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# Structural Studies of the System *trans*-Azobenzene/*trans*-Stilbene. I. A Reinvestigation of the Disorder in the Crystal Structure of *trans*-Azobenzene, $C_{12}H_{10}N_2$

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**Abstract.** $M_r = 182·22$, monoclinic, $P2_1/c$, $a = 15·219\ (4)$, $b = 5·7855\ (8)$, $c = 12·177\ (4)$ Å, $\beta = 112·42\ (2)°$, $V = 991·1\ (4)$ Å$^3$, $Z = 4$, $D_x = 1·189\ (1)$ Mg m$^{-3}$, $\lambda(\text{Mo}\ K\alpha) = 0·7107$ Å, $\mu = 0·41$ mm$^{-1}$, $F(000) = 384$, room temperature. A model in which disorder at one of the two crystallographically independent molecule sites was taken into account refined, using constraints and restraints, with 2121 diffractometer data to an $R$ of 0·061 ($R_w = 0·075$). The degree of misorientation is 17%. The molecules at the disordered site are approximately related to one another by 180° rotation around their longest axes.

**Introduction.** Several years ago Brown (1966*a*) reported the crystal structure of *trans*-azobenzene. Differences in thermal parameters and geometries between the two crystallographically independent molecules led him to suggest configurational disorder at one of the independent sites. A similar kind of disorder has been ascribed to the related structures of *p*-azotoluene (Brown, 1966*b*), *trans*-stilbene (Finder, Newton & Allinger, 1974; Hoekstra, Meertens & Vos, 1975; Bernstein, 1975; Bernstein & Mirsky, 1978) and dimethylstilbene (Valle, Busetti & Galiazzo, 1981).

The reinvestigation of *trans*-azobenzene was undertaken as part of a project designed to prepare and to carry out thermodynamical and structural studies on mixed crystals. The zone-levelling technique (Kolkert, 1974) was used for the preparation of homogeneous crystalline material and recently we succeeded in obtaining mixed single crystals of azobenzene and stilbene. Before undertaking the structure determination of a mixed crystal we decided to have a closer look at the mode of disorder of the title compound.

**Experimental.** Red, block-shaped crystals, 0·3 × 0·3 × 0·3 mm (m.p. 341·0 K), obtained by slow vacuum sublimation; sealed in capillary glass tube to avoid sublimation. Enraf–Nonius CAD-4 diffractometer, Zr-filtered Mo $K\alpha$ radiation. Room-temperature lattice parameters refined by fitting to $\theta$, $\varphi$, $\omega$ and $\kappa$ settings of 24 reflections. Corresponding cell dimensions by Brown (1966*a*) after transformation by (101/010/$\bar{1}$00): $a = 15·230$, $b = 5·756$, $c = 12·144$ Å, $\beta = 112·64°$; 3190 unique reflections ($2\theta \leq 70°$, $hkl$ range: $h$ −24–19, $k$ 0–9, $l$ 0–19), 2121 with $I > 2·5\sigma(I)$ subsequently used; $\omega$–$2\theta$ scan mode, one reflection monitored periodically (change in intensity < 3%), absorption ignored. Structure solved by *MULTAN* (Germain, Main & Woolfson, 1971), to give essentially the same structural parameters as published by Brown (1966*a*),

Both independent molecules (referred to as $A$ and $B1$) at sites $A$ and $B$ respectively have $\bar{1}$ symmetry. $\Delta\rho$ map clearly revealed four C atoms and the N atom belonging to a misoriented molecule (referred to as $B2$) at site $B$. *SHELX* (Sheldrick, 1976) was then enlisted in the structure determination. The four C and the two additional atoms were fitted to a regular hexagon.

Full-matrix refinement on $F$. H atoms introduced only for molecules $A$ and $B1$ and placed 1·0 Å from their carrier atoms, assuming $sp^2$ hybridization; positions adjusted according to the riding model. The benzene rings of molecules $B1$ and $B2$ were refined as rigid groups. Slack constraints (Waser, 1963) were simultaneously applied to some *exo*-ring distances, which were restrained to the values found in molecule $A$ (for restraints and geometry after constrained refinement see Table 2). The occupancy ratio at site $B$ was initially set at 0·85:0·15. [Lattice-energy calculations by Bernstein & Mirsky (1978) resulted in 20% as an upper bound for the degree of misorientation in the related structure of *trans*-stilbene.] Isotropic refinement reduced $R$ from 0·28 to 0·13. The atoms of molecule $B2$ were assigned an overall isotropic temperature factor, the remaining non-hydrogen atoms were refined anisotropically; for H atoms, only isotropic thermal parameters were varied.

To prevent correlation effects during anisotropic refinement, the population parameters were held at their attained values of 0·83 (1) and 0·17 (1) respectively. $w = 1/[\sigma^2(F) + 0·00477F^2]$. Final $R = 0·061$ ($R_w = 0·075$, $S = 0·3$). This $R$ has to be compared with a value of 0·075, using our intensities and Brown's model. The introduction of the disordered model must therefore be considered a significant improvement.

Difference synthesis essentially featureless with $|\Delta\rho| \leq 0·3$ e Å$^{-3}$; $(\Delta/\sigma)_{\text{ave}} = 0·26$, $(\Delta/\sigma)_{\text{max}} = 1·36$, scattering factors for N and C from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965).

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Table 1. *Positional* (×10⁴) *and thermal parameters* (×10⁴) *with their e.s.d.'s in parentheses*

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

| | $x$ | $y$ | $z$ | $U_{\mathrm{eq}}$ | $U_{\mathrm{eq}}$ (Brown, 1966*a*) |
|---|---|---|---|---|---|
| Molecule *A* | | | | | |
| N(1) | 4885 (1) | 1024 (2) | 5034 (1) | 418 (4) | 478 |
| C(2) | 4327 (1) | 1344 (2) | 5736 (1) | 375 (4) | 441 |
| C(3) | 3857 (1) | 3446 (3) | 5590 (2) | 475 (4) | 559 |
| C(4) | 3292 (1) | 3899 (3) | 6226 (2) | 537 (6) | 560 |
| C(5) | 3215 (1) | 2294 (3) | 7025 (2) | 534 (5) | 599 |
| C(6) | 3711 (1) | 219 (3) | 7192 (2) | 490 (5) | 560 |
| C(7) | 4262 (1) | −276 (3) | 6543 (1) | 412 (4) | 494 |
| Molecule *B*1 | | | | | |
| N(8) | 9697 (1) | 761 (2) | 9777 (1) | 521 (5) | 742 |
| C(9) | 9202 (1) | 538 (3) | 8522 (1) | 473 (6) | 620 |
| C(10) | 9293 (1) | −1333 (3) | 7851 (1) | 541 (7) | 627 |
| C(11) | 8774 (1) | −1385 (3) | 6627 (1) | 605 (8) | 739 |
| C(12) | 8164 (1) | 434 (3) | 6075 (1) | 582 (9) | 723 |
| C(13) | 8072 (1) | 2305 (3) | 6747 (1) | 632 (9) | 723 |
| C(14) | 8591 (1) | 2357 (3) | 7970 (1) | 584 (7) | 711 |
| Molecule *B*2 | | | | | |
| N(15) | 9928 (6) | −768 (6) | 9615 (2) | 562 (10) | |
| C(16) | 9278 (6) | −108 (12) | 8462 (2) | 562 (10) | |
| C(17) | 9192 (6) | −1633 (12) | 7539 (2) | 562 (10) | |
| C(18) | 8615 (6) | −1065 (12) | 6373 (2) | 562 (10) | |
| C(19) | 8124 (6) | 1030 (12) | 6129 (2) | 562 (10) | |
| C(20) | 8208 (6) | 2554 (12) | 7051 (2) | 562 (10) | |
| C(21) | 8785 (6) | 1985 (12) | 8218 (2) | 562 (10) | |

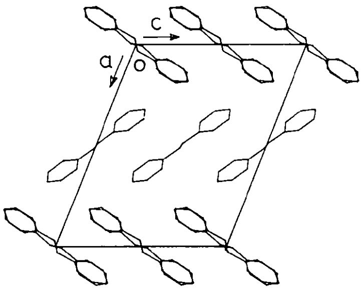

Fig. 1. Projection of the structure along **b**, showing the disorder at site *B*.

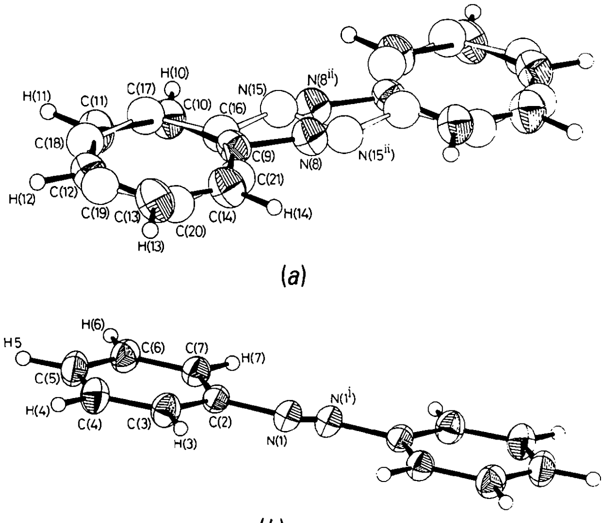

Fig. 2. (*a*) A composite view of the disordered molecules at site *B* with 50% probability plots for thermal ellipsoids of molecule *B*1. (*b*) View of the molecule at site *A* with 50% probability plots for thermal ellipsoids.

Table 2. *Bond distances* (Å) *and bond angles* (°) *in azobenzene with occasional restraints imposed during the refinement*

In the third column, values found by Brown (1966*a*) are given. Roman numerals indicate symmetry-related units according to the following code: (i) 1−*x*, −*y*, 1−*z*; (ii) 2−*x*, −*y*, 2−*z*.

| | Present work | Brown (1966*a*)* |
|---|---|---|
| Molecule *A* | | |
| N(1)–N(1$^{\mathrm{i}}$) | 1·247 (2) | 1·243 |
| N(1)–C(2) | 1·428 (2) | 1·433 |
| C(2)–C(7) | 1·389 (2) | 1·385 |
| C(2)–C(3) | 1·387 (2) | 1·384 |
| C(3)–C(4) | 1·384 (3) | 1·390 |
| C(4)–C(5) | 1·382 (3) | 1·368 |
| C(5)–C(6) | 1·391 (2) | 1·389 |
| C(6)–C(7) | 1·384 (3) | 1·379 |
| | | |
| N(1$^{\mathrm{i}}$)–N(1)–C(2) | 114·1 (1) | 113·6 |
| N(1)–C(2)–C(3) | 115·6 (1) | 115·5 |
| N(1)–C(2)–C(7) | 123·7 (1) | 124·1 |
| C(3)–C(2)–C(7) | 120·7 (1) | 120·3 |
| C(2)–C(3)–C(4) | 119·6 (2) | 119·4 |
| C(3)–C(4)–C(5) | 120·3 (2) | 120·4 |
| C(4)–C(5)–C(6) | 119·7 (2) | 119·9 |
| C(5)–C(6)–C(7) | 120·5 (2) | 120·3 |
| C(2)–C(7)–C(6) | 119·1 (1) | 119·6 |
| Molecules *B*1 and *B*2† | | |
| N(8)–N(8$^{\mathrm{ii}}$) | 1·240 (2) | 1·172 |
| N(15)–N(15$^{\mathrm{ii}}$) | 1·249 (6) | |
| Restraint | 1·246 | |
| | | |
| N(8)–C(9) | 1·429 (2) | 1·472 |
| N(15)–C(16) | 1·427 (9) | |
| Restraint | 1·429 | |
| | | |
| N(8$^{\mathrm{ii}}$)–N(8)–C(9) | 113·9 (1) | 111·1 |
| N(15$^{\mathrm{ii}}$)–N(15)–C(16) | 113·9 (5) | |
| Restraint | 114·0 | |
| | | |
| N(8)–C(9)–C(14) | 115·5 (1) | 112·7 |
| N(15)–C(16)–C(17) | 116·1 (6) | |
| Restraint | 115·6 | |
| | | |
| N(8)–C(9)–C(10) | 124·5 (1) | 127·0 |
| N(15)–C(16)–C(21) | 123·8 (5) | |
| Restraint | 124·4 | |

* Mean e.s.d.'s for bond lengths: 0·003 Å; mean e.s.d.'s for bond angles 0·2°.

† Intra-ring bond lengths are 1·395 Å; intra-ring bond angles are 120°.

**Discussion.** Final parameters are in Table 1.*

A projection of the structure along **b**, containing also the misoriented molecule at site *B*, is given in Fig. 1. It is noteworthy that this projection, as far as molecules *A* and *B*1 are concerned, remains practically unchanged when the structure is rotated by 180° about the [201] axis, which happens to be approximately perpendicular to the *c* axis. *ORTEP* views of the molecules, along with their numbering schemes, are presented in Fig. 2(*a*) and (*b*). Bond lengths and bond angles are given in Table 2.

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* Lists of structure factors, H-atom coordinates and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38542 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Selected torsion angles* (°) *in azobenzene*

| | |
|---|---|
| $N(1^i)-N(1)-C(2)-C(3)$ | −164·1 (1) |
| $N(1^i)-N(1)-C(2)-C(7)$ | 17·5 (2) |
| $N(8^{ii})-N(8)-C(9)-C(14)$ | −173·2 (1) |
| $N(8^{ii})-N(8)-C(9)-C(10)$ | 7·1 (2) |
| $N(15^{ii})-N(15)-C(16)-C(17)$ | 171·5 (7) |
| $N(15^{ii})-N(15)-C(16)-C(21)$ | −4·7 (11) |

From the list of relevant torsion angles (Table 3) it can be inferred that there are no drastic differences in the conformations of the centrosymmetric molecules, although the molecules at site *B* appear to be more planar than the molecule at site *A*. The composite view of molecules *B*1 and *B*2 (Fig. 2) shows that the molecular positions do not differ very much, as was already suggested by Brown (1966*a*). They are approximately related by a twofold axis, which runs in the direction of the longest molecular axis; the mean positional deviation after the twofold operation appears to be only 0·08 Å. The angle between the molecular planes of molecules *B*1 and *B*2 is 1·9°.

The inclusion of disorder in the structural model, submitted to refinement, has led to considerably lower temperature factors for molecule *B*1 compared to those found by Brown (1966*a*). However, the thermal motion of that molecule remains significantly larger than that of molecule *A*. This can be expected since, following Brown (1966*a*), at site *B* there is more available space. This also explains why disorder is only manifested at site *B* and it probably accounts for the fact that at that site the molecules are less distorted from planarity.

There are no intermolecular contacts which might be considered significantly less than the van der Waals radii.

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# Disordered Structure of 2,3-Dichloro-6,7-dimethylanthracene, $C_{16}H_{12}Cl_2$, for Sublimation-Grown (I) and Solution-Grown (II) Crystals

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**Abstract.** $M_r = 275{\cdot}18$, monoclinic, $P2_1/c$. (I) $a = 6{\cdot}174$ (1), $b = 7{\cdot}607$ (1), $c = 26{\cdot}835$ (4) Å, $\beta = 101{\cdot}14$ (1)°, $U = 1236{\cdot}6$ Å$^3$. (II) $a = 6{\cdot}180$ (1), $b = 7{\cdot}600$ (1), $c = 26{\cdot}810$ (3) Å, $\beta = 101{\cdot}15$ (1)°, $U = 1235{\cdot}4$ Å$^3$. $D_m = 1{\cdot}47$ (1), $D_x = 1{\cdot}478$ Mg m$^{-3}$, $Z = 4$, $F(000) = 568$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 0{\cdot}501$ mm$^{-1}$, room temperature. Refinement for (I) led to $R$ and $wR$ of 0·075 and 0·069 for 3633 reflections (0·044 and 0·062 for 2378 reflections with $I > 2{\cdot}3\sigma_I$). For (II) $R$ and $wR$ were 0·061 and 0·069 for 2842 reflections (0·044 and 0·064 for 2201 reflections with $I > 2{\cdot}3\sigma_I$). The 2,3,6,7 substituents show disorder of Cl and $CH_3$. For (I) the 2,3 sites are occupied on average by 0·606 Cl and 0·394 C and *vice versa* for 6,7, while for (II) the values are 0·792 Cl and 0·208 C.

**Introduction.** In previous publications (Jones & Welberry, 1980; Welberry & Jones, 1980; Welberry, Jones & Epstein, 1982; Epstein, Welberry & Jones, 1982) we have described our interest in disordered molecular crystals. Those studies characterized the structures of two polymorphs of 9-bromo-10-methylanthracene (BMA), in which the disorder occurred between the bromo and methyl substituents. In addition to the determination of the 'average' crystal structure a detailed study of the diffuse scattering was reported. As part of our continuing studies of disorder in such materials we now report the structure of 2,3-dichloro-6,7-dimethylanthracene. This compound represents an increase in the complexity of disorder problem studied, since each molecule now contains four disordered sites. In addition, our interest in this compound was aroused since preliminary investigations suggested that crystals

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