

The 1-pyrrolidinecarbodithioate anion (Fig. 3): the non-hydrogen atom arrangement is similar to that in tris(1-pyrrolidinecarbodithioato)iron(III) (Mitra, Raston & White, 1978), (FePy₃).

The mean C–S length is 1.719 Å. C(1)–S(2) is *ca* 10σ shorter than C(1)–S(1). The probable explanation of this discrepancy is, as in (E) and (iP), unsymmetrical intermolecular hydrogen bonding. C(1)–N(1) is *ca* 0.02 Å shorter than that in (M), (E) and (iP), and 0.014 Å longer than the mean value in (FePy₃). The bonds between the alkyl C atoms and the N atoms agree with those in the present cation and those in (FePy₃), and are intermediate between those in (E) and (iP).

Distances of some atoms from the least-squares plane through S(1), S(2), C(1), N(1), C(2) and C(5) are: S(1) 0.000 (1), S(2) 0.001 (1), C(1) –0.010 (3), N(1) –0.005 (2), C(2) 0.010 (3), C(5) 0.005 (4), C(3) 0.378 (4), and C(4) –0.196 (5) Å. The dithiocarbamate plane is a little bent, in agreement with observations in (M) and (E).

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Structure of 1,4-Difluoro-1,1,4,4-tetranitro-2,3-butanediol

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Abstract. C₄H₄F₂N₄O₁₀, monoclinic, *P*2₁/*c*, *a* = 5.5984 (5), *b* = 10.802 (1), *c* = 8.9371 (9) Å, β = 104.9 (4)°. *D_m* = 1.925 (measured by neutral buoyancy), *D_c* = 1.947 Mg m⁻³, *Z* = 2. The structure was solved by direct methods and refined by a full-matrix least-squares procedure to an *R* value of 0.03, observed reflections only. The F atom and hydroxyl group are *gauche* to one another and no intramolecular hydrogen bond is formed. A weak intermolecular hydrogen bond does exist between the hydroxyl group and a nitro group.

Introduction. The material was synthesized at these laboratories and provided to us as clear, colorless crystals. Preliminary cell dimensions were obtained from oscillation, Weissenberg and precession films, and the systematic absences observed (*h*0*l*, *l* = 2*n* + 1; 0*k*0, *k* = 2*n* + 1) indicated the space group to be *P*2₁/*c*. A crystal was mounted on a Picker FACS-I diffractometer (λ = 0.71069 Å) and cell-dimension and intensity data were collected. Cell-dimension data were gathered from 16 reflections measured at both positive and

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negative values of 2θ, and the intensity data were collected using an ω–2θ scan to 2θ_{max} = 55°. Of the 1879 intensity data collected, 1268 were crystallographically independent. The structure was solved by direct methods.* Full-matrix least-squares refinement using unit weights reduced the *R* value to 0.03 with anisotropic temperature factors for the non-hydrogen atoms. H atoms were given arbitrarily assigned isotropic values. Of the independent reflections, 888 had *I* ≥ 3σ(*I*). These were included in the refinement as were those of the remainder whose calculated structure factor was greater than the observed value, a total of 1010 reflections in the last cycle.† The *R* value for all reflections (1196 total) was 0.05. The scattering factors

* All calculations were performed using one or more versions of the XRAY calculational system (Stewart, 1972).

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33973 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	0.04030 (7)	0.54059 (3)	0.07217 (4)
C(2)	0.25047 (7)	0.47593 (3)	0.19051 (4)
H(1)	-0.0954 (7)	0.5515 (4)	0.1166 (4)
H(2)	0.0948 (9)	0.7023 (4)	0.0692 (5)
F(1)	0.42803 (4)	0.43566 (3)	0.13038 (3)
N(1)	0.36612 (7)	0.56504 (3)	0.32322 (4)
N(2)	0.16763 (6)	0.36536 (3)	0.27375 (4)
O(1)	0.22363 (7)	0.62996 (3)	0.36785 (4)
O(2)	0.58816 (6)	0.55946 (3)	0.37329 (4)
O(3)	0.29215 (7)	0.27318 (3)	0.28880 (4)
O(4)	-0.01347 (6)	0.38123 (3)	0.32096 (3)
O(5)	0.13279 (6)	0.65091 (3)	0.02687 (3)

for C, F, N and O were those of Cromer & Mann (1968) and for H those of Stewart, Davidson & Simpson (1965). The final positional parameters are given in Table 1.

Discussion. The fluorodinitromethyl group has received some attention as a new atom grouping in energetic materials such as explosives (Gilligan & Adolph, 1974) and propellants (Sickman, Kamlet, Rich, Heller & Kaplan, 1973). Further, studies have indicated interesting anomalies in the chemistry of the group, particularly the effect on carbanion chemistry (Kaplan & Burlinson, 1972; Adolph & Kamlet, 1966, 1969). Also, intramolecular hydrogen bonding has been suggested both for β -fluoro-alcohols (Hagen & Hedberg, 1973, and references therein) and β -nitro-alcohols (Lipczyńska-Kochany & Urbański, 1977). Finally, we wished to study the packing of the molecules because the density seemed abnormally high. We have developed a scheme for calculating densities based on group-volume additivity that is essentially similar to that of Immirzi & Perini (1977) and the observed value for this diol deviates from the estimated density ($\rho_o - \rho_{est} = 0.099 \text{ Mg m}^{-3}$), by nearly twice the average deviation of the

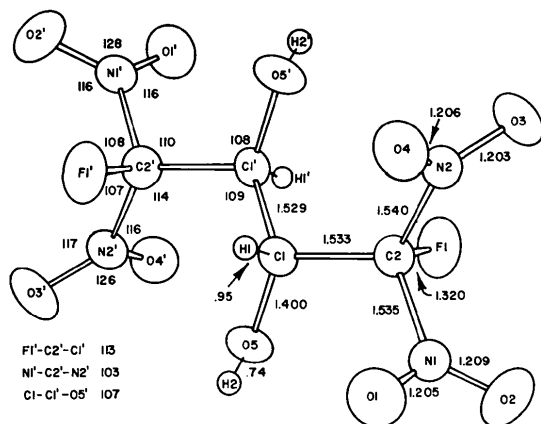


Fig. 1. ORTEP drawing (Johnson, 1965) of the molecule with bond lengths and angles.

354 solids we have examined. In order to determine the geometry of the fluorodinitromethyl group and to investigate the hydrogen bonding in β -substituted alcohols, we have determined the crystal structure of the title compound.

The bond lengths and angles for the non-hydrogen atoms and the numbering scheme are shown in Fig. 1. The molecule lies on a center of symmetry ($0, \frac{1}{2}, 0$) located midway between atoms C(1) and C(1'). The errors in the bond lengths range from 0.003 to 0.007 Å, with an average of 0.004 Å; in the angles the error range is 0.14–0.19° and the average is 0.16°. The bond lengths, angles and errors for the H atoms are: C(1)–H(1), 0.95 (2); O(5)–H(2), 0.74 (3) Å; C(1')–C(1)–H(1), 109 (1); O(5)–C(1)–H(1), 114 (1); C(2)–C(1)–H(1), 109 (1); C(1)–O(5)–H(2), 109 (2)°.

Bond lengths in the molecule are near anticipated values, although a little shorter than might be expected in certain cases. Thus the C–F bond at 1.320 Å may be compared with C–F lengths in a series of fluoro-halomethanes and ethanes that are reported to range from 1.398 Å in fluoroethane to 1.323 Å in carbon tetrafluoride, with shorter C–F distances associated with multiple F substitution on a single C atom (Gallaher, Yokozeki & Bauer, 1974, and references therein). Our own studies on *N*-trifluoroethyl-*N*,2,4,6-tetranitroaniline (Holden & Dickinson, 1969) gave C–F distances ranging from 1.29 to 1.36 Å. Also in this diol, the O–H bond length, 0.74 Å, is nearly 0.2 Å shorter than most reported values. Of the bond angles, C(1)–C(2)–F(1) (113°) is the most interesting since in β -fluoroethanol the equivalent angle is closed somewhat from the tetrahedral angle and the C–C–O angle is enlarged. The expansion of this angle here does not seem to be the result of overcrowding since the non-bonded separations do not reveal much intramolecular steric interaction: O(5) to F(1), 2.86; to N(1), 2.79; to O(1), 2.97; to C(2), 2.38; to N(2'), 2.78; to O(4'), 3.02; and F(1) to H(1'), 2.50 Å.

The F atom and the hydroxyl group are *gauche* to one another with dihedral angles F(1)–C(2)–C(1)–O(5), -67° , and C(2)–C(1)–O(5)–H(2), -103° . The *gauche* configuration was anticipated for this molecule from steric considerations, but it is interesting to note that given the *gauche* configuration for whatever reason, the hydroxyl group is oriented in such a way as to form a weak intermolecular hydrogen bond [$d(O \cdots O) = 2.99 \text{ Å}$, $\angle(O-H \cdots O) = 170^\circ$] with a nitro group of the molecule at $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$, as shown in Fig. 2, rather than an intramolecular or bifurcated system involving either the β -fluorine atom or a β -nitro group. Similarly, no intramolecular hydrogen bonding was discovered in NMR studies of β -fluoroethanol (Griffith & Roberts, 1974) or in the crystal structure of 2-methyl-2-nitro-1,3-propanediol (Marr, Kruger & Stewart, 1977). The intermolecular hydrogen-bonding scheme here is such that the

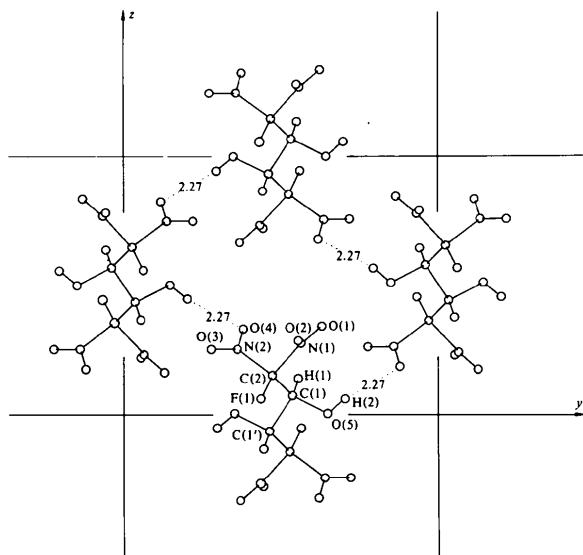


Fig. 2. Hydrogen-bonding scheme and packing of the molecules. Projection is onto the yz plane.

molecules form a relatively thick layer parallel to the yz plane [~ 6.6 Å elevation between O(2) and its centrosymmetrically related atom] and the molecular arrangement is relatively open as indicated by the 'hole' in the center of the cell, Fig. 2.

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Structure of 4-Formylamino- Δ^2 -1,2,4-triazoline-5-thione

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Abstract. $C_3H_4N_4OS$, orthorhombic, $Pna2_1$, $a = 8.508$ (17), $b = 6.599$ (13), $c = 10.382$ (21) Å, $V = 582.9$ Å³, $Z = 4$, $D_x = 1.47$, $D_m = 1.44$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.7107$ Å; final $R = 5.1\%$. The molecule has a non-planar structure which explains the non-cyclization to 3-triazolo[3,4-*b*]thiadiazole.

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