

## Molecular Conformation and Electronic Structure.

### IV. *p*-(*N*-Methylbenzylidene)-*p*-methylaniline (Form III)

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**Abstract.**  $C_{15}H_{15}N$ , monoclinic,  $P2_1/c$ ,  $a=9.878$  (5),  $b=4.884$  (1),  $c=12.018$  (3) Å,  $\beta=90.48$  (2)°,  $D_c=1.20$  g cm<sup>-3</sup>,  $Z=2$ ,  $D_m=1.18$  g cm<sup>-3</sup>. The compound was prepared by condensation of *p*-tolualdehyde and *p*-toluidine. It is trimorphic and all three polymorphs may be obtained from ethanolic solutions from which crystals for this study were grown; m.p. 90°C, lit. 93°C (Keasling & Schueler, 1950).

**Introduction.** Lattice constants were obtained from a least-squares fit of 15  $2\theta$  values ranging between 13° and 44° (Mo  $K\alpha$ ) as determined on a diffractometer. Systematic absences were  $h0l$  with  $l$  odd and  $0k0$  with  $k$  odd. The cell constants differ from those for the same substance reported earlier (Bürgi, Dunitz & Zust, 1968) establishing that this is a different crystal form. A third polymorph has also been isolated (Bernstein & Bar, 1975) and the latter two structures (forms I and II) will be reported elsewhere.

Intensities were measured on a Syntex  $P\bar{T}$  diffractometer (Mo  $K\alpha$ , graphite monochromatized, monochromator in parallel mode,  $\theta:2\theta$  scan). 1268 reflections for which  $2\theta \leq 54.0^\circ$  were measured, and after Lorentz and polarization corrections, 416 of these had  $F_o < 2.5\sigma(F_o)$  and were considered unobserved. Absorption corrections [ $\mu(\text{Mo } K\alpha)=0.75$  cm<sup>-1</sup>] were not applied.

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971). The presence of only two molecules in the unit cell requires *crystallographic* disorder about a center of symmetry similar to that found in two other benzylideneanilines (Bernstein & Izak, 1975a; Bernstein & Schmidt, 1972). Hence the scattering factor of the two atoms at the bridge was taken to be the average of C and N. Full-matrix least-squares refinement of the heavy atoms with anisotropic temperature factors converged at  $R=0.139$ . H atoms were located in a difference map at the chemically expected positions and when included in the refinement with isotropic temperature factors led to convergence at  $R=0.117$ .

At this stage the geometry of the benzene ring was

normal but the bond C(4)-X† was longer by 0.3 Å than the expected value of 1.47 Å. The difference map exhibited two peaks in the vicinity of the bridge, suggesting an additional *positional* disorder resembling that found in *p*-azotoluene (Brown, 1966) with which this polymorph is isostructural. Evidence for a similar type of positional disorder has been observed for one of the two crystallographically independent molecules in the structure of *trans*-stilbene (Hoekstra, Meertens & Vos, 1975). Anisotropic temperature factors are apparently sufficient to account for the small displacements due to disorder in the atoms of the benzene ring and the methyl group, but the bridge atom was assigned two orientations with occupancies corresponding to the positions and peak heights on the difference map. Subsequent least-squares refinement (including alternately occupancy and temperature factors for the disordered atoms) led to  $R=0.093$  (isotropic disordered atoms, others as above) and  $R=0.078$  (anisotropic disordered atoms,  $R=0.093$  including unobserveds),  $R_w=0.021$ . The anisotropic refinement of the disordered bridge atoms was required to remove a difference density peak of  $ca\ 0.8\ e\ \text{\AA}^{-3}$  which appeared between the two atom positions after the isotropic refinement. A difference map based on the final parameters did not exceed  $0.3\ e\ \text{\AA}^{-3}$  at any point. H atoms on the bridge were not located.

The function minimized was  $\sum w(|kF_o|^2 - |F_c|^2)^2$  with weights  $w=1.0/\sigma^2(F_o^2)$ . Scattering factors were taken from *International Tables for X-ray Crystallography* (1968), and computer programs used were *ORTEP* (Johnson, 1965) and locally modified versions of *ORFLS* (Busing, Martin & Levy, 1962) and *FORDAP* (Zalkin, 1962). The final positional and thermal parameters are listed in Table 1; bond lengths and angles are given in Fig. 1 and Table 2.†

†  $X=(C+N)/2$  and is used to designate the heavy atoms in the bridge.

‡ A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31648 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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Table 1. *Final positional 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 atoms to which they are bonded. Anisotropic thermal parameters 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,  $\exp[-8\pi^2 U \sin^2 \theta/\lambda^2]$ .

	<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>
X(1A)*	5438 (5)	9335 (10)	-328 (4)	293 (27)	451 (28)	580 (32)	66 (24)	-70 (24)	66 (24)
X(1B)†	5064 (7)	9392 (13)	453 (6)	265 (33)	293 (37)	746 (64)	41 (33)	81 (35)	-161 (41)
C(1)	8103 (3)	3388 (6)	1140 (3)	264 (18)	285 (16)	473 (21)	-20 (16)	-15 (16)	-92 (16)
C(2)	7133 (4)	4459 (7)	1846 (3)	393 (22)	467 (21)	586 (26)	28 (20)	-36 (21)	43 (21)
C(3)	6211 (4)	6410 (8)	1473 (4)	333 (22)	467 (23)	1031 (37)	98 (21)	-194 (26)	17 (24)
C(4)	6235 (4)	7335 (7)	385 (4)	377 (23)	320 (20)	1147 (38)	-7 (19)	88 (24)	-381 (25)
C(5)	7189 (4)	6225 (9)	-325 (4)	506 (25)	538 (25)	740 (28)	-30 (22)	169 (23)	-233 (23)
C(6)	8098 (4)	4302 (8)	49 (3)	426 (23)	480 (22)	497 (23)	26 (20)	40 (19)	-56 (19)
C(7)	9106 (4)	1293 (9)	1538 (4)	413 (23)	376 (21)	682 (30)	115 (20)	-8 (22)	-129 (22)

\* Occupancy 0.6.

† Occupancy 0.4.

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub>
H(2)	716 (4)	398 (9)	263 (3)	46 (13)
H(3)	566 (4)	714 (8)	203 (3)	43 (14)
H(5)	698 (5)	698 (9)	-119 (4)	90 (17)
H(6)	878 (4)	330 (8)	-51 (3)	42 (12)
H(7a)	934 (5)	133 (12)	230 (5)	97 (21)
H(7b)	894 (6)	-57 (15)	138 (5)	123 (28)
H(7c)	977 (6)	94 (13)	110 (5)	104 (24)

Table 2. *Geometric features of the bridge atoms (average values)*

C(4)-X	1.525 Å	C(3)-C(4)-X	117.6°
-X'	1.294	C(5)-C(4)-X	124.2
		C(4)-X-X'	109.0

**Discussion.** This study was undertaken as part of a series of structure determinations of benzylideneanilines designed ultimately to investigate the relationship between molecular conformation and electronic structure (Bernstein & Izak, 1975*b*; Eckhardt & Bernstein, 1972). The structure is of further interest since this compound represents a good example of *conformational polymorphism* (Panagiotopoulos, Jeffrey, LaPlaca & Hamilton, 1974).

The ORTEP plot of the molecule (Fig. 1), including the disordered bridge atoms, suggests, on the basis of the magnitudes and directions of the components of the thermal ellipsoids, that the two positions of the asymmetric unit due to the static *positional* disorder may be obtained by a rotation of the asymmetric unit about an axis perpendicular to the benzene ring and passing nearly through C(1). If the axis were to pass through the center of the ring, C(7) would be expected to exhibit disorder similar to X.

The geometric features of the ring (not corrected for rigid-body motion), including the C(1)-C(7) length, correspond to those expected for methyl-substituted benzene rings (Domenicano, Vaciago & Coulson, 1975). The average C-H distance (including methyl) is  $0.98 \pm 0.06$  Å.

The geometric features of the bridge atoms (Table 2) differ from other benzylideneanilines (Bernstein &

Table 3. *Plane of all heavy atoms in one ring and deviations (Å) from the plane*

$$6.287x + 3.551y + 3.028z - 6.639 = 0$$

*x, y, z* are fractional coordinates.

Atoms included in calculation	Others
C(1) 0.005	C(7) 0.012
C(2) -0.011	C(1') 0.108
C(3) -0.011	C(2') 0.123
C(4) 0.003	C(3') 0.124
C(5) -0.007	C(4') 0.110
C(6) -0.005	C(5') 0.119
	C(6') 0.117
	C(7') 0.101

Izak, 1975*b*) but the significance of these differences is questionable due to the disorder in the structure.

Crystallographic site symmetry (*i*) requires that the two phenyl rings in one molecule be parallel, but not necessarily coplanar. The displacements of the atoms of the second ring from the plane the first are given in Table 3. The planar conformation is similar to that in the di-*para*-substituted bromo and chloro (triclinic, metastable) derivatives (Bernstein & Izak, 1975*a*; Bernstein & Schmidt, 1972) but differs significantly from that found in other benzylideneaniline derivatives (Bürgi & Dunitz, 1970; Bernstein & Izak, 1975*b*) and at least one of the other two polymorphs of the title compound (Bernstein & Bar, 1975), all of which are non-planar. This benzylideneaniline structure, however, is the first one in which *positional* disorder is found in addition to the *crystallographic* disorder about a pseudo molecular center. The appearance of the latter mode of disorder in three compounds with identical modes of substitution but different substituents (Cl, Br,

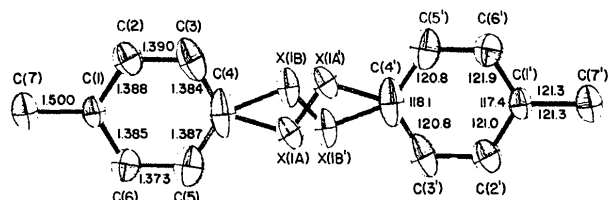


Fig. 1. ORTEP plot of the molecule. Geometric features of the bridge atoms are given in Table 2.

methyl) suggests, at least, a near isotropy of crystal forces around the center of the molecule, with the sum of intermolecular forces being of a magnitude estimated to be about 2 kcal mol<sup>-1</sup> (Bürgi & Dunitz, 1971), sufficient to compensate for the preference of the non-planar conformation over the planar one.

### References

- BERNSTEIN, J. & BAR, I. (1975). Unpublished results.  
 BERNSTEIN, J. & IZAK, I. (1975a). *J. Cryst. Mol. Struct.* In the press.  
 BERNSTEIN, J. & IZAK, I. (1975b). *J. Chem. Soc. Perkin II*. In the press.  
 BERNSTEIN, J. & SCHMIDT, G. M. J. (1972). *J. Chem. Soc. Perkin II*, pp. 951–955.  
 BROWN, C. J. (1966). *Acta Cryst.* **21**, 153–158.  
 BÜRGI, H. B. & DUNITZ, J. D. (1970). *Helv. Chim. Acta*, **52**, 1747–1764.  
 BÜRGI, H. B. & DUNITZ, J. D. (1971). *Helv. Chim. Acta*, **54**, 1255–1260.  
 BÜRGI, H. B., DUNITZ, J. D. & ZUST, C. (1968). *Acta Cryst.* **B24**, 463–464.  
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.  
 DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). *Acta Cryst.* **B31**, 221–234.  
 ECKHARDT, C. J. & BERNSTEIN, J. (1972). *J. Amer. Chem. Soc.* **94**, 3247–3249.  
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *MULTAN: A Computer Program for the Automatic Solution of Crystal Structures*.  
 HOEKSTRA, A., MEERTENS, P. & VOS, A. (1975). *Acta Cryst.* **B31**, 2813–2817.  
*International Tables for X-ray Crystallography* (1968). Vol. III, pp. 201–207. Birmingham: Kynoch Press.  
 JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.  
 KEASLING, H. H. & SCHUELER, F. W. (1950). *J. Amer. Pharm. Assoc.* **39**, 87–90.  
 PANAGIOTOPOULOS, N. C., JEFFREY, G. A., LAPLACA, S. J. & HAMILTON, W. C. (1974). *Acta Cryst.* **B30**, 1421–1430.  
 ZALKIN, A. L. (1962). *FORDAP: A Fourier Synthesis Program*. Lawrence Radiation Laboratories, Livermore, California.

*Acta Cryst.* (1976). **B32**, 1611

## A Cobalt (III) Complex with 1-(2-Thiazolylazo)-2-naphthol, [Co<sup>III</sup>(C<sub>13</sub>H<sub>8</sub>N<sub>3</sub>OS)<sub>2</sub>](Cl, I) · 2CHCl<sub>3</sub>

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**Abstract.** [Co<sup>III</sup>(C<sub>13</sub>H<sub>8</sub>N<sub>3</sub>OS)<sub>2</sub>](Cl<sub>0.7</sub>I<sub>0.3</sub>) · 2CHCl<sub>3</sub>, monoclinic, *P*2<sub>1</sub>/*a*, *a* = 16.487 (4), *b* = 21.750 (3), *c* = 10.045 (3) Å, β = 108.89 (3)°, *U* = 3408.1 Å<sup>3</sup>; *Z* = 4, *D<sub>m</sub>* = 1.69, *D<sub>c</sub>* = 1.69 g cm<sup>-3</sup>; μ = 9.9 cm<sup>-1</sup> (for Mo *K*α); *R* = 0.087 for 1125 reflexions collected by diffractometry. The cobalt atom is surrounded octahedrally by two terdentate ligands in the *mer* configuration. The 1-(2-thiazolylazo)-2-naphtholato group is coordinated to the cobalt atom through the phenolic oxygen atom, the azo nitrogen atom adjacent to the naphthol ring and the thiazole nitrogen atom, forming two five-membered chelate rings.

**Introduction.** As a part of a series of studies on the structures of metal chelates with 1-(2-thiazolylazo)-2-naphthol ('Htan'), the X-ray determination of the title compound was undertaken. A powder sample of [Co<sup>III</sup>(tan)<sub>2</sub>](Cl, I) was kindly supplied by Dr A. Kawase. Small green crystals of the complex were obtained from a chloroform solution by slow evaporation. The crystal used for the X-ray study had dimensions of 0.06 × 0.06 × 0.25 mm. Both the determination of cell constants and the collection of intensity data were carried out on a Rigaku automated four-circle diffractometer using Mo *K*α radiation monochromated with a graphite plate. The ω–2θ scan technique was

employed at a scan rate of 4° min<sup>-1</sup> in ω. The scan ranges were determined according to the formula 1.5° + 0.6° × tan θ. The background countings were taken at both sides of each peak for 10 s. Intensities were converted to the structure amplitudes in the usual manner, but an absorption correction was not applied. Thus 1125 independent reflexions with |*F*| > 3σ(|*F*|) were obtained.

The structure was solved by the heavy-atom method. Initially it was assumed that the crystal contained only chloride ions. On this supposition the structure was refined by the least-squares technique to give

Table 1. *Positional* (× 10<sup>4</sup>) and *thermal parameters*  
(a) Fractional atomic coordinates and isotropic temperature factors for the non-hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
O	1002 (14)	2670 (10)	1924 (22)	4.6 (5)
Co	639 (3)	2099 (2)	407 (5)	
Cl, I	3499 (4)	4797 (3)	4552 (7)	
S	1409 (7)	679 (5)	-1845 (11)	
S'	-1011 (7)	1102 (5)	2167 (11)	
Cl(1)	1354 (10)	5436 (7)	569 (15)	
Cl(2)	1490 (10)	4117 (7)	624 (16)	
Cl(3)	869 (11)	4748 (8)	2551 (22)	
Cl(1')	2234 (14)	3917 (8)	7013 (21)	
Cl(2')	1688 (21)	5125 (15)	6759 (28)	
Cl(3')	3214 (21)	4825 (12)	8502 (28)	