Crystallographic Studies of High-Density Organic Compounds: N,N'-Bis(2,2,2-trinitroethyl)oxamide

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Abstract. $C_6H_6N_8O_{14}$, $M_r = 414 \cdot 2$, triclinic, $P\bar{1}$, $a = 6 \cdot 6574$ (2), $b = 6 \cdot 6855$ (3), $c = 8 \cdot 9634$ (4) Å, $\alpha = 86 \cdot 715$ (6), $\beta = 81 \cdot 263$ (6), $\gamma = 76 \cdot 025$ (6)°, $D_{calc} = 1 \cdot 80$ Mg m^{-3} for $Z = 1$; Cu $K\alpha$ ($\lambda = 1 \cdot 5418$ Å) diffractometer data; 1251 intensities; 1151 I's $> 3\sigma$ above background; final $R = 0 \cdot 034$. The molecule lies on a center of symmetry and extends diagonally along the unit cell. The conformational properties of the $C(NO_2)_3$ groups found in several compounds are discussed. $O \cdots N$ distances between NO_2 groups suggest the presence of a substantial attractive interaction between the atoms.

Introduction. We are investigating the crystal structures of a number of high-density nitro-organics to explore the relationships between molecular structure and density in these kinds of materials. This paper summarizes our work on the crystallography of N,N'-bis(2,2,2-trinitroethyl)oxamide (I), one of only a handful of structures containing the $C-C(NO_2)_3$ moiety.

$$(O_2N)_3C-CH_2-NH-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-NH-CH_2-C(NO_2)_3$$

(I)
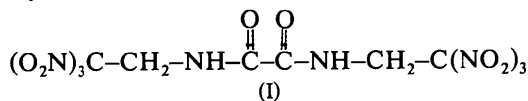
The compound was obtained from Dr H. Adolph of the Naval Surface Weapons Center in Silver Spring, Maryland as transparent flattened hexagonal crystals. The space group and approximate cell parameters were obtained from oscillation and Weissenberg photographs with Ni-filtered Cu radiation. Accurate cell parameters were determined and intensity measurements were made with a Picker FACS-I diffractometer and graphite-monochromated Cu radiation. A $0 \cdot 13 \times 0 \cdot 17 \times 0 \cdot 28$ mm crystal was mounted parallel to the long edge of the hexagonal face (b) and aligned to place this direction along the instrument's φ axis. The unit-cell parameters were determined by least squares from the 2θ values of 18 reflections manually centered at $\pm 2\theta$ (average $|2\theta_o - 2\theta_c| = 0 \cdot 002°$).

Intensities were measured with the 2θ–θ scan technique with a scan rate of 2° min^{-1} and 10 s backgrounds. The 2θ scan width was $2 \cdot 05° + 0 \cdot 29° \times$ tanθ. Four standards were measured at 100-reflection intervals during the data collection. 1343 reflections were measured to a 2θ maximum of 127°, giving 1251 unique data of which 1151 were more than 3σ above background. The structure was solved with the *MULTAN*-80 direct-methods system (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All of the C, N and O atoms were revealed in the first run. Structure refinement was by the method of full-matrix least squares with anisotropic temperature factors applied to C, N and O and isotropic terms for H. The quantity minimized was $\sum w(F_o - F_c)^2$, $w = [1/\sigma(F)]^2$. Those reflections for which $I_c < 3\sigma(I)$ were not included in the refinement. Scattering factors for C, N and O were calculated from the analytical expressions of Cromer & Mann (1968); the H terms were interpolated from the tabulated values of Stewart, Davidson & Simpson (1965). The final $R(\sum ||F_o| - |F_c||/\sum|F_o|)$ and weighted $R\{[\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}\}$ factors were $0 \cdot 034$ and $0 \cdot 032$, respectively. Atomic coordinates and thermal parameters are listed

Table 1. *Fractional coordinates and temperature factors* (Å^2) *with e.s.d.'s in parentheses*

A dagger denotes U_{eq}, the equivalent value of the anisotropic temperature-factor coefficient, calculated from $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

	x	y	z	U_{eq}/U_{iso}
C(1)	0·4999 (3)	0·3910 (3)	0·4768 (2)	0·017 (1)†
C(2)	0·4642 (3)	0·1947 (3)	0·2675 (2)	0·017 (3)†
C(3)	0·2541 (3)	0·1934 (3)	0·2214 (2)	0·017 (2)†
N(1)	0·4599 (3)	0·3866 (2)	0·3350 (2)	0·015 (2)†
N(2)	0·0726 (3)	0·2890 (3)	0·3397 (2)	0·029 (4)†
N(3)	0·2179 (3)	0·3113 (3)	0·0731 (2)	0·027 (4)†
N(4)	0·2369 (3)	−0·0249 (3)	0·1964 (2)	0·018 (2)†
O(1)	0·5326 (3)	0·2452 (2)	0·5629 (2)	0·022 (1)†
O(2)	0·0901 (3)	0·2261 (3)	0·4666 (2)	0·047 (4)†
O(3)	−0·0699 (3)	0·4177 (3)	0·2968 (3)	0·077 (5)†
O(4)	0·1255 (3)	0·2441 (3)	−0·0105 (2)	0·026 (3)†
O(5)	0·2879 (3)	0·4632 (2)	0·0532 (2)	0·037 (3)†
O(6)	0·3909 (3)	−0·1309 (2)	0·1247 (2)	0·034 (3)†
O(7)	0·0764 (3)	−0·0720 (3)	0·2469 (2)	0·030 (4)†
H(1)	0·455 (3)	0·489 (3)	0·280 (2)	0·041 (6)
H(2A)	0·569 (3)	0·168 (3)	0·177 (2)	0·037 (5)
H(2B)	0·496 (3)	0·085 (3)	0·340 (2)	0·037 (5)

in Table 1.* All calculations were done on Univac 1108 and 1100/42 computers in the University of Maryland's Computer Science Center with the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) of crystallographic programs.

Discussion. An *ORTEP* drawing (Johnson, 1971) of the structure as part of a packing diagram is shown in Fig. 1, and bond lengths and angles are shown in Fig. 2. The molecule has an extended conformation and is stretched diagonally across the unit cell. The origin has been chosen so that the center of the molecule is coincident with the crystallographic center of symmetry at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

At the time of writing the crystal structures of only four other $C-C(NO_2)_3$-group-containing compounds have been reported: (II) Lind (1970); (III) Gidaspov,

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36846 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
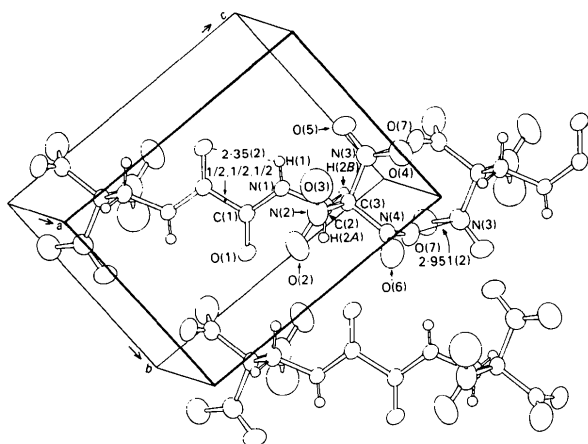

Fig. 1. An *ORTEP* packing diagram of (I) with the C, N and O atoms depicted as 50% probability boundary ellipses. H atoms are shown as 0·1 Å radius circles.
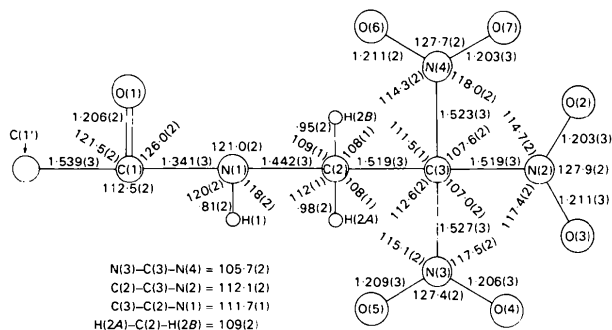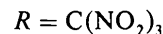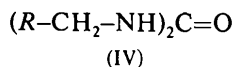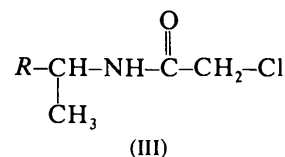

N(3)–C(3)–N(4) = 105·7(2)
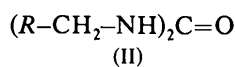C(2)–C(3)–N(2) = 112·1(2)
C(3)–C(2)–N(1) = 111·7(1)
H(2A)–C(2)–H(2B) = 109(2)

Fig. 2. Bond lengths (Å), angles (°) and e.s.d.'s (in parentheses).

Grigor'eva, Margolis, Makarenko, Popov & Selivanov (1971); (IV) Atovmyan, Gafurov, Golovina, Eremenko & Fedorov (1980).

$(R-CH_2-NH)_2C=O$
(II)

$R-CH-NH-C-CH_2-Cl$ (with O double bond on C, and CH₃ below the R–CH)
(III)

$(R-CH_2-NH)_2C=O$
(IV)

$R = C(NO_2)_3$

Two crystal forms of (IV) were reported, in space groups $Pn2_1a$ and $P2_1/a$, but errors in the fractional coordinates and/or cell parameters of the $P2_1/a$ form have not made it possible to use these data. If it is considered that the two $(NO_2)_3C-CH_2-NH$ halves of (I) and (II) are related by symmetry, and that the two $(NO_2)_3C-CH_2$ groups in the $Pn2_1a$ polymorph of (IV) are unique, there are five examples of the $C-C(NO_2)_3$ group contained in the four structures (I)–(IV).

With the exception of structure (III), which is of low accuracy, the bond lengths and angles of the several $C-C(NO_2)_3$ groups in (I), (II) and (IV) are essentially identical. The N–C–N angles are all 2–3° smaller than the ideal tetrahedral value of 109·5°, which is somewhat surprising since one might have expected that steric interactions among the three NO_2's would lead to larger angles. The shorter N–O distances and larger O–N–O angles in these compounds, relative to aromatic nitro groups, are undoubtedly due to enhanced electron delocalization to the nitro groups by the aryl substituents. The overall conformations of the $C-C(NO_2)_3$ groups in (I)–(III) are very similar to each other, but somewhat different from the two conformations found in (IV). For example, the O–N–C–C dihedral angles range from 34–56° in (I)–(III), whereas the corresponding range is 23–67° in (IV).

All of the $N-C-C(NO_2)_3$ conformations are staggered. However, in four of the five examples, the N–C bond is substantially displaced from the position at which it would bisect one of the $O_2N-C-NO_2$ angles [see Fig. 3 for compound (I)]. This skewing is undoubtedly coupled to the $C-NO_2$ bond twist angles to minimize the associated conformational energies. Perhaps one of the most curious structural features of the $C(NO_2)_3$ groups involves the O···N distances from one nitro group to another. The oxygen atoms in each of the nitro groups form one short and one long O···N contact to the central nitrogen atoms in the two neighboring nitro groups. The minimum O···N distances observed in the five $C(NO_2)_3$ groups are listed in the middle column of Table 2, while the right-most column gives the minimum possible O···N distance, obtained by rotating the oxygen atoms in each of the C–N–O units around the appropriate C–N bonds. With
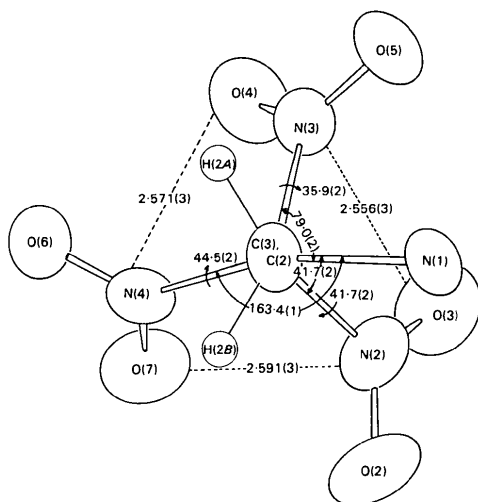
Fig. 3. A projection drawing of the C–C(NO$_2$)$_3$ group in (I) viewed down the C(3)–C(2) bond. The drawing includes torsion angles (°) about the C–N bonds, some torsion angles (°) about C(3)–C(2) and the minimum O···N contact distances (Å).

Table 2. *Observed and minimum calculated* O···N *distances* (Å) *in the* C(NO$_2$)$_3$ *groups of* (I)–(IV)

	Obs	Calc*
(I)	2·556 (3)	2·55
	2·571 (3)	2·53
	2·591 (3)	2·58
(II)	2·55	2·50
	2·55	2·55
	2·57	2·56
(III)	2·48	2·45
	2·54	2·53
	2·56	2·52
(IV)	2·54	2·54
	2·57	2·54
	2·59	2·50
	2·57	2·42
	2·58	2·58
	2·60	2·59

* Minimum distance obtained by rotating the appropriate N–O bond about its C–N bond.

only two exceptions, both in (IV), the minimum possible O···N distance is only 0·01–0·04 Å shorter than the observed contact. These small differences, coupled with the fact that the sum of the van der Waals radii of oxygen and nitrogen is *ca* 2·9 Å, suggest that the observed O···N distances reflect a substantial attractive interaction between the atoms. Given that the usual structures drawn for NO$_2$ show large negative charges on O and a full positive charge on N, it is proposed that there is an appreciable Coulombic attraction between
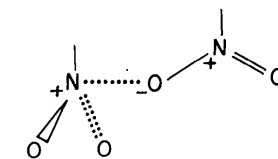

Fig. 4. Suggested model for nitro–nitro interaction.

the nitro groups in the C(NO$_2$)$_3$ substituent (Fig. 4). In (I), for example, the angles between the C–NO$_2$ planes are 78–90°, lending support to this proposal.

Bond lengths and angles in the central portion of (I) are very similar to values observed in other oxamides: *e.g.* oxamide (de With & Harkema, 1977) and N,N,N',-N'-tetramethyloxamide (Adiwidjaja & Voss, 1977).

A packing diagram is shown in Fig. 1. The oxamide hydrogen atoms form weak intramolecular N–H···O contacts, and no significant intermolecular contacts. There is a very weak C(2)–H(2B)···O(1) contact of 2·37 (3) Å with the molecule at 2–x, 1–y, 1–z (not shown in the figure). The 2·95 (3) Å O(7)···N(3) contacts, which join two molecules end-to-end, are simply van der Waals interactions.

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