

## Molecular Conformation and Electronic Structure.

V.\* The Crystal and Molecular Structure of *N*-(*p*-Methylbenzylidene)-*p*-methylaniline (Form II)

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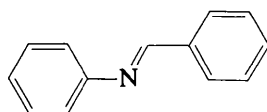
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The title compound is monoclinic, space group  $P2_1$ , with  $a = 6.891(1)$ ,  $b = 7.153(1)$ ,  $c = 12.600(1)$  Å,  $\beta = 102.70(1)^\circ$ ,  $Z = 2$ . The structure was solved by direct methods from 1432 intensities measured on a diffractometer and refined anisotropically to  $R = 0.046$ . It provides a good example of conformational polymorphism since, in contrast to polymorph III, the molecule has a non-planar conformation.

## Introduction

Benzylideneaniline (BA) is an excellent model compound for the investigation of the relationship between molecular conformation and electronic or structural influences.



BA

The conformation can be defined in terms of two geometric parameters: the rotations of the two phenyl rings with respect to the plane of the four atoms which form the bridge between them. Initial interest in this compound arose from its anomalous solution spectral properties in comparison with its isoelectronic analogues: *trans*-azobenzene (A) and *trans*-stilbene (S). The spectral differences have been shown to be a result of the non-planarity of BA compared with A and S (Skrabal, Steiger & Zollinger, 1975, and references therein). Subsequent to the original crystallographic studies of Bürgi & Dunitz (1970), investigations in this and other laboratories have revealed other interesting aspects of the structural chemistry of this family of compounds:

(1) Throughout the series the molecule exhibits a wide range of conformations, the angle between the plane of the aniline ring and the central atoms varying from 0 to  $55^\circ$ , while that between the benzylidene ring and the central atoms ranges from  $-25$  to  $6^\circ$  (Bernstein & Izak, 1976; Nakai, Shiro, Ezumi, Sakata &

Kubota, 1976; Meunier-Piret, Piret, Germain & Van Meerssche, 1972).‡

(2) In the majority of cases investigated, derivatives are substituted on one or both of the phenyl rings in the *para* position. In the earlier examples there appeared to be a fairly simple relationship between the degree of planarity, the electron-withdrawing or electron-donating power of the substituents and the three bond lengths between the bridge atoms (Bürgi & Dunitz, 1970; Bernstein & Izak, 1975). Recent studies suggest that a more complicated situation exists with no clear consistencies present in the available structural data (Bernstein & Izak, 1976).

(3) At least three of the BA's studied to date are polymorphic (Nakai *et al.*, 1976; Bernstein & Izak, 1976; Bernstein, Bar & Christensen, 1976) with significant changes in molecular conformation between polymorphs, *i.e.* they are examples of *conformational polymorphism* (Panagiotopoulos, Jeffrey, La Placa & Hamilton, 1974). Since the number of molecular conformational parameters is small, these cases provide excellent systems for detailed studies of the relationship between crystal structure and molecular conformation.

In pursuit of further information on all three of these aspects we undertook the structure determination of the title compound.

## Experimental

Crystals suitable for X-ray study were prepared by condensation of *p*-toluidine and *p*-tolualdehyde. The material is trimorphic and all crystalline forms have

\* Part IV: Bernstein, Bar &amp; Christensen (1976).

† In partial fulfilment of the requirements of the degree of MSc.

‡ See part III (Bernstein &amp; Izak, 1976) for a definition of these torsion angles. It has been brought to our attention that the sense of these angles is contrary to the IUPAC convention. In the interest of avoiding confusion at this stage we maintain the earlier convention.

been obtained under similar conditions by evaporation from ethanolic solution, m.p. 91°C [lit. 93°C (Keasling & Schueler, 1950)]. Weissenberg and precession photographs indicated monoclinic symmetry with systematic absences  $0k0$ ,  $k$  odd, compatible with space group  $P2_1$  or  $P2_1/m$ ; the former was confirmed during the course of the study.

Lattice constants were obtained from a least-squares fit of 15  $2\theta$  values determined on a diffractometer and ranging between 13 and 37° (Mo  $K\alpha$ ).

#### Crystal data

$C_{15}H_{15}N$ ,  $M_r = 209.19$ ; monoclinic,  $a = 6.891$  (1),  $b = 7.153$  (1),  $c = 12.600$  (1) Å,  $\beta = 102.70$  (1)°,  $U = 605.90$  Å<sup>3</sup>,  $D_c = 1.15$ ,  $D_m$  (floatation) = 1.17 g cm<sup>-3</sup>,  $Z = 2$ ;  $F(000) = 224$ ,  $\lambda(\text{Mo } K\alpha_1) = 0.71069$  Å,  $\mu(\text{Mo } K\alpha) = 0.72$  cm<sup>-1</sup>.

Intensities were measured on a Syntex  $P\bar{1}$  diffractometer with graphite-monochromatized Mo radiation and a crystal  $0.5 \times 0.5 \times 0.5$  mm. 1432 reflexions were measured with a  $2\theta/\theta$  scan (for  $2\theta \leq 54^\circ$ ). The scan rate varied from 2 to 24° min<sup>-1</sup> and was determined for each reflexion by a rapid prescan of the diffraction maxima. Absorption corrections were not applied. After Lorentz and polarization corrections, 313 reflexions had  $F_o < 2.5\sigma(F_o)$  and were considered unobserved.

#### Structure determination and refinement

The cell parameters and density indicated  $Z = 2$ , which is compatible with a general position in space group  $P2_1$ , but requires either one of two special positions in  $P2_1/m$ , corresponding to site symmetries  $m$  and  $\bar{1}$ . Both site symmetries are possible for the molecule, the former requiring a planar molecule, the latter parallelism of the two phenyl rings and disorder about the centre (Bernstein & Schmidt, 1972). Statistics of normalized structure factors ( $E$ ) supported the assignment of the

centrosymmetric space group, although packing considerations argued against site symmetry  $\bar{1}$ . However, a test of the crystals with the non-linear optical effect (Oudar & Chemla, 1975) was positive, dictating unambiguously the choice of the non-centrosymmetric space group.

The structure was solved, not without difficulty, with *MULTAN* (Germain, Main & Woolfson, 1972); hence we describe the solution in some detail. 1454  $\Sigma_2$  relationships among the 160 reflexions with  $|E| > 1.54$  were included in the phase determination by the weighted tangent formula. The 'weighted figure of merit' of the set of phases from which the structure was eventually obtained (2.33) was the highest of the 64 sets calculated, the 'residual' was the lowest (20.26), but the 'absolute figure of merit' (1.09) and ' $\psi$  zero' ( $0.42 \times 10^3$ ) were lower than for other sets of phases.

The 48 highest peaks from the  $E$  map corresponding to this set of phases are shown in Fig. 1. The distribution of peaks illustrates the ambiguity of locating the molecule in the unit cell because of the presence of multiple images of the molecule which are displaced from the correct one (Bürgi & Dunitz, 1971). The problem is common to structures of high molecular symmetry, particularly those containing phenyl rings, and has been encountered previously in the structure solution of a number of benzylideneanilines (Bürgi & Dunitz, 1971; Nakai *et al.*, 1976). Many peaks which proved to be atom positions in the solution were 'doubly degenerate', *i.e.* for a pair of  $x$  and  $z$  coordinates, two non-symmetry-related peaks (in space group  $P2_1$ ) could be found, differing only in their  $y$  values. This reflects an ambiguity in the choice of enantiomorph (see below) and is probably related to the pseudo centrosymmetry of the structure. The  $E$  map, therefore, did not yield a unique solution to the structure which was finally obtained by trial and error from the possibilities suggested by the map. Of the 16 heavy atoms in the asymmetric unit, 15 could be directly related to peaks in the set of 48 but only six of them were among the highest 16 peaks. The position of the remaining atom was calculated from geometric considerations. The trial structure based on these coordinates yielded through two cycles of least squares an  $R$  of 0.46 for 647 reflexions of  $\sin \theta/\lambda < 0.5$  Å<sup>-1</sup> with only positional parameters permitted to vary. Least-squares refinement was then continued in stages. Individual isotropic temperature factors were included, then the limit for  $\sin \theta/\lambda$  was increased to the limit of the data and anisotropic temperature factors for all atoms were introduced. The refinement converged at  $R = 0.25$ .

At this stage many geometric features of the molecule were not normal and the temperature factors of several atoms were unusually high. A difference map yielded a set of peaks whose  $x$  and  $z$  coordinates were essentially identical to those of the input atoms, but whose  $y$  coordinates were approximately related to the

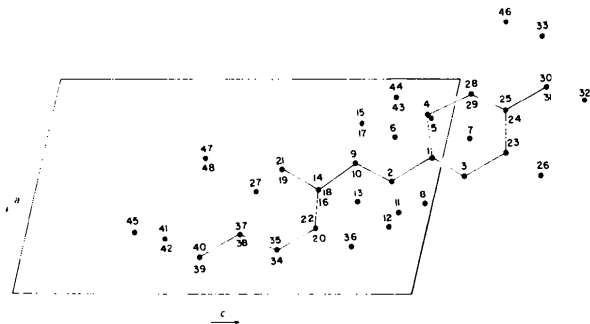


Fig. 1. The 48 highest peaks in the  $E$  map from which the structure was solved, projected down  $b$ . For an explanation of the points marked by two numbers see text. Peaks used in trial model which led to solutions are connected by lines.

Table 1. Final fractional coordinates and thermal parameters for non-hydrogen ( $\times 10^4$ ) and hydrogen ( $\times 10^3$ ) atoms

E.s.d.'s in parentheses are in units of the least significant digit. Hydrogen atoms are numbered according to the carbon atoms to which they are bonded. Anisotropic temperature factors are in the form  $\exp[-2\pi^2(\sum_i a_i^2 h_i^2 U_{ii} + 2\sum_{i < j} a_i^* a_j^* h_i h_j U_{ij})]$ ; isotropic,  $\exp[-8\pi^2 U_{iso} \sin^2 \theta / \lambda^2]$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>
N(1)	3881 (4)	2086 (4)	7842 (1)	548 (9)	699 (13)	659 (10)	26 (10)	18 (10)	139 (8)
C(1)	7163 (3)	2876 (4)	5417 (2)	726 (13)	570 (14)	647 (13)	-60 (12)	7 (11)	190 (11)
C(2)	8045 (3)	2040 (4)	6396 (2)	542 (11)	687 (15)	691 (14)	-3 (12)	-9 (12)	137 (10)
C(3)	7017 (3)	1779 (4)	7205 (2)	583 (11)	673 (16)	616 (12)	46 (12)	55 (12)	67 (10)
C(4)	5040 (3)	2365 (4)	7061 (1)	549 (11)	596 (14)	618 (12)	-5 (10)	-21 (11)	116 (9)
C(5)	4162 (3)	3171 (5)	6075 (2)	621 (13)	757 (18)	725 (14)	113 (13)	93 (13)	102 (11)
C(6)	5201 (4)	3428 (5)	5278 (2)	749 (14)	749 (17)	653 (15)	116 (14)	135 (13)	105 (12)
C(7)	4656 (4)	2386 (4)	8834 (2)	592 (12)	562 (13)	702 (13)	-2 (14)	-2 (11)	148 (11)
C(8)	3590 (3)	2085 (4)	9697 (2)	606 (11)	470 (12)	673 (12)	54 (10)	-5 (10)	161 (10)
C(9)	4482 (4)	2503 (4)	10766 (2)	689 (14)	667 (16)	732 (14)	-43 (12)	-65 (12)	120 (12)
C(10)	3487 (4)	2251 (5)	11584 (2)	952 (17)	706 (17)	628 (13)	63 (15)	-42 (13)	149 (13)
C(11)	1546 (4)	1601 (4)	11378 (2)	869 (15)	580 (15)	803 (16)	167 (14)	115 (13)	326 (13)
C(12)	668 (4)	1144 (5)	10313 (2)	656 (13)	726 (17)	805 (16)	39 (13)	57 (14)	240 (12)
C(13)	1654 (3)	1375 (4)	9486 (2)	609 (12)	742 (17)	662 (13)	19 (12)	-1 (13)	135 (11)
C(14)	8272 (6)	3100 (6)	1522 (3)	929 (21)	994 (27)	828 (20)	-37 (22)	100 (20)	361 (18)
C(15)	403 (7)	1419 (6)	12263 (3)	1273 (29)	979 (27)	870 (21)	286 (25)	219 (20)	537 (22)

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub>
H(2)	938 (3)	157 (4)	653 (2)	46 (7)
H(3)	763 (3)	119 (3)	792 (2)	26 (5)
H(5)	270 (4)	354 (5)	599 (2)	52 (8)
H(6)	456 (4)	409 (5)	460 (2)	66 (9)
H(7)	594 (4)	298 (5)	907 (2)	63 (9)
H(9)	582 (4)	298 (6)	1090 (2)	72 (9)
H(10)	416 (4)	242 (5)	1235 (2)	66 (9)
H(12)	-70 (4)	53 (6)	1012 (3)	69 (9)
H(13)	104 (3)	99 (4)	874 (2)	30 (6)
H(14a)	755 (8)	357 (10)	391 (4)	142 (22)
H(14b)	883 (6)	424 (8)	453 (4)	125 (17)
H(14c)	930 (7)	234 (9)	458 (4)	117 (20)
H(15a)	125 (5)	111 (7)	1285 (2)	78 (12)
H(15b)	-23 (5)	265 (6)	1235 (2)	80 (11)
H(15c)	-54 (8)	21 (10)	1201 (4)	170 (24)

input coordinates by the relations  $y' = y + 0.2$  for  $y \leq 0.2$  and  $y' = y - 0.2$  for  $y \geq 0.2$ , i.e. the enantiomorph of the initial solution obtained by reflexion through a mirror plane at  $y \approx 0.2$ .

Further full-matrix refinement based on the  $y'$  coordinates thus obtained yielded an  $R$  of 0.11 with anisotropic temperature factors and all observed data. The molecule was then divided into two blocks corresponding to the *p*-methylbenzylidene and *p*-toluidine moieties, and H atom coordinates based on positions determined from a difference map were included with individual isotropic temperature factors. At convergence  $R$  was 0.046 (0.051 including unobserveds) and  $R'$  0.014 with goodness of fit 1.66.

At all stages of refinement the weight ( $w$ ) of an individual reflexion was  $1.0/\sigma^2(F_o^2)$ . The function minimized was  $\sum w(|kF_o|^2 - |F_c|^2)^2$ . The electron density in the difference map based on the final parameters did not exceed  $0.38 \text{ e } \text{Å}^{-3}$ .

Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Computer programs used, in addition to *MULTAN*, were locally modified versions of *ORFLS* (Busing, Martin & Levy, 1962) and *FORDAP* (Zalkin, 1962). Final positional parameters are given in Table 1.\*

### Thermal motion

Rigid-body analysis (Schomaker & Trueblood, 1968) was carried out separately on three groups of atoms: (1) the tolyl group with the N on the bridge, (2) the tolyl group with the C on the bridge, (3) the entire molecule. The r.m.s. differences between the observed and calculated  $U_{ij}$  values were respectively 0.0032, 0.0034 and 0.0059  $\text{Å}^2$  (the discrepancy indices  $\{[\sum (U_{obs.} - U_{calc.})^2 / U_{obs.}^2]^{1/2}\}$  were 0.049, 0.047 and 0.100), compared with the mean standard deviations of the experimental  $U_{ij}$ 's ( $\sigma U_{ij}$ ) of 0.0013, 0.0015 and 0.0014  $\text{Å}^2$ . If the rigid-body analysis is valid here, it is valid only for groups 1 and 2 and not for the whole molecule. The pertinent data for these two groups are summarized in Table 2.

The directional properties of the librational motion are consistent with those found in other derivatives of benzylideneaniline: the principal libration axis for each group is parallel to the *para* axis of the ring (Bernstein & Schmidt, 1972; Bernstein & Izak, 1975, 1976; Bürgi & Dunitz, 1970). Although the molecules themselves have different conformations and the packing modes

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32319 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

differ throughout the series, the repetition of this pattern of rigid-body motion strongly suggests that these motions are true molecular properties.

Table 2. Summary of the rigid-body analysis for the two phenyl groups

The calculation is referred to the origin which symmetrizes **S** and reduces the trace of **T**.

#### Group 1

The centre of mass of the axial system of inertia is referred to the crystal axes  $x = 0.2561$ ,  $y = 0.1845$ ,  $z = 1.0540$ .

The transformation matrix from the crystal system to the axial system of inertia is

$$\begin{pmatrix} 4.6284 & 0.8694 & -10.8406 \\ 4.5776 & 2.4021 & 6.3635 \\ 2.2486 & -6.6795 & 0.8775 \end{pmatrix}$$

Tensor elements ( $\times 10^4$ )

	11	22	33	12	23	13
L(rad <sup>2</sup> )	195 (18)	34 (3)	44 (3)	1 (5)	6 (3)	5 (8)
T(Å <sup>2</sup> )	647 (10)	596 (13)	422 (21)	-21 (11)	20 (13)	-23 (12)
S(rad Å)	10 (8)	-8 (7)	-2 (10)	13 (6)	-22 (4)	-23 (4)

R.m.s. amplitudes	Components of molecular axes			
	L	M	N	
L	8.0°	0.9993	0.0106	0.0346
	3.9	0.0357	-0.4345	-0.8999
	3.2	0.0055	0.9006	-0.4346
T	0.27 Å	-0.2432	-0.9699	-0.0110
	0.25	-0.9688	-0.2423	0.0513
	0.20	-0.4711	0.0231	0.9986

#### Group 2

The centre of mass of the axial system of inertia is referred to the crystal axes  $x = 0.6052$ ,  $y = 0.2595$ ,  $z = 0.6257$ .

The transformation matrix from the crystal system to the axial system of inertia is

$$\begin{pmatrix} -4.7508 & -0.9077 & 10.6723 \\ -4.7404 & 3.0057 & -5.3624 \\ -1.5464 & -6.4252 & -4.0161 \end{pmatrix}$$

Tensor elements ( $\times 10^4$ )

	11	22	33	12	23	13
L(rad <sup>2</sup> )	187 (19)	47 (4)	31 (3)	8 (8)	1 (3)	-12 (10)
T(Å <sup>2</sup> )	629 (11)	526 (14)	471 (25)	-13 (11)	4 (14)	-24 (13)
S(rad Å)	0 (9)	3 (7)	-2 (11)	-3 (6)	-12 (3)	-10 (4)

R.m.s. amplitudes	Components of molecular axes			
	L	M	N	
L	7.9°	-0.9955	-0.0534	0.0777
	3.9	-0.0436	0.9915	0.1226
	3.1	-0.0836	0.1186	-0.9894
T	0.25 Å	0.9857	-0.0294	-0.1661
	0.24	0.0530	0.9888	0.1394
	0.22	0.1602	-0.1462	0.9762

## Results and discussions

### Molecular geometry

Table 3 gives the best planes for various molecular fragments. The group C(4)–N–C(7)–C(8) does not deviate significantly from planarity. The normal to plane 2 makes angles of 41.7 and -3.0° with the normals to the aniline and benzylidene rings respectively. This conformation is consistent with the geometry encountered in other non-planar benzylideneanilines (Bernstein & Izak, 1976, and references therein) but is in marked contrast to its conformational polymorph form III which is essentially planar (Bernstein, Bar & Christensen, 1976).

Bond lengths (not corrected for rigid-body motion) and angles are given in Fig. 2. The features of the rings, including the C(1)–C(14) and C(11)–C(15) lengths, correspond to those expected for a benzene ring substituted by a methyl group (Domenicano, Vaciano & Coulson, 1975). C(4)–N, C(7)–C(8) and C(7)–N are 1.411, 1.456 and 1.265 Å; those of the parent compound (Burgi & Dunitz, 1970) are 1.460, 1.496 and 1.237 Å. We pointed out earlier (Bernstein & Izak, 1976) that the apparently consistent trend of these bond lengths as a result of substitution of the two phenyl rings (in the first few structures of the series) breaks down in *p*-nitrobenzylidene-*p*-dimethylamino-

Table 3. Equations of some least-squares planes in the form  $Ax + By + Cz + D = 0$ , where  $x$ ,  $y$  and  $z$  are fractional coordinates

Deviations (Å) of relevant atoms from the plane are given in square brackets.

Plane 1: C(1)–C(6)

A	B	C	D
-1.549	-6.424	-4.018	5.129

[C(1) -0.005, C(2) 0.002, C(3) 0.005, C(4) -0.009, C(5) 0.006, C(6) 0.000, N 0.037, C(7) -0.675, C(8) -0.663, C(9) -1.499, C(10) -1.512, C(11) -0.711, C(12) 0.147, C(13) 0.178, C(14) -0.772, C(15) 0.040, H(7) -1.352]

Plane 2: C(4), N, C(7), C(8)

A	B	C	D
2.067	-6.783	0.415	0.279

[C(1) 0.034, C(2) 0.823, C(3) 0.822, C(4) 0.009, C(5) -0.760, C(6) -0.752, N -0.009, C(7) -0.010, C(8) 0.010, C(9) -0.045, C(10) -0.047, C(11) -0.015, C(12) 0.081, C(13) 0.082, C(14) -0.073, C(15) -0.091, H(7) -0.140]

Plane 3: C(8)–C(13)

A	B	C	D
2.272	-6.675	0.822	-0.231

[C(1) -0.078, C(2) 0.760, C(3) 0.768, C(4) -0.085, C(5) -0.903, C(6) -0.904, N -0.098, C(7) -0.040, C(8) -0.010, C(9) 0.001, C(10) 0.010, C(11) -0.014, C(12) 0.005, C(13) 0.007, C(14) -0.050, C(15) -0.079, H(7) -0.127]

aniline (I). This is planar and because of the presence of the strong electron-withdrawing and electron-donating groups at the extremities would be expected to exhibit the shortest C(4)—N, C(7)—C(8) and the longest C(7)—N lengths in the series, if there were a simple relationship between degree of planarity and the contribution of resonance structures and the electronic structure. The respective bond lengths for (I) are 1.416, 1.460 and 1.258 Å (Nakai *et al.*, 1976). In spite of the fact that the molecule in the present structure is symmetrically substituted with relatively weak electron-donating groups, the bond lengths in question are equal (to within  $2\sigma$ ) to those in (I). On the other hand, in the structure of *p*-dimethylaminobenzylidene-*p*-nitroaniline (II), C(4)—N (1.399 Å) is the shortest in the whole series found to date, although the nitrophenyl ring is twisted about this bond by 45° (Nakai *et al.*, 1976). The situation is further confused by the observation that N—C(7) in the latter structure is 1.279 Å, which is one of the longest bond lengths in the series while C(7)—C(8) (1.452 Å) is essentially equal to that found in the present structure.

Nakai *et al.* (1976) have suggested an alternative model to account for some of the variations in planarity and bond length. The model is based on a competition between two intramolecular charge-

transfer effects: the first (*CT-1*), as a result of a difference in electron-donating and electron-withdrawing power of *p,p'*-substituents, would lead to increasing planarity with an increase of the effect, while in the second (*CT-2*), charge transfer between the lone-pair electrons on the N and an electron-withdrawing group on the aniline ring (in the *para* position) would stabilize the non-planar conformation. Thus in (II) (Nakai *et al.*, 1976), *p*-methylbenzylidene-*p*-nitroaniline (Bürgi & Dunitz, 1970) and benzylideneaniline-*p*-carboxylic acid (III) (Bürgi & Dunitz, 1970), the electron-withdrawing groups stabilize the non-planar conformation (*CT-2*), while in (I) the planar conformation is preferred (*CT-1*) (Nakai *et al.*, 1976; Skrabal, Steiger & Zollinger, 1975). Nakai *et al.* (1976) also noted that the C(4)—N distance decreases with increasing *CT-2* effect. The present structure is not consistent with this model. The non-planar conformation cannot be stabilized by *CT-2* since the methyl group normally acts as a weak electron donor, although it is true that the molecule is less non-planar by 13° than BA itself. Furthermore, the planar conformation found in form III (Bernstein, Bar & Christensen, 1976) cannot be stabilized by effects of the *CT-1* type since the two *para* substituents are identical. Moreover, the argument based on the relationship between the strength of *CT-2* and C(4)—N length is not

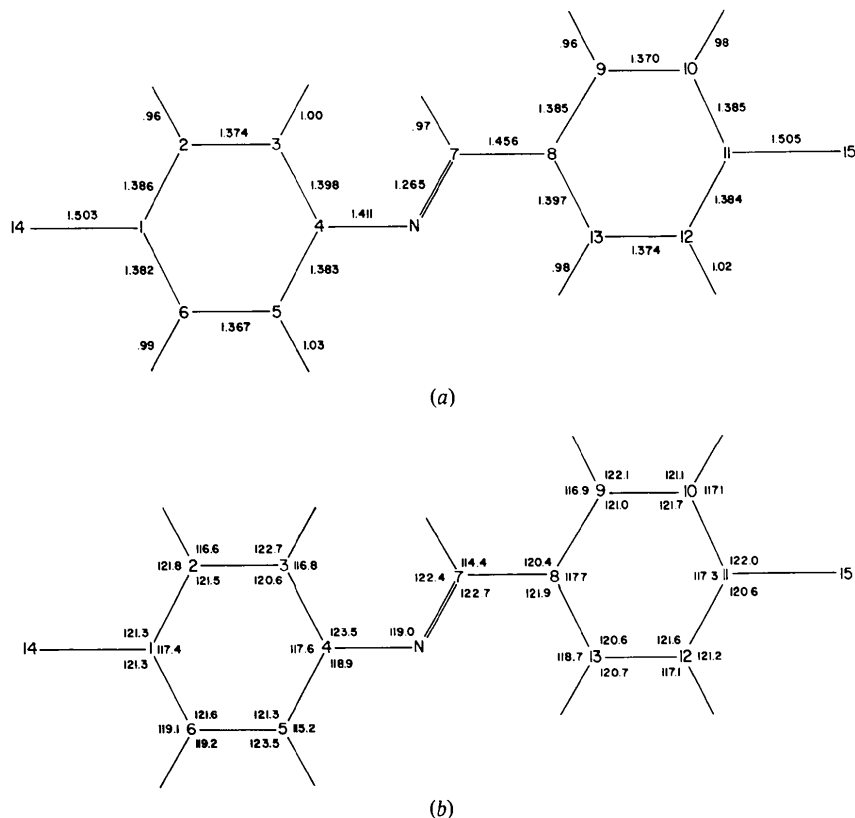


Fig. 2. (a) Bond lengths (Å), e.s.d.'s are  $\sim 0.004$  Å ( $\sim 0.06$  Å for C—H bonds). (b) Bond angles (°), e.s.d.'s are C—C—C  $0.2^\circ$ ; C—C( $sp^2$ )—H  $1.5^\circ$ ; C—C( $sp^3$ )—H  $3.5^\circ$ .

compatible with the results found in this structure since the relative shortness of the bond cannot be attributed to either effect.

On the basis of the data presently available we conclude that there is no simple relationship between bond length (or bond order), molecular planarity and substituent.

Furthermore, recent calculations on another example of conformational polymorphism, the two forms of *N*-(*p*-chlorobenzylidene)-*p*-chloroaniline (III), strongly suggest that conformational changes, at least in these symmetrically substituted benzylideneaniline systems, can be well accounted for by crystal forces (Bernstein & Hagler, 1977).

### Packing

The packing viewed along [010] is shown in Fig. 3. One feature is that the end of one molecule is near the middle of its closest neighbour. This arrangement is of the 'imbricated packing' type (Lesser, de Vries, Reed & Brown, 1975, and references therein) which is a necessary (but apparently not sufficient) condition for a material to form a nematic mesophase.

The definition is qualitative at best but many of the benzylideneanilines appear to have packing of the imbricated type, which intuitively is a very efficient mode of packing for this family of molecules, being composed of two bulky groups bridged by a smaller one. An exception is found in the polymorphic III. The metastable, triclinic polymorph is of the imbricated packing type (Bernstein & Schmidt, 1972), while the stable orthorhombic form (Bernstein & Izak, 1976) clearly is not.

Short intermolecular distances are given in Table 4. Most of these values are very close to the sum of the van der Waals radii. In this structure the molecular volume is 605.9 Å<sup>3</sup> which is significantly greater than in form III (579.8 Å<sup>3</sup>), in which the molecule is essentially planar. In an earlier example of conformation polymorphism in benzylideneanilines, compound III,

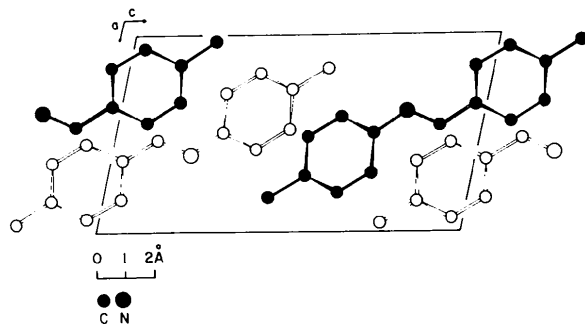


Fig. 3. A view of the structure down [010].

Table 4. Intermolecular distances (Å)

	Symmetry	Translation along			Distance
		<i>a</i>	<i>b</i>	<i>c</i>	
C(1)···C(6)	2	1	-1	1	3.59
C(1)···H(6)	2	1	-1	1	2.96
C(2)···H(6)	2	1	-1	1	2.87
C(3)···H(6)	2	1	-1	1	3.00
H(3)···H(13)	1	1	0	0	2.35
C(7)···C(9)	2	1	-1	2	3.56

Symmetry code: (1)  $x, y, z$ ; (2)  $x, \frac{1}{2} + y, z$ .

the large difference in molecular conformation between the two polymorphs was not manifested in any change in molecular volumes, probably because in both polymorphs molecular site symmetry required disorder.

The cell constants of form I of the present compound (Bürgi, Dunitz & Züst, 1968) indicate that the long molecular axis lies nearly parallel to *c* (26.7 Å) as in the present structure. However, *a* is shorter (6.07) and *b* is longer (7.73 Å). On the basis of these cell constants, packing considerations lead us to predict that form I is a third conformational polymorph in which the angle between the aniline ring and the central bridge will be larger than in form II. The structure is currently being investigated in our laboratory.

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## The Crystal Structure of Bis(tetrathiotetracene) Triiodide, a One-Dimensional Organic Metal

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The crystal structure of the organic metal  $\text{TTT}_2\text{I}_3$  has been determined at room temperature from X-ray diffraction data collected on a diffractometer. The crystals are orthorhombic, *Abam*, with  $a = 18.394(12)$ ,  $b = 4.962(5)$ ,  $c = 18.319(11)$  Å,  $d_m = 2.16$ ,  $d_c = 2.156$  g cm<sup>-3</sup>,  $Z = 2$ . Diffuse streaks on precession photographs indicate a disordered lattice incommensurate along **b** with  $b' = 9.54$  Å =  $1.92b$ . The structure was solved in the subcell by Patterson and Fourier methods and refined by full-matrix least-squares calculations to  $R_1 = 0.042$ . The structure consists of planar TTT radical cations with  $2/m$  crystallographic symmetry stacked uniformly along **b**, the axis of high electrical conductivity, with a 3.32 Å interplanar spacing and a ring-bond overlap. A short S...S contact [3.373(2) Å] links stacks in (100) planes. The I atoms are present as triiodide ions lying in chains along  $2_b$  axes parallel to the TTT stacks. For some crystal domains the triiodide ions lie on the incommensurate lattice but for others they are forced to conform to the subcell dimensions by a close hydrogen approach. The dual nature of the triiodide ions also causes a possible disorder in the TTT moieties. These disorders are possibly the reason no metal–insulator transitions are observed down to 3.3 K.

### Introduction

Isett & Perez-Albuerna (1977) have prepared and studied a novel ion-radical salt of tetrathiotetracene (TTT) and iodine with stoichiometry  $\text{TTT}_2\text{I}_3$ . They report that single crystals of  $\text{TTT}_2\text{I}_3$  have a room-temperature electrical conductivity of  $1000 \Omega^{-1} \text{cm}^{-1}$  along the needle axis which rises to  $3000 \Omega^{-1} \text{cm}^{-1}$  in the range 40 to 80 K and then decreases to  $100 \Omega^{-1} \text{cm}^{-1}$  at 4 K. The temperature dependence of the conductivity is essentially metallic and there is no evidence of a metal–semiconductor transition down to 3.3 K. This behavior places  $\text{TTT}_2\text{I}_3$  among the best organic ‘metals’ known to date, such as TTF–TCNQ (tetrathiofulvalene/tetracyanoquinodimethane) (Ferraris,

Cowan, Walatka & Perlstein, 1973) and HMTSF–TCNQ (hexamethylenetetraselenofulvalene–tetracyanoquinodimethane) (Bloch, Cowan, Bechgaard, Pyle, Banks & Poehler, 1975).

We have determined the crystal structure of  $\text{TTT}_2\text{I}_3$  to provide a sound structural basis for the interpretation of the high conductivity of this material.

### Experimental

Brown, long, square, prismatic (*b*) crystals, grown in vacuum by cosublimation of TTT and iodine, were supplied by Dr L. C. Isett of the Eastman Kodak Research Laboratories. Crystal data, given in Table 1,