining cell parameters. $2\theta_{\text{max}} = 50^\circ$; range of hkl : $-11 \leq h \leq 11$, $0 \leq k \leq 12$, $-9 \leq l \leq 0$ for (I) and $-10 \leq h \leq 0$, $-7 \leq k \leq 0$, $-10 \leq l \leq 10$ for (II), standards, 400, 040, 002 for (I) and 310, 031, 103 for (II), monitored every 100 reflections with random variation of $\pm 1.5\%$ [$\pm 2.5\%$ for (II)] over data collection, $\theta/2\theta$ mode, scan width [$2\theta(K\alpha_1) - 1.0$] to [$2\theta(K\alpha_2) + 1.0$]°, scan rate a function of count rate ($10^\circ \text{ min}^{-1}$ minimum, $60^\circ \text{ min}^{-1}$ maximum); 898 [1022 for (II)] reflections measured, 800 [873 for (II)] unique, R_{int}

$= 0.01$, 757 [683 for (II)] observed [$F_o > 3\sigma(F_o)$]. Data corrected for Lorentz and polarization effects, but not for absorption.

The least-squares program used is part of the MicroVAX version of the *SHELXTL* system (Sheldrick, 1980). $\sum w(|F_o| - |F_c|)^2$ minimized where $w = 1/[\sigma^2(|F_o|) + g(F_o)^2]$. For (I), $g = 0.00025$ and 146 parameters were refined: atom coordinates for all atoms, anisotropic temperature factors for non-H atoms and isotropic temperature factors for H atoms; $(\Delta/\sigma)_{\text{max}} = 0.01$, $R = 0.030$, $wR = 0.032$, $S = 1.21$; final difference Fourier excursions 0.12 and $-0.15 \text{ e } \text{Å}^{-3}$. For (II), $g = 0.00023$ and 79 parameters were refined: atom coordinates and anisotropic temperature factors for non-H atoms, H atoms on C(2) were fixed (C–H = 0.96 Å and angles set at 109.7°), coordinates refined for H atoms on C(3), all H thermal parameters fixed; $(\Delta/\sigma)_{\text{max}} = 0.021$, $R = 0.047$, $wR = 0.062$, $S = 1.54$; final difference Fourier excursions 0.21 and $-0.25 \text{ e } \text{Å}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).^{*} Atom numbering for Tables 1–4, atom coordinates, bond distances and bond angles for molecules (I) and (II), respectively, follows that shown in Figs. 1 and 2.

Related literature. No structures containing the nitrocyanamide group appear in the 1988 edition of the Cambridge Structural Database. Structures containing nitramine groups (N–NO₂) adjacent to multiple bonds (other than nitriles) have been reported by Boileau, Wimmer, Gilardi, Stinecipher, Gallo & Pierrot (1988) and by Glass, Blount, Butler, Perrotta & Oliveto (1972).

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^{*} Lists of structure factors, anisotropic thermal parameters and H-atom coordinates for both compounds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51732 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^2$) for molecule (I)

	x	y	z	U_{eq}^*
C(1)	-0.3871	0.1926 (2)	0.5099	2.7 (1)
C(2)	-0.4467 (4)	0.0866 (3)	0.4170 (5)	3.2 (1)
C(3)	-0.5811 (4)	0.0469 (3)	0.4034 (5)	3.6 (1)
C(4)	-0.6574 (4)	0.1119 (3)	0.4807 (5)	3.6 (1)
C(5)	-0.5993 (4)	0.2177 (3)	0.5725 (5)	3.9 (1)
C(6)	-0.4634 (4)	0.2586 (3)	0.5883 (5)	3.5 (1)
C(7)	-0.2426 (4)	0.2394 (3)	0.5206 (6)	3.3 (1)
N(8)	-0.1257 (3)	0.1586 (2)	0.6334 (4)	2.8 (1)
N(9)	0.0093 (3)	0.1668 (2)	0.6214 (4)	3.4 (1)
C(10)	-0.1416 (4)	0.0634 (3)	0.7250 (5)	3.2 (1)
N(11)	-0.1535 (4)	-0.0172 (3)	0.8066 (5)	4.8 (1)
O(12)	0.0983 (3)	0.0895 (2)	0.7017 (5)	4.2 (1)
O(13)	0.0246 (3)	0.2515 (2)	0.5358 (5)	4.4 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Bond lengths (\AA) and angles ($^\circ$) for molecule (I)

C(1)—C(2)	1.387 (4)	C(1)—C(6)	1.389 (4)
C(1)—C(7)	1.512 (4)	C(2)—C(3)	1.384 (4)
C(3)—C(4)	1.377 (4)	C(4)—C(5)	1.378 (4)
C(5)—C(6)	1.397 (4)	C(7)—N(8)	1.481 (3)
N(8)—N(9)	1.407 (3)	N(8)—C(10)	1.332 (4)
N(9)—O(12)	1.222 (3)	N(9)—O(13)	1.211 (3)
C(10)—N(11)	1.144 (4)		
C(6)—C(1)—C(2)	119.5 (2)	C(7)—C(1)—C(2)	120.6 (2)
C(7)—C(1)—C(6)	119.9 (3)	C(3)—C(2)—C(1)	120.1 (3)
C(4)—C(3)—C(2)	120.7 (3)	C(5)—C(4)—C(3)	119.6 (3)
C(6)—C(5)—C(4)	120.3 (3)	C(5)—C(6)—C(1)	119.7 (3)
N(8)—C(7)—C(1)	110.6 (2)	N(9)—N(8)—C(7)	118.1 (2)
C(10)—N(8)—C(7)	125.7 (2)	C(10)—N(8)—N(9)	115.2 (2)
O(12)—N(9)—N(8)	116.3 (2)	O(13)—N(9)—N(8)	116.0 (2)
O(13)—N(9)—O(12)	127.6 (2)	N(11)—C(10)—N(8)	178.6 (3)

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for molecule (II)

	x	y	z	U_{eq}^*
N(1)	2010 (2)	2719 (4)	365 (3)	32 (1)
C(2)	2945 (3)	4130 (5)	-406 (3)	33 (1)
C(3)	4537 (3)	4253 (5)	402 (3)	29 (1)
C(4)	1171 (3)	3480 (5)	1329 (3)	30 (1)
N(5)	461 (3)	4231 (5)	2113 (3)	46 (1)
N(6)	2019 (3)	434 (4)	191 (3)	29 (1)
O(7)	1324 (2)	-638 (3)	962 (2)	37 (1)
O(8)	2707 (3)	-253 (4)	-732 (3)	43 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Bond lengths (\AA) and angles ($^\circ$) for molecule (II)

N(1)—C(2)	1.476 (4)	N(1)—C(4)	1.348 (4)
N(1)—N(6)	1.395 (3)	C(2)—C(3)	1.509 (4)
C(3)—C(3A)	1.517 (6)	C(4)—N(5)	1.144 (4)
N(6)—O(7)	1.218 (3)	N(6)—O(8)	1.212 (4)
C(2)—N(1)—C(4)	124.0 (2)	C(2)—N(1)—N(6)	120.4 (2)
C(4)—N(1)—N(6)	115.5 (2)	N(1)—C(2)—C(3)	113.0 (2)
C(2)—C(3)—C(3A)	111.7 (3)	N(1)—C(4)—N(5)	176.5 (3)
N(1)—N(6)—O(7)	116.8 (2)	N(1)—N(6)—O(8)	115.8 (2)
O(7)—N(6)—O(8)	127.5 (2)		

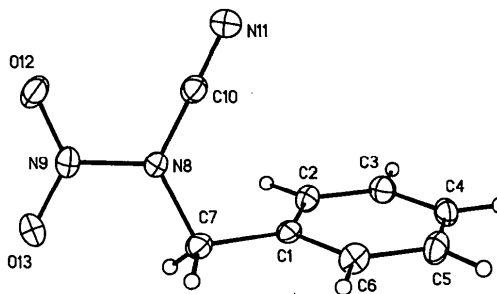


Fig. 1. Perspective drawing of the results of the X-ray study on molecule (I). The ellipsoids are shown at the 40% probability level.

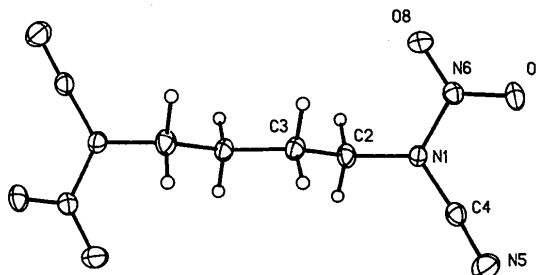


Fig. 2. Perspective drawing of the results of the X-ray study on molecule (II). Ellipsoids are shown at the 40% probability level.

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