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The Crystal Structure of and Twinning in *γ-o*-Nitroaniline*

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Crystals of *γ-o*-nitroaniline, $C_6H_6N_2O_2$, are monoclinic, space group $P2_1/a$ with $a = 15{\cdot}45$ (2), $b = 10{\cdot}01$ (2), $c = 8{\cdot}57$ (1) Å; $\beta = 107{\cdot}4$ (2)°; $\rho_o = 1{\cdot}446$ g cm^{-3}, ρ_c for $Z = 8$, $1{\cdot}451$ g cm^{-3}. The structure was solved by direct methods with the help of 647 reflexions. The asymmetric unit in the structure consists of two crystallographically independent molecules *A* and *B* which are related approximately by a pseudo twofold axis normal to the (100) plane and passing through the point $(0,\frac{1}{4},-\frac{1}{4})$. The presence of the pseudo axis explains the occurrence of twinning in the crystals as well as the presence of diffuse streaks in some of the Weissenberg photographs.

Introduction

The twinning in *γ-o*-nitroaniline is described by Herbstein (1965); he also gives detailed references of earlier work on this structure. *γ-o*-Nitroaniline crystals are monoclinic; however, the crystals are usually polysynthetically twinned and show pseudo-orthorhombic symmetry. Single untwinned crystals of *γ-o*-nitroaniline were grown from bromobenzene in this laboratory and, in the present paper, the structure of this compound is reported and the probable method of twinning is described on the basis of the crystal structure. The proposed method of twinning explains the diffuse streaks observed by Herbstein (1965) in the Weissenberg photographs of the twinned crystal.

Experimental

The crystals grown from a solution in bromobenzene in the course of a couple of months were untwinned, monoclinic, with $a = 15{\cdot}45$ (2), $b = 10{\cdot}01$ (2), $c = 8{\cdot}57$ (1) Å; $\beta = 107{\cdot}4$ (2)°; space group, $P2_1/a$; $\rho_o = 1{\cdot}446$ g cm^{-3}; ρ_c (for $Z = 8$) $= 1{\cdot}451$ g cm^{-3}. The values of *a* and *β* differ substantially from those obtained by Herbstein (1965) from measurements on twinned crystals. The crystal data reported by him are: $a = 15{\cdot}28$ (3), $b = 10{\cdot}00$ (5), $c = 8{\cdot}54$ (3) Å; $\beta = 105{\cdot}5$ (1·0)°; $\rho_o = 1{\cdot}44$ g cm^{-3}, $\rho_c = 1{\cdot}46$ g cm^{-3}; the crystals were twinned on the (100) plane.

Data were collected with unfiltered Cu radiation from the zero to seventh layer Weissenberg photographs about the *c* axis; 647 reflexions were observed.

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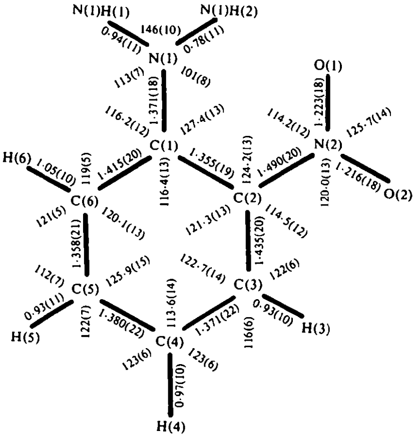
Determination of the structure

The structure was determined by direct methods using Long's (1965) program, and refined by the full-matrix least-squares method using program *LALS* of Gantzel, Sparks & Trueblood (1961), and Cruickshank's weighting scheme. Hydrogen atoms of the aromatic ring were placed at the expected positions and those of the NH_2 groups were obtained from a three-dimensional difference Fourier map. The final R is 10·9%; the atomic parameters along with their e.s.d.'s are given in Table 1, and intramolecular bond lengths and angles in Fig. 1.

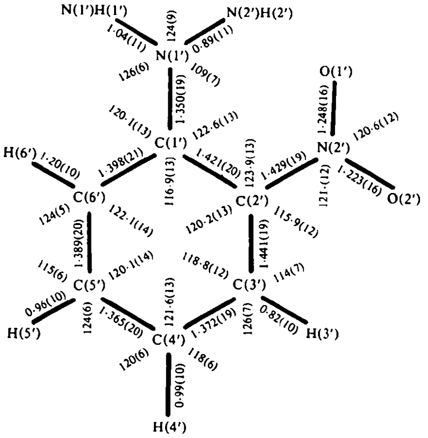
Description of the structure and discussion

Molecular structure

The asymmetric unit consists of two crystallographically independent molecules *A* and *B* of *o*-nitroaniline. In view of the rather large e.s.d.'s, the differences in the molecular dimensions of *A* and *B* are unlikely to be significant; the mean molecular dimensions are normal. In both *A* and *B*, the N of the amino group is hydrogen bonded to an O of the nitro group (NH···O distance, 2·64 and 2·67 Å in *A* and *B* respectively, and ∠N—H···O, nearly 150° in both molecules). The nitro group is known to undergo large librations, but in *o*-nitroaniline the librations are small presumably because of hydrogen bonding with the neighbouring amino group.



Molecule *A*



Molecule *B*

Fig. 1. Bond lengths (Å) and angles (°) with e.s.d.'s (in parentheses).

Crystal structure and twinning

The crystal structure is shown in (010) projection in Fig. 2. The crystallographically independent molecules *A* and *B* are related approximately by a non-crystallographic twofold axis normal to the (100) plane and passing through the point $(0,\frac{1}{4},-\frac{1}{4})$ (shown in Fig. 2). Thus if the structure above the twin plane in Fig. 2 is rotated about the pseudo twofold axis by 180°, the intermolecular contacts near the (100) plane remain

Table 1. *Final atomic parameters and their estimated standard deviations (in parentheses)*

	x	*y*	*z*
(*a*) Non-hydrogen atoms ($\times 10^4$)			
C(1)	682 (9)	2965 (14)	−4359 (15)
C(2)	1045 (9)	1952 (14)	−5006 (16)
C(3)	2009 (11)	1789 (14)	−4621 (16)
C(4)	2615 (10)	2664 (16)	−3640 (17)
C(5)	2209 (10)	3687 (17)	−3035 (17)
C(6)	1303 (10)	3852 (15)	−3309 (15)
N(1)	−219 (8)	3213 (13)	−4577 (14)
N(2)	502 (10)	936 (14)	−6160 (15)
O(1)	−318 (8)	1039 (11)	−6419 (11)
O(2)	883 (7)	70 (12)	−6703 (12)
C(1′)	874 (11)	2083 (14)	−3 (15)
C(2′)	1242 (10)	3124 (14)	1128 (14)
C(3′)	2210 (9)	3306 (14)	1748 (14)
C(4′)	2764 (9)	2468 (14)	1213 (16)
C(5′)	2421 (10)	1449 (15)	149 (17)
C(6′)	1491 (10)	1235 (14)	−413 (14)
N(1′)	−23 (8)	1817 (12)	−544 (12)
N(2′)	705 (9)	4042 (12)	1719 (13)
O(1′)	−135 (7)	3889 (10)	1273 (12)
O(2′)	1054 (6)	4978 (10)	2600 (12)
(*b*) Hydrogen atoms ($\times 10^3$)			
H(3)	226 (7)	108 (10)	−503 (11)
H(4)	326 (6)	260 (11)	−344 (11)
H(5)	254 (6)	432 (12)	−232 (12)
H(6)	105 (6)	462 (10)	−273 (10)
N(1)H(1)	−33 (6)	407 (12)	−424 (12)
N(1)H(2)	−43 (6)	255 (12)	−497 (11)
H(3′)	237 (6)	399 (10)	229 (10)
H(4′)	342 (6)	269 (10)	151 (10)
H(5′)	278 (6)	75 (11)	−11 (11)
H(6′)	114 (7)	31 (10)	−127 (11)
N(1′)H(1′)	−32 (7)	94 (12)	−110 (12)
H(1′)H(2′)	−33 (7)	255 (12)	−47 (11)

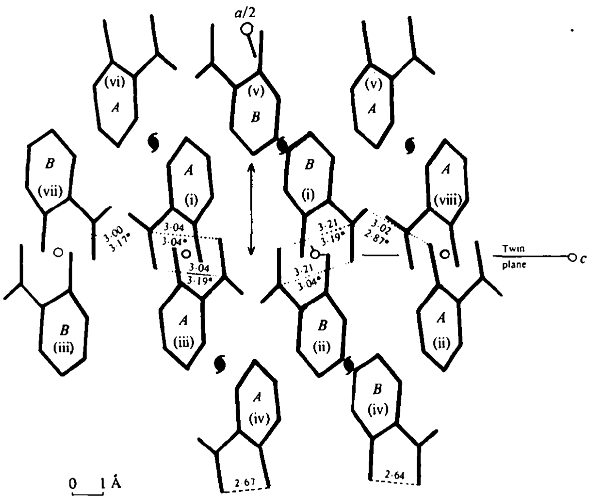


Fig. 2. Structure projected on (010). Symmetry code: (i) x,y,z; (ii) $\bar{x},\bar{y},\bar{z}$; (iii) $\bar{x}, \bar{y}, -1-z$; (iv) $x-\frac{1}{2}, \frac{1}{2}-y, z$; (v) $\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}$; (vi) $\frac{1}{2}-x, \frac{1}{2}+y, -1-z$; (vii) $x, y, z-1$; (viii) $x, y, z+1$. An asterisk indicates an intermolecular contact after rotation about the pseudo twofold axis.

unaffected to a good approximation. Some of the intermolecular contacts near the twin plane before and after rotation are shown in the figure. The similarity of the contacts probably explains why the crystal is twinned so easily on the (100) plane.

It is reported by Herbstein (1965) that the reflexions on the *hk*0 Weissenberg photographs of γ-*o*-nitroaniline crystals are sharp, but those on the *hk*1 photographs are joined by weak diffuse streaks running parallel to *a**. It seems that the individual untwinned regions in the crystal are in general thick enough to give sharp reflexions in the X-ray photographs. However, there are also regions in the crystal where twinning occurs after only a few molecular layers; these regions lead to continuous diffuse streaks. The absence of diffuse streaks in the *hk*0 Weissenberg photographs can be explained as follows.

The parameters of equivalent positions in the (001) projection in space group $P2_1/a$ are: x,y; $\frac{1}{2}+x, \frac{1}{2}-y$; $\frac{1}{2}-x, \frac{1}{2}+y$; $\bar{x},\bar{y}$. On applying the twin operation of rotation about the pseudo twofold axis, the parameters become: $x, \frac{1}{2}-y$; $\frac{1}{2}+x, y$; $\frac{1}{2}-x, \bar{y}$; $\bar{x}, \frac{1}{2}+y$. It can be seen that the twin operation alters the x parameters of the first set of points by half; thus corresponding to the point x,y in the first set, there is a point $\frac{1}{2}+x, y$ in the second set and so on. This implies that the structure factors $F(hk0)$ with h even will remain unaffected by twinning and will continue to be sharp. In principle, $F(hk0)$ with h odd should show diffuse streaks; however, these diffuse streaks are imperceptible because $F(hk0)$ with h odd are very weak due to the near cancellation of scattering from molecules *A* and *B*. This is apparent in the structure factor tables.*

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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 33492 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Crystal Structure of 5-Benzoyloxyoctaethylporphyrin

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5-Benzoyloxyoctaethylporphyrin, $C_{43}H_{50}N_4O_2$, monoclinic, $P2_1/c$, $a = 15{\cdot}105\ (1)$, $b = 20{\cdot}729\ (2)$, $c = 12{\cdot}721\ (1)$ Å, $\beta = 112{\cdot}05\ (2)^\circ$, $D_m = 1{\cdot}18$, $D_c = 1{\cdot}177$ g cm^{-3} for $Z = 4$. The structure was solved by direct methods, and refined to $R = 0{\cdot}0474$, $R_w = 0{\cdot}0510$ for 4076 reflections measured on an automatic diffractometer. The central porphyrin system is distinctly non-planar, and adopts a shallow saucer shape. A 'half-hydrogen' atom has been located attached to each central nitrogen atom; however, it is not clear whether these are truly representative of N—H tautomerism, or are crystallographic artifacts.