$C_{33}H_{32}$

figuration of (2) is not suited for the deviation (downwards) of C(21), as it brings H(8) [buttressed by H(tert-Bu 7)] quite close to H(tert-Bu 9). In this case the second-best way to relieve the repulsion is by twisting the naphthalene unit around the C(9)—C(18) axis through the deviation of C(19), whereby the relief of the repulsion is not appreciably effective. The resulting increment of strain energy in (2) was found to be borne largely by the increased distortion of the phenanthrene unit from planarity, which was shown by the calculated torsional energy difference between (2) and (3) (8·9 and 1·4 kJ mol^{-1} for the phenanthrene and naphthalene unit, respectively).

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Crystallographic Studies of High-Density Organic Compounds. 1,4-Difluoro-1,1,4,4-tetranitro-2,3-dinitrooxybutane

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Abstract. $C_4H_2F_2N_6O_{14}$, $M_r = 396·1$, monoclinic, $P2_1/c$, $a = 7·6975 (9)$, $b = 5·7890 (8)$, $c = 14·722 (3)$ Å, $\beta = 101·74 (2)°$, $D_{calc} = 2·05$ Mg m^{-3}, $Z = 2$; Cu $K\alpha$ ($\lambda = 1·5418$ Å) diffractometer data; 1045 unique intensities; $811 \geq 3\sigma$ above background; final $R = 0·054$. The molecule lies on a center of symmetry. The overall structure and conformation is similar to that of 1,4-difluoro-1,1,4,4-tetranitro-2,3-butanediol. The $RO-NO_2$ distance of $1·515 (5)$ Å, which is substantially longer than other O—N single bonds, may account for the facile hydrolysis of the nitrate ester linkage. There are no short intermolecular contacts that would account for the exceptional crystal density.

Introduction. The fluorodinitromethyl group is of interest as a functional group for energetic materials such as explosives. We are currently investigating the structures of a number of high-crystal-density, polynitro-group-containing organic compounds as the first step in an investigation of the relationships between crystal density and structure in these types of compounds. In this paper, the structure of the title compound (I) is reported, and compared with the structure of the diol (II) (Dickinson & Holden, 1979).

$$ (NO_2)FC-\underset{\underset{O-X}{|}}{\overset{\overset{O-X}{|}}{CH}}-CH-CF(NO_2)_2 $$

(I) X = NO_2, (II) X = H
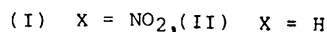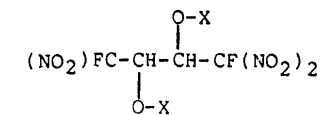
(I) was obtained from Dr H. Adolph, Naval Surface Weapons Center, Silver Spring, Maryland, as opaque white needles. The compound is moisture-sensitive, undergoing hydrolysis to the alcohol (II). A crystal with maximum dimensions of 0·3 mm was quickly transferred from its storage desiccator to a pre-dried capillary tube which was then sealed with dental wax.

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 made with a Picker FACS-I diffractometer and graphite-monochromated Cu radiation (Cu $K\alpha$, $\lambda =$

1·5418 Å). The unit-cell parameters were determined by least-squares calculations from the 2θ values of 12 reflections manually centered at $\pm 2\theta$ (average $|2\theta_o - 2\theta_c| = 0.006°$).

Intensities were measured with the θ–2θ scan technique with a scan rate of $2°$ min^{-1} and 10 s backgrounds. The 2θ scan width was calculated from $1.5° + 0.3°$ tan θ. Four standards were measured at 100-reflection intervals to monitor intensity fluctuations and crystal decomposition. Intensity corrections ranged from 1.0–1.077. 1201 reflections were measured to a 2θ maximum of 127° giving 1045 unique reflections. 811 were 3σ above background. The structure was solved with the direct-methods subprogram *PHASE* of the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The 13 non-H atoms in the asymmetric unit showed up as the strongest peaks in an E map calculated with 170 phases. The structure was refined by the method of full-matrix least squares with anisotropic temperature factors applied to the C, N, O and F atoms and an isotropic term for the 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, O and F 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 0·054 and 0·066, respectively. Atomic coordinates and temperature factors are listed in Table 1.* All calculations were performed on a

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* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36940 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and isotropic temperature factors* (Å^2)

An asterisk denotes U_{eq}, the equivalent value of the anisotropic temperature-factor coefficients, calculated from the expression: $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$. The U_{ij} values have been deposited. The e.s.d. of the last significant digit is given in parentheses.

	x	y	z	U
C(1)	0·4028 (4)	0·4617 (6)	0·4930 (2)	0·035 (7)*
C(2)	0·3119 (5)	0·4734 (6)	0·3903 (2)	0·037 (8)*
F	0·4067 (3)	0·3835 (4)	0·3351 (1)	0·051 (6)*
N(1)	0·2692 (4)	0·7289 (6)	0·3597 (2)	0·034 (5)*
N(2)	0·1286 (4)	0·3595 (5)	0·3702 (2)	0·031 (6)*
N(3)	0·2957 (4)	0·1811 (7)	0·5947 (2)	0·048 (5)*
O(1)	0·0546 (4)	0·3350 (5)	0·4342 (2)	0·045 (7)*
O(2)	0·0753 (4)	0·3060 (6)	0·2896 (2)	0·032 (7)*
O(3)	0·3370 (4)	0·7996 (6)	0·2988 (2)	0·074 (4)*
O(4)	0·1714 (4)	0·8238 (5)	0·4022 (2)	0·056 (2)*
O(5)	0·4028 (3)	0·2265 (4)	0·5209 (2)	0·040 (3)*
O(6)	0·2438 (4)	0·3420 (6)	0·6303 (2)	0·076 (3)*
O(7)	0·2885 (5)	−0·0231 (6)	0·6068 (2)	0·072 (6)*
H(1)	0·339 (4)	0·552 (6)	0·535 (2)	0·023 (8)

Univac 1108 computer at the University of Maryland's Computer Science Center with the XRAY system (Stewart *et al.*, 1976) of crystallographic programs.

Discussion. An *ORTEP* drawing (Johnson, 1971) of the molecule is shown in Fig. 1, and bond lengths and angles are given in Fig. 2. The conformations of (I) and the diol (II) are very similar and both molecules straddle crystallographic centers of symmetry situated midway between C(1) and C(1′). A comparison of the O—C—C(F)(NO$_2$)$_2$ fragments in the two structures with Nyburg's (1974) best-molecular-fit program gave an r.m.s. deviation of 0·182. Small variations in several torsion angles associated with the fluorodinitromethyl groups account for the major differences between the structures. The conformations around the C(1)—C(2) bonds are essentially identical, but there are *ca* 15°
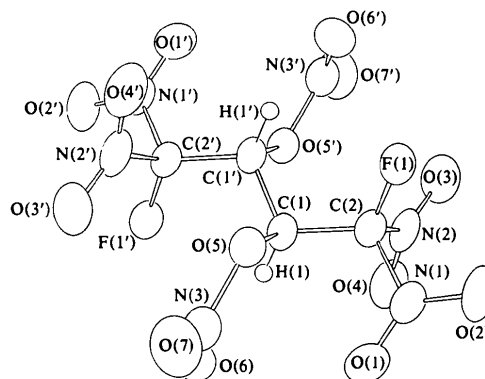

Fig. 1. *ORTEP* drawing of (I) with the C, N, O and F atoms depicted as 50% probability boundary ellipses. H atoms are shown as 0·1 Å radius circles.
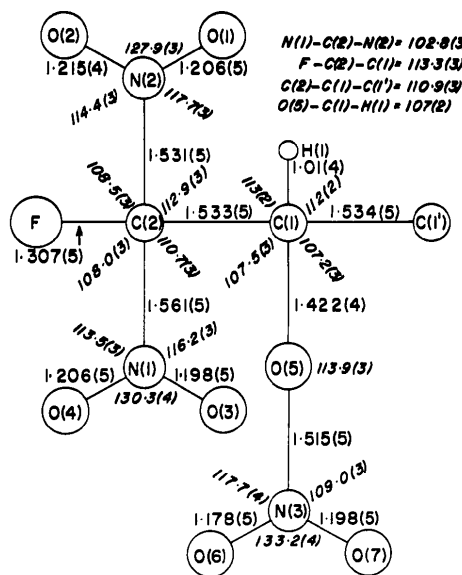

Fig. 2. Bond lengths (Å) and angles (°) with e.s.d.'s (in parentheses).

Table 2. *Molecular dimensions of the* C—O—NO$_2$ *group in some nitrate esters*

$$C \diagdown O-N \diagup\diagup O' \diagdown O'$$

| Compound	Reference	C—O	O—N	$\langle$N—O'$\rangle$	C—O—N
4,4-Difluoro-1,1,4,4-tetranitro-2,3-dinitrooxybutane	Present work	1·422 (4) Å	1·515 (5) Å	1·188 (5) Å	13·9 (3)°
cis-Benzocyclobutene-1,2-diol dinitrate	Allen & Trotter (1970)	1·451 (4)[a]	1·387 (4)	1·195 (4)	113·6 (3)
		1·443 (4)[a]	1·411 (4)	1·194 (4)	113·1 (3)
cis-1,2-Acenaphthenediol dinitrate	Mak & Trotter (1964)	1·467 (13)[a]	1·408 (12)	1·193 (12)	115·7 (9)
		1·468 (13)[a]	1·410 (12)	1·200 (12)	115·4 (9)
Pentaerythritol tetranitrate	Trotter (1963)	1·462 (14)	1·404 (12)	1·214 (14)	112·6 (7)
Ethyl 2-nitro-3-nitrooxy-3-(4-nitrophenyl)propionate	Couldwell (1979)	1·454 (3)	1·422 (2)	1·189 (3)	114·6 (2)
N-Nitrobis(2-nitrooxyethyl)amine	Halfpenny & Small (1978)	1·451 (4)[a]	1·393 (4)	1·122 (7)	113·6 (3)
		1·448 (5)[a]	1·405 (4)	1·199 (7)	112·9 (3)

(a) Two molecules per asymmetric unit.

differences in each of the C—N conformations. On the basis of this, it is somewhat surprising that the closest non-bonded F···O(2) and F···O(3) contacts in the CF(NO$_2$)$_2$ groups, which are presumably responsible for the NO$_2$ conformations, differ by no more than 0·03 Å between the two structures.

Bond lengths and angles in (I) and (II) are quite similar, the largest differences occurring between C(2)—N(1) [(I) = 1·561 (5), (II) = 1·540 (4) Å] and C(1)—O(5) [(I) = 1·422 (4), (II) = 1·400 (4) Å]. In the case of C(1)—O(5), differences between the OH and ONO$_2$ groups might be responsible for this variation. The fluorodinitroethyl lengths and angles are close to those observed in N-nitrobis(2-fluoro-2,2-dinitroethyl)amine (Bhattacharjee & Ammon, 1982; Atovmyan, Gafurov, Golovina & Eremenko, 1978) and tris-(2-fluoro-2,2-dinitroethyl)amine (Atovmyan, Gafurov, Golovina & Eremenko, 1980).

The Cambridge Crystallographic Data Centre (1981) files were searched for examples of nitrate esters, and the results are listed in Table 2 together with the data for (I). The various bond lengths and angles are quite similar, with the exception of O—N [O(5)—N(3) in (I)]. In (I) this bond is longer by *ca* 0·1 Å than any of the corresponding linkages given in the table, and longer than typical O—N single bonds. For example, the $\langle$O—N$\rangle$ distance in 1,3,5-triacetoxyhexahydro-1,3,5-triazine is 1·462 (2) Å (Jerslev, Brehm & Gabrielsen, 1977). In addition, C—O [C(1)—O(5) in (I)] appears to be short compared to the other corresponding values in Table 2, although the C—OH distance in the diol (II) is even shorter at 1·400 (4) Å. Because these differences might reflect an 'incorrect' position for O [O(5) in (I)], and because the opacity of the crystal could be indicative of some amount of hydrolysis of the ester, a careful inspection of the final difference map was made. The difference electron density ranged from +0·32 to −0·28 e Å^{-3} over the whole map, and there were no features in the

vicinity of the C—O—NO$_2$ group that could be interpreted as arising from partial hydrolysis of the nitrate ester. Although we cannot offer a simple rationale for this O—N bond distance on a structural basis, the facile hydrolysis of (I) to the alcohol (II) suggests that the bond is weaker than normal and therefore could well be longer than normal. Crystals of the corresponding formate ester, which become opaque on standing in air for a few weeks, are presently being investigated to determine if these molecules also exhibit an abnormal bond length.
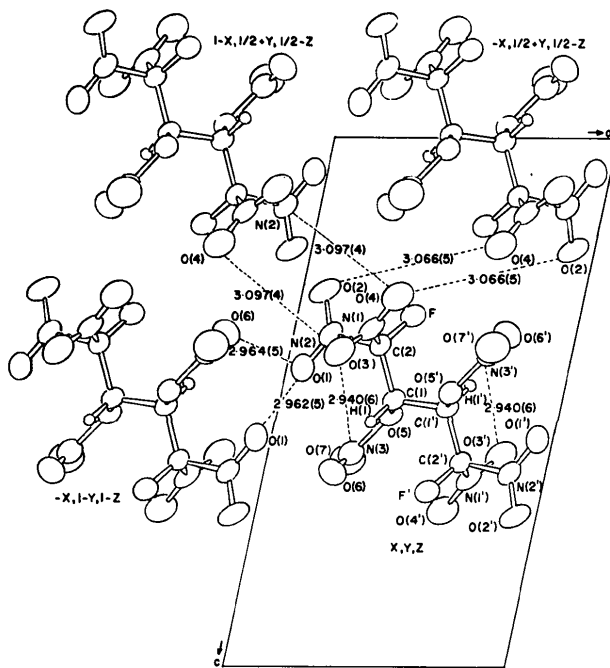
Fig. 3. Packing view down **b**; some contact distances (Å) and e.s.d.'s (in parentheses) are given.

The crystal-packing arrangements in the nitrate ester (I) (see Fig. 3) and alcohol (II) (Dickinson & Holden, 1979) are quite different. The latter contains a 2·27 Å O—H···O contact, and all of the remaining inter-molecular distances are greater than the sums of the appropriate van der Waals radii (1·5 Å for N and 1·4 Å for O). The principal intermolecular contacts in (I) (see Fig. 3) are of the O···O type, and range from 2·96–3·07 Å. The shortest intermolecular N···O distance is 3·10 Å. That these distances are all larger than the values that would be expected on the basis of van der Waals radii of 1·5 Å for N and 1·4 Å for O is not unexpected, since the outer perimeters of the molecule bristle with NO_2's which presumably supplement the molecule's electrostatic defenses.

The densities of (I) and (II), 2·05 and 1·95 Mg m^{-3}, respectively, seem anomalously high in view of the absence of apparent close contacts that would reflect the reduction of empty space in the crystal lattices. It is concluded that the high crystal densities result from compounds which exhibit higher than normal molecular densities. The high molecular densities can be presumed to arise from having relatively compact molecules composed of sizable fractions of the denser N, O and F atoms compared to the less dense C and H atoms.

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Pyridoxine*

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Abstract. $C_8H_{11}NO_3$, $M_r = 169·18$, orthorhombic, space group $Pn2_1a$, $a = 12·377$ (2), $b = 4·652$ (1), $c = 14·112$ (2) Å, $V = 812·54$ Å^3, $Z = 4$, $D_c = 1·38$, $D_o = 1·40$ Mg m^{-3}, $R = 0·048$ for 724 reflections with $|F_o| > 2\sigma(F_o)$. The pyridoxine molecule occurs as the non-dipolar form in which the phenolic group remains un-ionized.

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* 5-Hydroxy-6-methyl-3,4-pyridinedimethanol.

Introduction. The crystal structure of neutral pyridox-ine (PN) has been determined as part of our research on the structures and spectra of vitamin B$_6$ derivatives (K. J. Franklin & Richardson, 1980; T. A. Franklin & Richardson, 1980; Thompson, Balenovich, Hornich & Richardson, 1980; Longo & Richardson, 1980). The IR spectrum of PN suggested that the stable tautomer was the non-dipolar form (T. A. Franklin & Richardson, 1980). This has been confirmed by the present structure.