

Molecular Conformation and Electronic Structure.
VI.* The Structure of *p*-Methyl-*N*-(*p*-methylbenzylidene)aniline (Form I)

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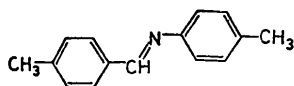
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Abstract

The crystal structure of the first polymorphic form of the title compound [form II: Bar & Bernstein (1977). *Acta Cryst.* B33, 1738–1744; form III: Bernstein, Bar & Christensen (1976). *Acta Cryst.* B32, 1609–1611] has been determined by X-ray single-crystal structure analysis. Crystals of form I, C₁₅H₁₅N, *M_r* = 209.19, are monoclinic, *a* = 6.089 (2), *b* = 7.751 (2), *c* = 26.766 (3) Å, β = 103.16 (3)°, *U* = 1230.07 Å³, space group *P*2₁/*c*, *Z* = 4; *D_c* = 1.12, *D_m*(flotation) = 1.12 Mg m⁻³, *F*(000) = 448, μ(Cu *K*α) = 0.431 mm⁻¹. The structure has been solved, not without difficulty, by direct methods and refined to a conventional *R* of 0.075 on 1374 reflections. Bond lengths and angles agree well among this structure and the other two polymorphs. The molecular conformation differs significantly from the conformation of form II, but agrees with the planar conformation of form III. The mode of disorder observed here differs from those of previously determined benzylideneanilines.

Introduction

Two studies (Bernstein & Hagler, 1978; Hagler & Bernstein, 1978) recently demonstrated the utility of employing conformational polymorphism to investigate the role of crystal forces in influencing molecular conformation. The model system employed in the first of these was *p*-chloro-*N*-(*p*-chlorobenzylidene)aniline in which the packing was dominated by van der Waals forces. As part of a program to investigate whether the phenomena observed are characteristic of conformational polymorphism or unique to that particular system we undertook the structure determination of form I of the dimethyl analogue (MeMe) of benzylideneaniline.



* Part V: Bar & Bernstein (1977).

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The structures of the two other known polymorphs have been reported earlier (see *Abstract* for references).

Experimental

Crystals suitable for X-ray study were prepared by condensation of *p*-tolualdehyde and *p*-toluidine. The material is at least trimorphic and all crystalline forms may be obtained from ethanolic solution. Crystals of MeMe, m.p. 363 K [lit. 366 K (Keasling & Schueler, 1950)] were obtained as nearly square plates by slow evaporation of an ethanolic solution.

We initially started work on this compound in early 1973 and confirmed the cell constants earlier reported by Bürgi, Dunitz & Züst (1968). After a hiatus of several months the crystals were no longer suitable for single-crystal studies. In the course of repeated and varied attempts to obtain good single crystals we discovered forms II and III. Only by synthesizing and recrystallizing the material in a laboratory completely isolated from ours (across town) were we successful in obtaining form I again. Hence, for a number of years this appeared to be a case of a 'disappearing crystal form' (Woodward & McCrone, 1975) but, in agreement with Jacewicz & Nayler (1979), we were finally successful, once again, in obtaining suitable crystals for data collection. The cell constants reported in the *Abstract* are based on a least-squares fit of 15 reflections with *2θ* values in the range 6–34° (Cu *K*α, λ = 1.5418 Å).

Intensities were collected on a Syntex *P* $\bar{1}$ diffractometer, using graphite-monochromatized Cu radiation. 1998 reflections were measured and, after Lorentz and polarization corrections, 616 of these having *F_o* ≤ 3σ(*F_o*) were considered unobserved.

Structure determination and refinement

The structure was solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1972). We discuss the solution in some detail because of the difficulties encountered and their relevance to a fairly

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large class of organic compounds. A total of 1516 Σ_2 relationships among the 180 reflections with E values > 1.87 were included in the phase determination by the weighted tangent formula. The E map obtained for the best set by most of the usual criteria except ' ψ zero' (Fig. 1) was not easily interpreted.

While at least two translationally related molecular images could be obtained from the map, neither of these was the correct structure. As in some other structures of fairly high symmetry and containing coplanar phenyl rings, multiple images are displaced from the correct one (Bürgi & Dunitz, 1971a; Huber & Ahmed, 1980; Carrell & Glusker, 1980). In this case the approximate average of the two images proved to be the correct structure.

The difference map based on the converged isotropically refined trial structure using *SHELX* (Sheldrick, 1976) revealed two peaks in the vicinity of the bridge atoms, suggesting a fairly widespread type of positional disorder found for instance in one of the molecules in the structure of *trans*-stilbene (Hoekstra, Meertens & Vos, 1975).

The refinement was continued with isotropic temperature factors for all heavy atoms and refinement of occupancy for the disordered atoms, to an R of 0.184 for 530 reflections with $\sin \theta < 0.6$. At this stage the geometry of the benzene rings was normal, but the geometry of the bridge atoms differed from the expected values. The exocyclic single bonds were lengthened and the bridge double bond was shortened by 0.13 Å for the orientation with greatest occupancy, while for the second orientation the bridge double bond was longer by 0.36 Å than the expected value of 1.27 Å (Bürgi & Dunitz, 1971b). The refinement was continued with individual isotropic temperature factors and bond-length constraints for the disordered atoms, then the limit for $\sin \theta$ was increased to the limit of the data and anisotropic temperature factors for all atoms were introduced. The refinement converged at $R = 0.094$. The H atoms were located on a difference map and included in the refinement (with isotropic temperature factors) which converged at $R = 0.075$ (0.096 including unobserveds), $R_w = 0.091$ excluding eight

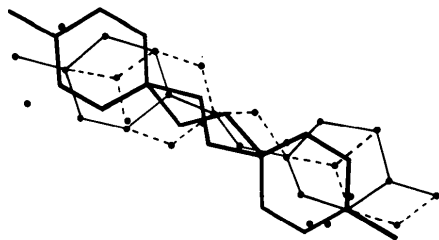


Fig. 1. The 30 highest peaks in the E map from which the structure was solved. Trial models which failed are connected by thin lines and dashed lines. The correct final model is shown with heavy lines.

Table 1. Atomic coordinates ($\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for H atoms) and U_{eq} ($\times 10^4$) expressed as $(U_{11}U_{22}U_{33})^{1/3}$

	x	y	z	U_{eq} (Å ²)
N	1608 (9)	7765 (8)	8468 (2)	734 (36)
N'*	1907 (13)	7741 (10)	8159 (3)	668 (47)
C(1)	3750 (6)	8156 (4)	6739 (1)	721 (19)
C(2)	1701 (6)	8901 (5)	6747 (1)	791 (22)
C(3)	884 (6)	8882 (5)	7185 (1)	845 (24)
C(4)	2053 (6)	8132 (4)	7635 (1)	792 (22)
C(5)	4078 (6)	7332 (5)	7616 (1)	791 (22)
C(6)	4895 (6)	7363 (5)	7180 (1)	762 (21)
C(7)	770 (12)	8419 (9)	8041 (2)	688 (46)
C(7')*	342 (16)	8507 (12)	8304 (3)	695 (61)
C(8)	231 (9)	8063 (6)	8841 (1)	1014 (30)
C(9)	-1803 (8)	8799 (7)	8880 (1)	1033 (31)
C(10)	-2599 (7)	8739 (5)	9318 (2)	983 (27)
C(11)	-1378 (6)	7912 (4)	9752 (1)	779 (21)
C(12)	648 (6)	7168 (5)	9715 (1)	879 (25)
C(13)	1417 (7)	7236 (5)	9280 (2)	998 (28)
C(14)	4738 (10)	8203 (10)	6270 (2)	1236 (41)
C(15)	-2206 (9)	7850 (7)	10241 (2)	1097 (35)
H(2)	95 (5)	933 (4)	646 (1)	
H(3)	-48 (5)	929 (4)	719 (1)	
H(5)	461 (5)	689 (4)	791 (1)	
H(6)	630 (5)	685 (4)	718 (1)	
H(7)	-43 (10)	936 (7)	807 (2)	
H(7')*	-71 (14)	872 (10)	799 (3)	
H(9)	-272 (5)	934 (4)	860 (1)	
H(10)	-418 (5)	913 (4)	934 (1)	
H(12)	151 (5)	656 (4)	1000 (1)	
H(13)	305 (5)	675 (4)	926 (1)	
H(14)	377 (8)	883 (8)	601 (2)	
H(14)	407 (8)	743 (7)	603 (2)	
H(14)	609 (7)	876 (6)	635 (2)	
H(15)	-133 (6)	699 (5)	1040 (1)	
H(15)	-348 (6)	725 (5)	1023 (1)	
H(15)	-256 (6)	889 (5)	1036 (1)	

* Primed atoms are the disordered pairs of the unprimed ones with occupancy 0.6.

reflections (106, 224, 218, 112, 020, 220, 2,0,10, 2,0,12) which showed strong signs of extinction and were removed from the refinement. A difference map based on the final parameters of all atoms shows no peak higher than 0.16 e \AA^{-3} . Final positional parameters are given in Table 1.* Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1968).

Results and discussion

Molecular geometry

Molecular dimensions (Fig. 2) are compatible, within experimental error, with those obtained for the other

* Structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36238 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

two polymorphs of MeMe (Bernstein, Bar & Christensen, 1976; Bar & Bernstein, 1977), and with those expected for a benzene ring substituted by a methyl group (Domenicano, Vacigo & Coulson, 1975). The mode of disorder is such that the small atomic displacements in the two positions of the benzene ring are absorbed by the anisotropic temperature factors, which exhibit a pattern consistent with the expected displacements of the atoms in the rings. The unusual geometric features of the disordered bridge atoms have no chemical significance but are a consequence of the positional disorder observed in this case and in many members of the series of benzylideneanilines (Bernstein & Bar, 1980). This molecule is the first which is in a general position and exhibits this mode of disorder with no crystallographic symmetry restrictions. The positional disorder could be statistical (*i.e.* equal occupancy of the two orientations) or non-statistical (unequal occupancy of the two orientations) as observed here.

We have observed positional disorder in combination with orientational disorder about a center of symmetry in form III of MeMe (Bernstein, Bar & Christensen, 1976) and about a twofold axis in the 1:2 π -molecular complex of benzylideneaniline with *sym*-trinitrobenzene (Bar & Bernstein, 1981). A mode of positional disorder similar to that found here was observed in *p*-azotoluene (Brown, 1966*b*) and in one of the two independent molecules in *trans*-stilbene (Hoekstra, Meertens & Vos, 1975). Experimental evidence suggests a similar situation in *trans*-azobenzene (Brown, 1966*a*; Gabe & LePage, 1980).

The existence of disorder leads to concentration of electron density towards the center of the molecule. As

a result, the bridge double bond undergoes apparent shortening, the exocyclic single bonds are concomitantly lengthened and the bond angles are smaller than the true values.

Table 2 gives the best planes for each of the aromatic rings and for the four central atoms of the molecule; both rings are planar to within 0.016 Å, while the disordered bridge atoms lie within 0.046 Å of their best plane. The most important feature of the molecular geometry in terms of conformational polymorphism is the angle of twist of the rings about the exocyclic single bonds. The angle of rotation of the aniline ring about N—C(8) is 2.3° and of the benzylidene ring about C(4)—C(7), 2.8°, while for the second orientation the angle of twist of the aniline ring about N'—C(4) is 10.2° and of the benzylidene ring about C(7')—C(8) 9.9°. The angle of twist of the phenyl rings about the exocyclic single bonds (*i.e.* planes I \wedge III and planes II \wedge III) are both 4.9°. The essentially planar conformation is similar to that found in form III of MeMe (Bernstein, Bar & Christensen, 1976), which is disordered about a center of symmetry and the phenyl rings are rotated by equal amounts (4.6°) about the N—phenyl and CH—phenyl bonds. However, the conformation differs significantly from that found in form II of MeMe which is not disordered (Bar & Bernstein, 1977) and in which the molecular conformation approximates that for the lowest free molecule

Table 2. *Best planes*

Equations of least-squares planes in the form $Ax + By + Cz + D = 0$, where x, y, z are fractional coordinates, with deviations of relevant atoms from the planes in Å

	A	B	C	D
Plane 1: C(1)—C(6)	0.418	0.861	0.291	9.777
Plane 2: C(8)—C(13)	0.415	0.855	0.310	10.301
Plane 3: C(4)—C(7)— C(7')—N'—N—C(8)	0.491	0.818	0.298	9.425

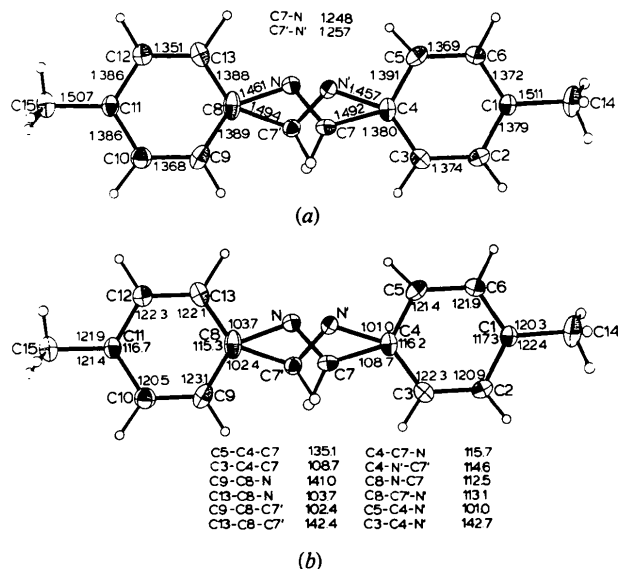


Fig. 2. (a) Bond lengths in MeMe, form I, e.s.d.'s 0.007 Å; (b) bond angles, e.s.d.'s 0.4°. The angles involving bridge atoms are provided for reference only since they are affected by the disorder (see text).

	Plane 1	Plane 2	Plane 3
C(1)	0.012 (3)	-0.210 (3)	0.094 (3)
C(2)	-0.008 (4)	-0.230 (4)	-0.043 (4)
C(3)	-0.008 (4)	-0.207 (4)	-0.090 (4)
C(4)	0.016 (3)	-0.156 (3)	-0.001 (3)
C(5)	-0.013 (4)	-0.187 (4)	0.088 (4)
C(6)	-0.004 (4)	-0.202 (4)	0.144 (4)
C(7)	0.085 (7)	-0.068 (7)	-0.008 (7)
C(7')	0.167 (9)	0.028 (9)	0.046 (9)
C(8)	0.113 (5)	0.003 (5)	-0.012 (5)
C(9)	0.107 (5)	-0.002 (5)	-0.135 (5)
C(10)	0.085 (4)	0.0 (4)	-0.202 (4)
C(11)	0.062 (3)	0.001 (3)	-0.154 (3)
C(12)	0.062 (3)	0.0 (4)	-0.037 (4)
C(13)	0.084 (4)	-0.002 (4)	0.028 (4)
C(14)	0.059 (7)	-0.189 (7)	0.195 (7)
C(15)	0.056 (5)	0.021 (5)	-0.207 (5)
N	0.077 (6)	-0.053 (6)	0.032 (6)
N'	-0.019 (8)	-0.165 (8)	-0.042 (8)

energy (Bürgi & Dunitz, 1971*b*; Bernstein, Engel & Hagler, 1981), with a torsion angle of 41.7° about the N—phenyl bond and -3.0° about the CH—phenyl bond. Thus, two of the three polymorphic forms of MeMe are planar while form II is non-planar, and this system serves as another example of conformational polymorphism (Corradini, 1973; Panagiotopoulos, Jeffrey, LaPlaca & Hamilton, 1974), in which a molecule adopts significantly different conformations in different crystal polymorphs.

The conformational energetics of benzylidene-anilines have been extensively studied, including *ab initio* calculations (Bernstein, Engel & Hagler, 1981, and references therein). They indicate that the conformation in which the aniline ring is rotated about 45° out of the plane of the remaining atoms is favored over a planar conformation by 6.57 kJ mol^{-1} . Hence in the present structure, the lattice and disorder must supply energy of this order of magnitude to stabilize this otherwise unfavorable conformation.

Packing

The packing is shown in Fig. 3; it differs significantly from the packing of the other two polymorphs of MeMe. The shortest intermolecular distance is between N' and C(3), 3.46 \AA .

The molecular volumes in forms I–III of MeMe are 307.5 , 303.0 and 289.9 \AA^3 . Since both forms I and III consist of essentially planar molecules the planarity does not seem to be a factor in the packing efficiency. The opposite case is encountered with the two polymorphs of *p*-chloro-*N*-(*p*-chlorobenzylidene)-aniline wherein the molecular volumes are essentially identical for the planar triclinic form (284.3 \AA^3) (Bernstein & Schmidt, 1972) and the non-planar orthorhombic form (284.2 \AA^3) (Bernstein & Izak, 1976). The lattice-energy minimizations which were carried out on this system (Bernstein & Hagler, 1978) favor the triclinic structure over the orthorhombic one by about 4.39 kJ mol^{-1} (6–12 potential), which is consistent with the stabilization required for the higher-energy planar molecule.

It is generally held that for polymorphic systems the higher-density material is thermodynamically more stable (*i.e.* has a higher melting point and/or heat of sublimation) (Burger & Ramberger, 1979; Kitaigor-

odskii, 1973). On this basis form III would be expected to be the most stable of the three forms and form I the least stable, yet the molecular energy for both of these is significantly higher than that in form II. Thus this polymorphic system appears to be a good test for the general applicability of the computational aspects of conformational polymorphism and the relevant calculations are currently under way.

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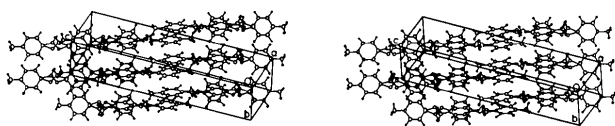


Fig. 3. Stereoscopic view of the structure in a direction perpendicular to the best plane of the bridge atoms of the reference molecule (indicated by filled circles).

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***cis*-5-Hydroxy-1,3-dimethyl-6-phenylthio-5,6-dihydrothymine,
cis-5-Hydroxy-6-(*p*-hydroxyphenyl)-1,3-dimethyl-5,6-dihydrothymine and
cis-5-Hydroxy-6-(*o*-hydroxyphenyl)-1,3-dimethyl-5,6-dihydrothymine**

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Abstract

The structures of three adducts formed by the photooxidation of dimethylthymine, with nucleophiles such as phenol and thiophenol, have been determined to help elucidate mechanistic pathways for such reactions. The reaction with thiophenol produced an adduct (I, $C_{13}H_{16}N_2O_3S$) which crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.100$ (3), $b = 11.326$ (3), $c = 11.026$ (3) Å, $\beta = 96.2$ (1)°, $Z = 4$, $V = 1378.06$ Å³ and $d_x = 1.35$ Mg m⁻³. The reaction with phenol yielded two products (II and III, $C_{13}H_{16}N_2O_4$) both of which showed unexpected carbon-carbon ring coupling indicating a different reaction mechanism from that which gave (I). (II) and (III) both crystallize in the monoclinic space group $P2_1/c$ with cell dimensions of $a = 13.056$ (4), $b = 8.317$ (3), $c = 13.478$ (6) Å, $\beta = 117.4$ (1)°, $V = 1299.35$ Å³ and $d_x = 1.35$ Mg m⁻³ for (II) and $a = 8.363$ (3), $b = 12.434$ (3), $c = 12.406$ (5) Å, $\beta = 103.6$ (1)°, $V = 1253.87$ Å³ and $d_x = 1.40$ Mg m⁻³ for (III). $Z = 4$ for both (II) and (III). Final weighted R factors were 0.055 (2240 independent reflections) for (I), 0.092 (2111 independent reflections) for (II) and 0.073 (1274 independent reflections) for (III).

Introduction

Reactions involving post-irradiation treatment of photo-oxidized pyrimidines with various nucleophiles are being studied as possible mechanistic models for the

formation of protein-nucleic acid cross-linkages (Ryang & Wang, 1978). It was expected that treating dimethylthymine in this manner with phenol and thiophenol would give analogous products. However, this did not turn out to be the case indicating that the reaction pathway is dependent upon the nature of the attacking nucleophile (Burrows, Ryang, Wang & Flippen-Anderson, 1979). The reaction with thiophenol yielded a *cis* thiophenol adduct (*cis*-5-hydroxy-1,3-dimethyl-6-phenylthio-5,6-dihydrothymine, I) as expected while the reaction with phenol gave a 3:2 mixture of *cis*-5-hydroxy-6-(*p*- or *o*-hydroxyphenyl)-1,3-dimethyl-5,6-dihydrothymine (II and III) both of which turned out to be unexpected carbon-carbon coupling products. X-ray single-crystal studies have been performed on (I), (II) and (III) and are reported here. The X-ray structure work confirmed the structures and established the stereochemistry for molecules (I) and (II). For molecule (III) the X-ray results established both the structure and the stereochemistry.

