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Structure of *p,p'*-Dinitrobenzanilide*

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Abstract. $C_{13}H_9N_3O_5$, $M_r = 287{\cdot}2$, monoclinic, $P2_1/n$, $a = 6{\cdot}230\,(1)$, $b = 17{\cdot}922\,(4)$, $c = 11{\cdot}562\,(2)$ Å, $\beta = 105{\cdot}50\,(1)°$, $V = 1244{\cdot}0\,(4)$ Å^3, $Z = 4$, $D_m = 1{\cdot}53\,(2)$, $D_x = 1{\cdot}537$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 9{\cdot}24$ cm^{-1}, $T = 293$ K, $F(000) = 592$, $R = 0{\cdot}062$, $wR = 0{\cdot}064$ for 1004 reflections with $I \geq 3\sigma(I)$. The amide plane makes an angle of 16·4 (4) and 17·5 (4)° respectively with the two benzene rings. The benzene rings are at 3·0 (1)° with respect to each other.

Introduction. Aromatic polyamides form a class of polymers which have high thermal and mechanical stability compared with other classes of polyamides. Hence they are used in the manufacture of fibres (Northolt & Van Aartsen, 1973). The title compound was of interest as a monomer of one such polymer.

Experimental. Yellow needle-shaped single crystals by evaporation of dimethyl acetate, D_m by flotation, 0·22 × 0·50 × 0·55 mm, three-dimensional intensity data using Enraf–Nonius CAD-4 four-circle automated diffractometer, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, cell parameters refined with 24 reflections in the range $22 \leq 2\theta \leq 90°$. 2026 unique reflections collected with $0 \leq h \leq 7$; $0 \leq k \leq 21$; $-13 \leq l \leq 13$ in the range $4 \leq 2\theta \leq 130°$ in $\omega/2\theta$ scan mode, two standard reflections (132, $1\bar{3}5$) checked periodically showed no variation in intensity. 1004 reflections with $I \geq 3\sigma(I)$ were considered as observed. The data were corrected for Lorentz and polarization effects but not for absorption. A default run (no random group input; automatic origin fixing) of *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) gave the structure. Least-squares refinement was carried out using *SHELX*76 (Sheldrick, 1976). Hydrogens from difference Fourier map. The non-hydrogens refined anisotropically. Hydrogens not refined but included in structure-factor calculations with assigned temperature factors of the non-hydrogen atoms to which they are attached. Final $R = 0{\cdot}062$ and $wR = 0{\cdot}064$, individual weighting scheme based on counting statistics, $w = 0{\cdot}0627/[\sigma^2(F_o) + 0{\cdot}0007F_o^2]$, final $(\mathrm{shift/e.s.d.})_{\max} = 0{\cdot}533$ and $(\mathrm{shift/e.s.d.})_{\mathrm{ave}} = 0{\cdot}116$, goodness of fit $S = 1{\cdot}40$ for 190 parameters. The final difference Fourier map had no peaks $\geq 0{\cdot}6$ e Å^{-3}. The scattering factors are as in *International Tables for X-ray Crystallography* (1974).

Discussion. Table 1 gives the fractional coordinates with the equivalent isotropic temperature factors for non-hydrogen atoms. The average e.s.d.'s in bond lengths and bond angles involving non-hydrogen atoms are 0·009 Å and 0·4° respectively. The bond lengths and bond angles for non-hydrogen atoms are shown in Figs. 1 and 2 respectively. The bond lengths and angles of the benzamide group agree with those reported in the literature.‡

There is an interaction between O3 and HC9 [HC9···O3 2·248 (5) Å] and between O3 and HC3 [HC3···O3 2·428 (5) Å], both less than the sum of the van der Waals radii of oxygen and hydrogen, 2·62 Å (Nyburg & Faerman, 1985; Srinivasan, Meena Hariharan & Vijayalakshmi, 1987). This is reflected in the angles C5—C4—C7, 126·7 (5), C3—C4—C7, 114·1 (5), C9—C8—N2, 125·7 (4), C13—C8—N2, 114·5 (4), N2—C7—O3, 125·0 (5) and N2—C7—C4, 114·1 (5)°.

The widening of the angles in the two nitro groups, O1—N1—O2 and O4—N3—O5, 123·4 (4) and 123·6 (4)°, indicates lone-pair interactions between the oxygens. The small torsion angles of C2—C1—N1—O1, −2·0 (8), and C10—C11—N3—O4, −4·3 (8)°, show that the nitro groups are nearly coplanar with the benzene rings to which they are attached. The small torsion angles also show enhanced C—N π-bond character and therefore increased negative charge on the O atoms of the nitro groups. Similar widening of the angle in the nitro groups is found in 2,4-dinitro-5-ethyleneiminobenzamide (Iball, Scrimgeour & Williams, 1975) and 3,5-diamino-2,4,6-dinitrobenzamide (Ammon & Bhattacharjee, 1982).

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‡ Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52301 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional parameters and equivalent isotropic temperature factors of non-hydrogen atoms with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}(Å^2)
C1	0·3515 (9)	0·0796 (3)	0·9178 (5)	0·039 (2)
C2	0·5390 (9)	0·1072 (3)	0·8918 (5)	0·048 (2)
C3	0·6210 (10)	0·0713 (4)	0·8088 (6)	0·052 (3)
C4	0·5253 (10)	0·0097 (4)	0·7520 (5)	0·051 (2)
C5	0·3389 (11)	−0·0183 (3)	0·7779 (5)	0·058 (2)
C6	0·2464 (10)	0·0171 (4)	0·8614 (5)	0·052 (2)
C7	0·6409 (12)	−0·0214 (4)	0·6561 (6)	0·063 (3)
C8	0·6590 (9)	−0·1272 (3)	0·5284 (5)	0·048 (2)
C9	0·8425 (9)	−0·1070 (3)	0·4898 (5)	0·050 (3)
C10	0·8952 (9)	−0·1476 (3)	0·4001 (5)	0·050 (2)
C11	0·7670 (10)	−0·2064 (3)	0·3517 (5)	0·043 (2)
C12	0·5860 (10)	−0·2281 (3)	0·3896 (5)	0·054 (3)
C13	0·5324 (10)	−0·1876 (3)	0·4776 (6)	0·054 (2)
N1	0·2608 (8)	0·1173 (3)	1·0070 (4)	0·048 (2)
N2	0·5836 (9)	−0·0904 (3)	0·6213 (5)	0·068 (2)
N3	0·8292 (10)	−0·2470 (3)	0·2535 (5)	0·060 (2)
O1	0·3611 (8)	0·1715 (3)	1·0578 (4)	0·081 (2)
O2	0·0942 (8)	0·0931 (3)	1·0274 (4)	0·076 (2)
O3	0·7692 (8)	0·0159 (2)	0·6212 (4)	0·071 (2)
O4	0·9829 (10)	−0·2228 (3)	0·2169 (4)	0·083 (2)
O5	0·7256 (10)	−0·3023 (3)	0·2145 (5)	0·085 (2)

The amide plane is at an angle of 16·4 (4) and 17·5 (4)° respectively with the two benzene rings 1 and 2. The two benzene rings are at 3·0 (1)° with respect to each other. Angles between the benzene ring and amide plane ranging from planarity to 65° have been observed in the literature depending on the substituents attached to the benzene ring. The values in the present compound, 16·4 (4) and 17·5 (4)°, compare with those in procainamide hydrochloride (Peeters, Blaton, De Ranter, Denisoff & Molle, 1980), 17·6°, in *p*-chlorobenzamide (Taniguchi, Nakata, Takaki & Sakurai, 1978), 17·9°, and in *N,N'*-ethylenedibenzamide (Palmer & Brisse, 1980), 19·0°. The angle between the amide plane and benzene may depend on the strength of the intermolecular forces and the steric repulsion between the *ortho* hydrogen and the imino hydrogen and the amide oxygen (Penfold & White, 1959). The predominance of one factor over the other may decide the angle between the amide plane and the benzene ring.

C—H···O-type intermolecular hydrogen bonds link centrosymmetrical molecules forming dimers about the centres of inversion. C5 is linked by a hydrogen bond to O5 at the symmetry position $-\frac{1}{2} + x$, $-\frac{1}{2} - y$, $\frac{1}{2} + z$ with C5···O5 3·331 (9), HC5···O5 2·493, C5—HC5 0·925 Å and angle C5—HC5···O5 150·8°; and C10 is linked by a hydrogen bond to O3 at the symmetry position $2 - x$, $-y$, $1 - z$ with C10···O3 3·205 (7), HC10···O3 2·499, C10—HC10 0·889 Å and angle C10—HC10···O3 137·0°. The packing of the molecules in the unit cell down the *a* axis is shown in Fig. 3.

There is also an N—H···O type of interaction between N2 and O5 ($-\frac{1}{2} + x$, $-\frac{1}{2} - y$, $\frac{1}{2} + z$) with N2···O5 3·335 (9), HN2···O5 2·335, N2—HN2 1·14 Å and angle N2—HN2···O5 145°. However the geometry is not such as to allow one to call it unequivocally a hydrogen bond. It may be noted that N—H···O hydrogen bonds are a common feature of benzamide crystal structures.

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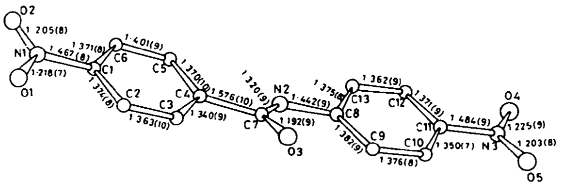

Fig. 1. Bond lengths (Å) involving non-hydrogen atoms.

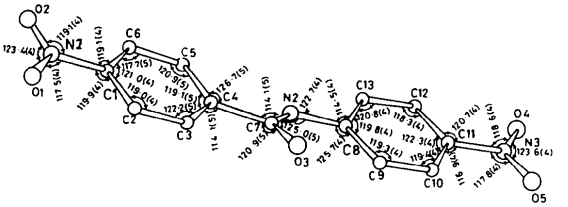

Fig. 2. Bond angles (°) involving non-hydrogen atoms.

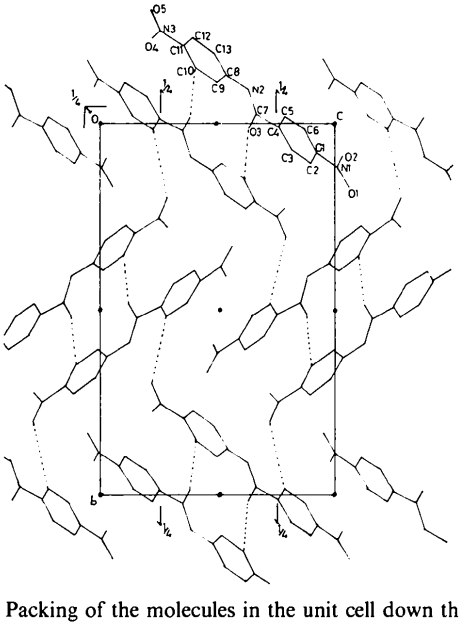

Fig. 3. Packing of the molecules in the unit cell down the *a* axis.

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Structure of Diethyl 2,3-*O*-Fluorenylidene-L-tartrate

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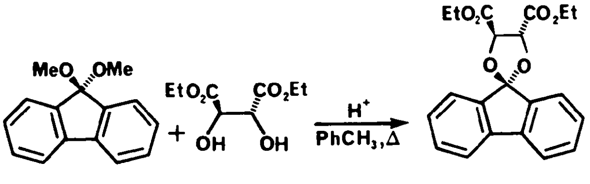
Abstract. $C_{21}H_{20}O_6$, $M_r = 368{\cdot}39$, orthorhombic, $P2_12_12_1$, $a = 11{\cdot}669\ (2)$, $b = 14{\cdot}975\ (2)$, $c = 10{\cdot}663\ (2)$ Å, $V = 1863\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}31$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}90$ cm^{-1}, $F(000) = 7768$, $T = 203$ K, $R = 0{\cdot}064$ for 1233 unique data with $I > 2\sigma(I)$. The molecular structure is very close to having idealized twofold geometry with the two substituents on the acetal carbon displaced 1·06 and 1·28 Å with respect to the dioxolane ring and the two ethoxycarbonyl groups on the 4 and 5 positions in equatorial positions; the torsional angle about the backbone is 87·4 (6)°.

Introduction. We have synthesized a homochiral dioxolane derived from fluorenone dimethylacetal and diethyl tartrate as part of a program in chiral organometallic reagents. The structure of the dioxolane, reported here, contains several remarkable features important for the study and possible application of homochiral dioxolanes in stereoselective synthesis.



Experimental. The acid-catalyzed reaction of diethyl-L-tartrate with fluorenone dimethylacetal in refluxing toluene gives the title compound. It is isolated as white prisms after purification by column chromatography and recrystallization from acetone/pentane. A colorless block approximately 0·20 × 0·40 × 0·40 mm in size was used for data collection in a thermostated nitrogen cold stream on a Rigaku AFC-6S diffractometer (Mo $K\alpha$ radiation, graphite monochromator, 203 K) using ω–2θ scans with a variable scan width where $\Delta\omega = (1{\cdot}05 + 0{\cdot}30\tan\theta)°$ and a scan rate of 2·0° min^{-1} in ω. Lattice parameters were determined from 25 reflections in the range $25{\cdot}0 < 2\theta < 28{\cdot}1°$. Weak reflections with $I < 10{\cdot}0\sigma(I)$ were rescanned a maximum of three times and counts accumulated. Stationary background counts were recorded at each side of the reflections; the ratio of peak:background counting time was 2:1. Three intensity standards were monitored every 200 reflections; no appreciable decay occurred. The crystal system was confirmed by a check of equivalent reflections and the space group determination was obtained from an analysis (Calabrese, 1972) of systematically absent reflections ($h00$: $h = 2n + 1$; $0k0$: $k = 2n + 1$; $00l$: $l = 2n + 1$) and Laue symmetry. A total of 8499 reflections, to a maximum 2θ of 55·1°, were collected in the range $-12 \le h \le 12$, $-15 \le k \le 15$, $-11 \le l \le 11$. Of 2472 unique reflections ($R_{\rm int} = 0{\cdot}060$), 1233 had $I > 2\sigma(I)$ and were used in the structure solution and refinement. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985). H atoms were included in calculated positions with isotropic thermal parameters at 120% of $B_{\rm eq}$ of the neighboring C atom. Full-matrix least-squares refinement of the structure, using the

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