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## Crystallographic Studies of High-Density Organic Compounds: 5-Fluoro-2,4,6-trinitro-1,3-benzenediamine

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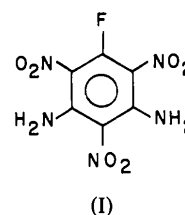
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**Abstract.** C<sub>6</sub>H<sub>4</sub>FN<sub>5</sub>O<sub>6</sub>, *M<sub>r</sub>* = 261.1, monoclinic, *Pc*, *a* = 7.5048 (4), *b* = 5.1195 (3), *c* = 11.7645 (6) Å, β = 99.625 (6)°, *D<sub>c</sub>* = 1.95 Mg m<sup>-3</sup> for *Z* = 2; Cu Kα (λ = 1.5418 Å) diffractometer data; 722 intensities; 713 *I*'s > 3σ above background; final *R* = 0.040. The effects of the amino and nitro substituents are exhibited by the benzene ring. The nitro groups flanking the F are rotated out of the ring plane by about the same amount, ca 20°, while the torsion angle for the third nitro is 3°. All of the H atoms are involved in strong intramolecular hydrogen bonds to adjacent nitro O atoms. Three of the four H atoms participate in weaker intermolecular hydrogen bonds which appear to control the crystal packing. On the basis of crystal-packing-coefficient calculations, it is concluded that the high crystal densities of this compound and of the analogous 3,5-diamino-2,4,6-trinitrophenol are due to efficient intermolecular packing arrangements which minimize free space in the unit cells.

**Introduction.** The densities of organic crystals containing only C, H, N, O or F atoms average to about 1.3 Mg m<sup>-3</sup>.<sup>\*</sup> The crystal densities of hydrocarbons are invariably smaller than the average, while the values for molecules containing several N, O or F atoms can be substantially larger. For example, the densities of

naphthalene (C<sub>10</sub>H<sub>8</sub>), glucose (α-D-glucopyranose, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) and hexanitrobenzene (C<sub>6</sub>N<sub>6</sub>O<sub>12</sub>) are 1.14, 1.56 and 1.99 Mg m<sup>-3</sup>, respectively. We are investigating the crystal structures of a number of high-density, polynitro-substituted organic molecules to understand better the relationships between molecular structure, crystal packing and density. The first structure reported (Bhattacharjee & Ammon, 1981) in the series, that of 3,5-diamino-2,4,6-trinitrophenol (DATNP), was characterized by a strong OH...O<sub>2</sub>N intramolecular interaction. Herein, we report the structure of a similar compound, *viz* 5-fluoro-2,4,6-trinitro-1,3-benzenediamine (I), which lacks the dominant OH of the phenol.



The compound, obtained from Dr H. Adolph, Naval Surface Weapons Center, White Oak, Maryland, crystallized as transparent yellow needles from acetonitrile. 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 measure-

<sup>\*</sup> Stine (1981) reported an average crystal density of 1.29 Mg m<sup>-3</sup> for 2051 C, H, N, O or F containing compounds selected from the Cambridge Crystallographic Files.

ments were made with a Picker FACS-I diffractometer and graphite-monochromated Cu radiation. A  $0.48 \times 0.22 \times 0.11$  mm crystal was mounted parallel to the long axis ( $b$ ) and aligned to place this direction along the instrument's  $\phi$  axis. The unit-cell parameters were determined by least squares from the  $2\theta$  values of 12 reflections manually centered at  $\pm 2\theta$  (average  $|2\theta_o - 2\theta_c| = 0.003^\circ$ ).

Intensities were measured by  $\theta$ - $2\theta$  scans with a scan rate of  $2^\circ \text{ min}^{-1}$  and 10 s backgrounds. The  $2\theta$  scan width was calculated from  $1.5^\circ + 0.29^\circ \tan \theta$ . Five standards were monitored every 100 reflections during data collection. 956 reflections were measured to a  $2\theta$  maximum of  $127^\circ$  giving 722 unique reflections. 713 were  $3\sigma$  above background. The *MULTAN* 80 system (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) was used for the structure solution revealing all atoms except one nitro group, which was subsequently located in a difference map. The structure was refined by the method of full-matrix least squares with anisotropic temperature factors for the C, N, O and F atoms. The four amino H atoms were not well behaved during refinement, and they were subsequently fixed at calculated positions in the plane of the benzene ring. Individual isotropic temperature factors were included for these atoms. 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 0.040 and 0.042 respectively. Atomic coordinates and thermal parameters are listed in Table 1.\* All calculations were made on a Univac 1108 computer at 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) is given in Fig. 1 and bond lengths and angles are listed in Table 2. The benzene ring is planar; the maximum deviation of a ring atom from the six-atom plane is  $0.017 \text{ \AA}$ . As in DATNP, the molecule exhibits the characteristics of both nitro- and amino-group substitution (Holden & Dickinson, 1977). Thus the average of the four benzene-ring bond lengths at amino-group substitutions is  $1.434 (9) \text{ \AA}$  and agrees with the value of  $1.433 (7) \text{ \AA}$  in DATNP. The average internal C—C—C angles at the benzene-ring atoms bearing the amino and nitro substituents are  $116.5 (6)$  and  $121.4 (6)^\circ$  respectively while in DATNP, these values are  $116.4 (4)$  and  $122.1 (4)^\circ$  respectively.

The N(3), N(1) and N(5) nitro groups are twisted by angles of  $3.4 (8)$ ,  $17.8 (8)$  and  $23.2 (8)^\circ$ , respectively, out of the benzene-ring plane, the last two angles being associated with the  $\text{NO}_2$ 's flanking the F. That the two sets of intramolecular  $\text{F} \cdots \text{NO}_2$  interactions are the same can be seen from these data, the associated bond lengths and angles, and the essentially equal  $\text{F} \cdots \text{O}$  distances. These latter contacts,  $2.45 \text{ \AA}$  average, are about  $0.3 \text{ \AA}$  less than the appropriate van der Waals

Table 1. Fractional coordinates and isotropic thermal factors ( $\text{\AA}^2$ )

An asterisk denotes  $U_{\text{eq}}$ , the equivalent value of the anisotropic temperature factor coefficients, calculated from the expression:  $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$ . 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)	0.4594 (9)	0.005 (1)	0.1812 (5)	0.03 (1)*
C(2)	0.3037 (9)	-0.039 (1)	0.1031 (6)	0.033 (8)*
C(3)	0.2969 (9)	-0.239 (1)	0.0163 (5)	0.03 (1)*
C(4)	0.4605 (9)	-0.387 (1)	0.0183 (5)	0.03 (1)*
C(5)	0.6227 (8)	-0.336 (1)	0.0969 (6)	0.03 (1)*
C(6)	0.6171 (8)	-0.133 (1)	0.1791 (6)	0.025 (5)*
F	0.4549	0.1785 (7)	0.2645	0.029 (2)*
N(1)	0.1439 (8)	0.120 (1)	0.1103 (5)	0.04 (1)*
N(2)	0.1507 (8)	-0.279 (1)	-0.0604 (5)	0.030 (4)*
N(3)	0.4563 (8)	-0.600 (1)	-0.0611 (5)	0.04 (1)*
N(4)	0.7742 (8)	-0.465 (1)	0.0948 (6)	0.04 (1)*
N(5)	0.7759 (9)	-0.066 (1)	0.2631 (5)	0.026 (8)*
O(1A)	0.1617 (8)	0.327 (1)	0.1639 (5)	0.04 (1)*
O(1B)	-0.0049 (8)	0.043 (1)	0.0619 (5)	0.04 (1)*
O(3A)	0.5950 (8)	-0.728 (1)	-0.0646 (5)	0.05 (1)*
O(3B)	0.3164 (7)	-0.6632 (9)	-0.1259 (5)	0.027 (9)*
O(5A)	0.7862 (8)	0.151 (1)	0.3059 (5)	0.023 (7)*
O(5B)	0.8955 (8)	-0.230 (1)	0.2890 (5)	0.041 (6)*
H(2A)	0.03 (1)	-0.18 (2)	-0.052 (8)	0.25 (3)
H(2B)	0.14 (2)	-0.43 (3)	-0.12 (1)	0.25 (7)
H(4A)	0.89 (2)	-0.42 (3)	0.16 (1)	0.25 (6)
H(4B)	0.78 (2)	-0.61 (2)	0.038 (9)	0.25 (5)

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36679 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

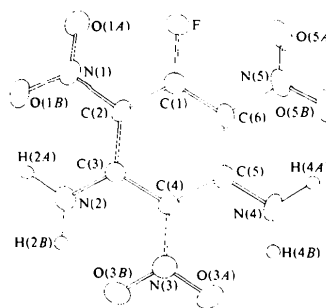
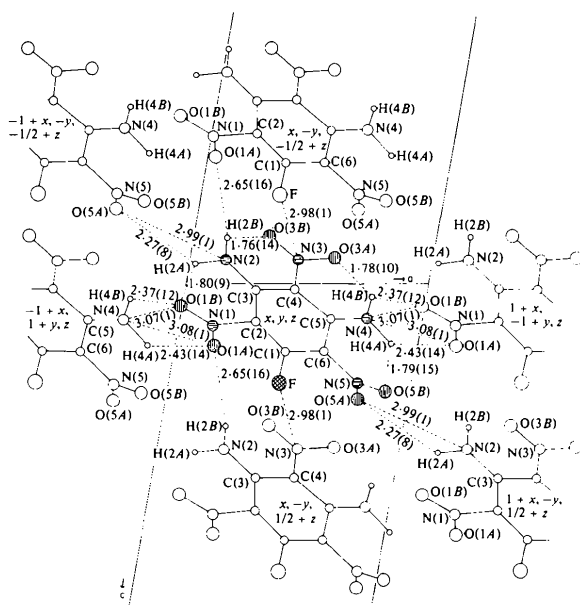


Fig. 1. An *ORTEP* drawing of (I) with the C, N, and O atoms depicted as 50% probability boundary ellipsoids. H atoms are shown as  $0.1 \text{ \AA}$  radius circles.

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

C(1)–C(2)	1.378 (9)	C(6)–N(5)	1.456 (8)
C(1)–C(6)	1.380 (9)	N(1)–O(1A)	1.230 (8)
C(1)–F	1.329 (7)	N(1)–O(1B)	1.229 (8)
C(2)–C(3)	1.441 (9)	N(3)–O(3A)	1.237 (9)
C(2)–N(1)	1.462 (9)	N(3)–O(3B)	1.233 (8)
C(3)–C(4)	1.442 (9)	N(5)–O(5A)	1.217 (8)
C(3)–N(2)	1.315 (8)	N(5)–O(5B)	1.228 (8)
C(4)–C(5)	1.425 (9)	N(2)–H(2A)	1.06 (9)
C(4)–N(3)	1.430 (9)	N(2)–H(2B)	1.0 (2)
C(5)–C(6)	1.426 (9)	N(4)–H(4A)	1.1 (1)
C(5)–N(4)	1.320 (9)	N(4)–H(4B)	1.0 (1)
C(6)–C(1)–C(2)	122.7 (6)	C(5)–C(6)–N(5)	121.2 (6)
C(1)–C(2)–C(3)	120.8 (6)	C(2)–N(1)–O(1A)	119.1 (5)
C(2)–C(3)–C(4)	115.7 (5)	C(2)–N(1)–O(1B)	119.2 (5)
C(3)–C(4)–C(5)	123.1 (6)	C(4)–N(3)–O(3A)	119.9 (6)
C(4)–C(5)–C(6)	117.2 (6)	C(4)–N(3)–O(3B)	121.8 (6)
C(5)–C(6)–C(1)	120.4 (5)	C(6)–N(5)–O(5A)	118.9 (6)
C(6)–C(1)–F	118.8 (5)	C(6)–N(5)–O(5B)	119.3 (6)
C(2)–C(1)–F	118.4 (6)	O(1A)–N(1)–O(1B)	121.7 (6)
C(1)–C(2)–N(1)	119.0 (6)	O(3A)–N(3)–O(3B)	118.3 (6)
C(3)–C(2)–N(1)	120.2 (5)	O(5A)–N(5)–O(5B)	121.9 (6)
C(2)–C(3)–N(2)	121.6 (6)	C(3)–N(2)–H(2A)	119 (5)
C(4)–C(3)–N(2)	122.6 (6)	C(3)–N(2)–H(2B)	121 (7)
C(3)–C(4)–N(3)	117.7 (5)	C(5)–N(4)–H(4A)	117 (8)
C(5)–C(4)–N(3)	119.2 (6)	C(5)–N(4)–H(4B)	121 (6)
C(4)–C(5)–N(4)	122.7 (6)	H(2A)–N(2)–H(2B)	120 (9)
C(6)–C(5)–N(4)	120.2 (6)	H(4A)–N(4)–H(4B)	121 (10)
C(1)–C(6)–N(5)	118.4 (6)		

Fig. 2. Intermolecular packing view down *b*, giving some contact distances (Å) and e.s.d.'s (in parentheses).

radii sum. In DATNP, the structural requirements of the intramolecular  $\text{OH}\cdots\text{O}_2\text{N}$  interaction produce  $\text{NO}_2$  torsion angles of  $5.6^\circ$  for the hydrogen-bond participant and  $52.5^\circ$  for the nonparticipant. For the three  $\text{NO}_2$  groups in DATNP, the C–N and N–O lengths, and C–N torsion and O–N–O angles show clearly the effects of varying degrees of conjugation

with the benzene ring. Similar trends are found between the N(3) nitro group and the F-flanking N(1) and N(5) substituents in (I).

A packing drawing is shown in Fig. 2. Each of the amine H atoms is involved in a strong intramolecular  $\text{H}\cdots\text{O}$  interaction with an adjacent nitro O atom; the range of the  $\text{H}\cdots\text{O}$  distances is 1.76–1.80 Å. The N(4) amino group forms a double intermolecular hydrogen bond to the N(1) nitro group in a nearby molecule. The  $\text{H}\cdots\text{O}$  distances are 2.37 (12) and 2.43 (14) Å, and the associated  $\text{N}\cdots\text{O}$  contacts are 3.07 (1) and 3.08 (1) Å. The N(2) amino group forms only a single contact with a nitro group:  $\text{H}(2\text{A})\cdots\text{O}(5\text{A}) = 2.27$  (8),  $\text{N}(2)\cdots\text{O}(5\text{A}) = 2.99$  Å. The fourth and remaining N–H does not appear to be involved in any significant intermolecular interactions. These  $\text{H}\cdots\text{O}$  intermolecular distances correspond to weak interactions, since the sum of the van der Waals radii of H and O is 2.4–2.6 Å.

The overall packing network is very similar to that observed in DATNP. Here there are three  $\text{H}\cdots\text{O}$  intermolecular contacts: the associated ( $\text{H}\cdots\text{O}$ ,  $\text{N}\cdots\text{O}$ ) distances are 2.30 (7) and 3.006 (7), 2.35 (6) and 2.945 (6), and 2.22 (7) and 2.995 (6) Å. The  $\text{NH}_2$  and  $\text{NO}_2$  groups involved in this last contact may be further associated by a weaker  $\text{N}–\text{H}\cdots\text{O}$  contact with parameters of 2.70 (7) and 3.100 (6) Å. The absence of any intermolecular contacts involving the OH group undoubtedly is an important factor in establishing the overall similarities with (I). When corrections are made for the different numbers of molecules per unit cell, the similarities also extend to the cell constants. The values of  $a = 7.5$ ,  $b = 5.1$ ,  $c = 11.8$  Å in (I) can be compared with  $b = 8.9$ ,  $a = 5.0$ ,  $c/2 = 10.3$  Å in DATNP. The angles of inclination of the benzene rings to the short axes are  $48^\circ$  in (I) and  $44^\circ$  in DATNP.

Packing calculations, based on the atomic radii listed by Kitaigorodsky (1973), have been carried out for 43 polynitro-organic compounds. The packing coefficients (PC = total molecular volume/unit-cell volume) range from 0.70 in  $[\text{FC}(\text{NO}_2)_2\text{CH}_2\text{C}(\text{=NH})_2]$  to 0.81 in 2,4,6-trinitro-1,3,5-benzenetriamine. The PC's of (I) and DATNP, 0.80 and 0.79 respectively, are near the top of the 0.70–0.81 range suggesting that the high crystal densities observed for these compounds are due to efficient intermolecular packing arrangements which limit the amount of free space in the unit cells.

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## Structure and Conformation of an Antidepressant Drug, Nitroxazepine Hydrochloride Monohydrate\*†

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**Abstract.**  $C_{18}H_{20}N_3O_4^+ \cdot Cl^- \cdot H_2O$ ,  $M_r = 395$ , orthorhombic,  $Pn2_1a$ ,  $a = 7.710$  (4),  $b = 11.455$  (3),  $c = 21.199$  (3) Å,  $Z = 4$ ,  $V = 1872.4$  Å<sup>3</sup>,  $D_m = 1.38$ ,  $D_c = 1.403$  g cm<sup>-3</sup>,  $F(000) = 832$ ,  $\mu(Cu K\alpha) = 20.94$  cm<sup>-1</sup>. Intensities for 1641 reflections were measured on a Nonius CAD-4 diffractometer; of these, 1470 were significant. The structure was solved by direct methods and refined to an  $R$  index of 0.045 using a block-diagonal least-squares procedure. The angle between the least-squares planes through the benzene rings is 125.0 (5)° and the side chain is folded similarly to one of the independent molecules of imipramine hydrochloride.

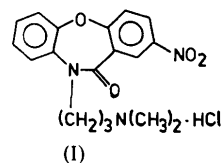
**Introduction.** Nitroxazepine, a dibenzoxazepine derivative, is an antidepressant (Nagarajan, Kulkarni & Venkateswarlu, 1968; Nagarajan, Venkateswarlu, Kulkarni, Nagana Goud & Shah, 1974; Nagarajan, David, Grewal & Govindachari, 1974; David & Grewal, 1974) belonging to the group containing imipramine, clomipramine, amitriptyline and doxepin (Maj, 1981).

\* IUPAC name: 10-(3-dimethylaminopropyl)-2-nitro-10,11-dihydrodibenz[*b,f*]oxazepin-11-one hydrochloride monohydrate. Registered name: Sintamil®.

† Contribution No. 626 from CIBA-GEIGY Research Centre.

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As the hydrochloride salt (Sintamil®) (I) has been found to be a safe and effective drug in the clinic (Nagarajan, David, Kaul, Maller, Rao & Grewal, 1975; Gupta & Marthak, 1981) with distinct advantages over imipramine (Gupta & Mankodi, 1972; Gordon, 1976; Kaiser, 1981). In attempts to relate the conformation of tricyclic antidepressants to their activity and their influence on the uptake of the biogenic amines norepinephrine and serotonin, the three-dimensional structure of (I) has been determined by X-ray studies and the results are presented here.



The space group and preliminary unit-cell parameters were determined from precession photographs. Systematic absences indicated that the space group could be either  $Pn2_1a$  or  $Pnma$ . The measured density indicated the presence of four water molecules in the unit cell. A crystal of dimensions 0.17 × 0.32 × 0.40 mm was used for data collection. A total of 1641