C₁₄H₁₅NO

C1—C2—C6—C7	2.3 (3)	C6—C7—C10—C1	−54.5 (2)
C1—C2—C6—C5	122.0 (2)	C8—C7—C10—C1	56.0 (3)
C1—C2—O3—N4	−117.3 (3)	C6—C7—C8—C9	69.6 (3)
O3—C2—C6—C7	−115.5 (2)	C10—C7—C8—C9	−37.0 (3)
O3—C2—C6—C5	4.2 (3)	C7—C8—C9—C1	2.2 (3)
C6—C2—O3—N4	−4.6 (3)	C5—C51—C56—C55	−179.8 (3)
C2—O3—N4—C5	3.1 (3)	C5—C51—C52—C53	179.9 (3)
O3—N4—C5—C6	−0.1 (3)	C52—C51—C56—C55	−0.2 (5)
O3—N4—C5—C51	179.3 (2)	C56—C51—C52—C53	0.3 (5)
N4—C5—C6—C2	−2.7 (3)	C51—C52—C53—C54	0.7 (6)
N4—C5—C51—C52	−4.8 (4)	C52—C53—C54—C55	−1.7 (6)
N4—C5—C51—C56	174.8 (3)	C53—C54—C55—C56	1.8 (6)
N4—C5—C6—C7	106.6 (3)	C54—C55—C56—C51	−0.8 (5)

Structure solution was by direct methods using *DIRDIF* (Beurskens *et al.*, 1990). Non-H atoms were located with *DIRDIF* using the *ORIENT* option with the norbornane rigid group, taken from *DIRDIF ORBASE*, as an input model. Refinement was performed by full-matrix least squares using *SHELX*76 (Sheldrick, 1976). All the non-H atoms were refined with anisotropic displacement parameters. H atoms were located from a difference Fourier map and fixed at a distance of 0.95 Å from their parent atom. H atoms were included in the structure-factor calculations and given displacement parameters equal to $1.1U_{eq}$ of their parent atom, but their parameters were not refined. *PARST* (Nardelli, 1983) was used for molecular geometry calculations and molecular graphics were prepared using *PLUTO* (Motherwell & Clegg, 1978).

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Influence of Crystal Environment on Molecular Conformation: p-Bromo-N-(p-dimethylaminobenzylidene)aniline

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Abstract

p-Bromo-N-(p-dimethylaminobenzylidene)aniline, $C_{15}H_{15}BrN_2$, (1), comprises two independent molecules with markedly different conformations. Molecule *A* is essentially planar along its entire length (including the dimethylamino group) whereas molecule *B* deviates considerably from planarity with an interplanar angle of 145.8 (3)° between the two phenyl rings and the NMe₂ group twisted by 10 (2)° out of the plane of the phenyl ring to which it is bound. While polymorphism and crystal packing effects are well documented for benzylidene derivatives, this is an interesting example with two quite distinct conformations in the same crystal phase. The differences are accounted for in terms of crystal-packing effects. The structure highlights the ability of particular molecular arrangements to stabilize a less favourable molecular conformation.

Comment

Recently, we embarked on a programme to develop molecular materials which exhibit non-linear optical properties (Houlton, Jassim, Roberts, Silver, McArdle, Cunningham & Higgins, 1992; Houlton, Miller, Silver, Jassim, Ahmet, Axon, Bloor & Cross, 1993). Two classes of compound have been considered: organometallic and organic derivatives.

Compounds in the latter class have been based on benzylidene and contain the dimethylamino donor group and a range of p-aniline acceptor groups. This type of compound has been predicted, on the basis of MO calculations, to have a small dipole moment but large hyperpolarizability (Tsunekawa, Gotoh, Mataki, Kondoh, Fukuda & Iwamoto, 1990).

Previous studies have used benzylidene derivatives in order to produce materials with useful optical properties, e.g. considerable second harmonic generation has been observed for N-(4-nitrobenzylidene)-3-acetamido-4-methoxyaniline (Tsunekawa, Gotoh, Mataki, Kondoh, Fukuda & Iwamoto, 1990). Studies of the liquid-crystalline properties of a number of derivatives have also been reported (Leadbetter, Mazid, Kelly, Goodby & Gray, 1979; Bryan & Forcier, 1980; Gane & Leadbetter, 1981).

There have been a number of structural studies on N-benzylideneaniline and its substituted derivatives as they provide useful models for the investigation of molecular geometry and electronic or crystal-packing modes (Bürgi & Dunitz, 1970; Bernstein, 1972; Bernstein & Schmidt, 1972; Bernstein & Izak, 1976; Nakai, Shiro, Ezumi, Sakato & Kubota, 1976). In addition to the wide range of geometries exhibited by different derivatives, polymorphism is also observed (Bernstein & Hagler, 1978; Hagler & Bernstein, 1978; Bernstein, Anderson & Eckhardt, 1979; Bar & Bernstein, 1984, 1987).

Here we report the crystal and molecular structure of p-bromo-N-(p-dimethylaminobenzylidene)aniline (1) and discuss the result, which is unexpected, by comparison with known related structures. Fig. 1

Br—⟨benzene ring⟩—N=CH—⟨benzene ring⟩—NMe$_2$

(1)
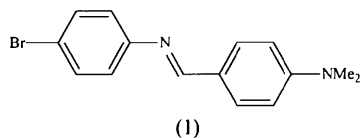
shows the appropriate numbering schemes for molecules A and B of (1). All corresponding bond lengths in molecules A and B are the same to within experimental error. However, the conformations of the two molecules are markedly different. A number of other benzylidene derivatives also exhibit independent molecules in their unit cells, notably N-benzylidene-p-bromoaniline and N-(p-dimethyl-aminobenzylidene)-p-nitroaniline; however, in these compounds the unique molecules do not exhibit significantly different geometries. Packing effects were cited to explain the differences in molecular geometry in N-(p-dimethylaminobenzylidene)-p-nitroaniline. The angles α and β are used in the discussion of N-benzylideneaniline structures; these are defined as the angles between the four atoms in the bridge and the aniline (α) and benzyl (β) rings. In (1) the bridge atoms are C(4), N(1), C(7), C(8)

(molecule A) and C(24), N(3), C(27), C(28), (molecule B). Values for these angles typically range from 0 to 55° for α and -26 to 6° for β (Bernstein & Izak, 1976). In (1), α and β fall within this range with $\alpha = 3$ (7), 28.9 (5) and $\beta = 3$ (6), -6.6 (1.7)° for molecules A and B, respectively. By comparison, N-benzylidene-p-bromoaniline has angles of $\alpha = 39.0$, 46.2° and $\beta = -11.1$, -9.4°, and for N-(p-dimethylaminobenzylidene)-p-nitroaniline $\alpha = 41.5$, 49.0°, $\beta = -11.4$, -7.7°. Clearly some explanation is needed to account for the very different conformations observed for (1).
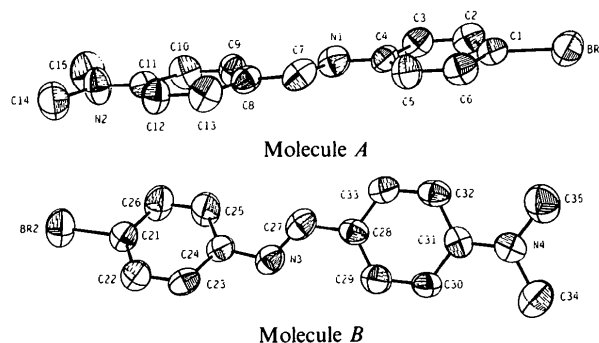

Molecule A

Molecule B

Fig. 1. Molecular structure of p-bromo-N-(p-dimethylamino-benzylidene)aniline (1) showing the atomic numbering scheme for molecules A and B. Displacement ellipsoids are drawn at the 50% probability level.

Nakai, Shiro, Ezumi, Sakato & Kubota (1976) have discussed two intramolecular charge-transfer mechanisms for N-benzylideneanilines which contain donor and acceptor groups that influence the molecular conformation. Type (I) is due to the contributions of the quinoid structure through charge transfer from donor to acceptor groups whereas type (II) involves charge transfer from the bridge-N-atom lone-pair electrons to the acceptor group. These two mechanisms are maximized by different geometries; type (I) is facilitated by a planar arrangement, i.e. decreasing the twist angle, while type (II) increases with increased twist. An additional factor is the steric interaction between the ortho H atom of the aniline ring and the CH bridge H atom. However, a number of the known structures are essentially planar, suggesting that the interaction is not sufficiently large to prevent such conformations.

A comparison of the bond lengths in (1) and other derivatives is quite instructive. The bridge bond lengths of (1) and N-(p-bromobenzylidene)-p-bromoaniline are the same. When compared with N-benzylideneaniline, (1) shows some degree of resonance with the quinoid form with appropriate lengthening and shortening of alternate bonds. The C=N bond length in N-benzylidene-p-bromoaniline is slightly longer than in (1), especially when the average of the

two independent molecules is calculated. The most directly comparable derivative is N-(p-dimethyl-aminobenzylidene)-p-nitroaniline in which the three averaged bridge-bond lengths are C—N = 1.399 (3), N=C = 1.279 (4) and C—C = 1.452 (3) Å. These are alternately short, long and short compared with (1) and demonstrate the considerably stronger electron-withdrawing nature of the NO_2 group relative to Br; they also indicate considerable resonance in the N-(p-dimethylaminobenzylidene)-p-nitroaniline derivative, despite the non-planar arrangement between donor and acceptor groups. From these comparisons it appears that the bromophenyl group is not particularly electron withdrawing, but some evidence for resonance is seen in both A- and B-type molecules.

Table 3 contains short intermolecular distances that are defined as A···A, B···B and A···B-type contacts, the majority of which are A···B. There are no non-H-atom B···B contacts of <3.7 Å. Molecules of type A are involved in a head-to-tail interaction between Br(1) and H(141) of 3.001 (8) Å. This distance is less than the sum of van der Waals radii and represents a $\delta^+\cdots\delta^-$ interaction. It is perhaps significant that it is the planar molecule A that has the head-to-tail interaction as this has the greater potential for resonance between the donor and acceptor groups, although this is not discernible from the bond lengths.

Ab initio calculations have been performed on N-benzylideneaniline and a number of model compounds (Bernstein, Engel & Hagler, 1981). It was shown that rotations of up to 45° in α were stabilizing, while those in β were destabilizing. These results explain the smaller range of β values observed compared to α. Hence, non-planar geometries are the more stable free-molecule conformations, although planar structures can be stabilized by the crystal environment.

In (1), the difference in energy between the two quite extreme examples of conformation in the crystal cannot be large. It is suggested that the most stable molecular conformation for (1) is close to that of B. The almost planar geometry of A is a result of crystal forces stabilizing the geometry, an example of which is the $\delta^+\cdots\delta^-$ interaction between Br(1) and H(141) shown in Fig. 2. This compound demonstrates the ability of the crystalline phase to support quite different molecular geometries in the same crystal.
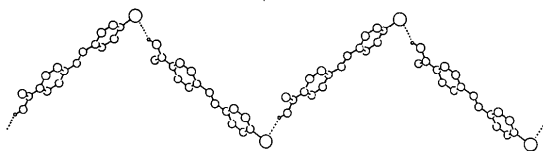

Fig. 2. Head-to-tail alignment of A, viewed down the c axis.

Experimental

Crystal data

$C_{15}H_{15}BrN_2$	Mo $K\alpha$ radiation
$M_r = 303.21$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/c$	reflections
$a = 10.778$ (2) Å	$\theta = 16–22°$
$b = 23.669$ (10) Å	$\mu = 2.97$ mm^{-1}
$c = 11.483$ (2) Å	$T = 293$ K
$\beta = 111.57$ (1)°	Needle
$V = 2724.2$ Å^3	$1 \times 0.25 \times 0.13$ mm
$Z = 8$	Yellow
$D_x = 1.48$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.02$
diffractometer	$\theta_{max} = 25°$
ω–2θ scans	$h = -12 \rightarrow 12$
Absorption correction:	$k = -28 \rightarrow 28$
none	$l = -14 \rightarrow 14$
11679 measured reflections	3 standard reflections
6706 independent reflections	frequency: 120 min
2440 observed reflections	intensity variation: 2%
$[I > 3.0\sigma(I)]$	

Refinement

Refinement on F	$w = 1/[\sigma^2(F) + (0.02F)^2 + 1]$
$R = 0.037$	(Killean & Lawrence,
$wR = 0.044$	1969)
$S = 0.575$	$(\Delta/\sigma)_{max} < 0.03$
2440 reflections	$\Delta\rho_{max} = 0.51$ (6) e Å^{-3}
325 parameters	$\Delta\rho_{min} = -0.15$ (6) e Å^{-3}
H-atom parameters not	Atomic scattering factors
refined	from *International Tables*
	for X-ray Crystallography
	(1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Br(1)	0.05293 (8)	0.29038 (3)	0.65807 (7)	5.73 (2)
Br(2)	−0.57222 (8)	−0.26768 (4)	0.27578 (7)	6.65 (2)
N(1)	−0.2784 (5)	0.0952 (2)	0.3587 (5)	5.0 (1)
N(2)	−0.6836 (6)	−0.1085 (2)	0.0977 (5)	5.9 (2)
N(3)	−0.1835 (5)	−0.1040 (2)	0.6362 (4)	4.6 (1)
N(4)	0.1931 (6)	0.1027 (2)	0.9281 (5)	5.6 (2)
C(1)	−0.0540 (6)	0.2305 (3)	0.5634 (5)	4.3 (2)
C(2)	−0.0292 (6)	0.2062 (3)	0.4660 (6)	4.8 (2)
C(3)	−0.1044 (6)	0.1625 (3)	0.4011 (5)	4.7 (2)
C(4)	−0.2105 (6)	0.1411 (2)	0.4309 (5)	4.2 (2)
C(5)	−0.2339 (6)	0.1668 (3)	0.5290 (6)	4.8 (2)
C(6)	−0.1586 (6)	0.2103 (3)	0.5953 (5)	4.9 (2)
C(7)	−0.3748 (7)	0.0733 (3)	0.3758 (6)	5.2 (2)
C(8)	−0.4492 (6)	0.0251 (3)	0.3058 (6)	4.7 (2)
C(9)	−0.4173 (6)	−0.0024 (3)	0.2149 (6)	5.1 (2)
C(10)	−0.4916 (7)	−0.0462 (3)	0.1461 (6)	5.6 (2)

C(11)	−0.6069 (6)	−0.0661 (3)	0.1667 (6)	4.5 (2)
C(12)	−0.6366 (7)	−0.0387 (3)	0.2609 (6)	5.1 (2)
C(13)	−0.5613 (7)	0.0049 (3)	0.3271 (6)	5.5 (2)
C(14)	−0.7990 (8)	−0.1281 (4)	0.1221 (7)	7.4 (2)
C(15)	−0.6576 (9)	−0.1342 (3)	−0.0048 (7)	7.5 (2)
C(21)	−0.4545 (6)	−0.2149 (3)	0.3856 (6)	4.8 (2)
C(22)	−0.4377 (6)	−0.2132 (3)	0.5094 (5)	4.8 (2)
C(23)	−0.3515 (6)	−0.1756 (3)	0.5883 (5)	4.7 (2)
C(24)	−0.2772 (6)	−0.1387 (3)	0.5469 (5)	4.2 (2)
C(25)	−0.2971 (7)	−0.1408 (3)	0.4200 (6)	6.2 (2)
C(26)	−0.3836 (7)	−0.1785 (3)	0.3402 (6)	6.5 (2)
C(27)	−0.1522 (6)	−0.0570 (3)	0.6032 (6)	4.7 (2)
C(28)	−0.0552 (6)	−0.0178 (3)	0.6875 (5)	4.3 (2)
C(29)	0.0166 (6)	−0.0303 (3)	0.8121 (6)	4.8 (2)
C(30)	0.0994 (6)	0.0087 (3)	0.8907 (6)	4.8 (2)
C(31)	0.1143 (6)	0.0625 (3)	0.8485 (6)	4.4 (2)
C(32)	0.0419 (6)	0.0744 (3)	0.7214 (6)	4.7 (2)
C(33)	−0.0371 (6)	0.0346 (3)	0.6446 (6)	5.0 (2)
C(34)	0.2681 (8)	0.0905 (3)	1.0585 (7)	6.4 (2)
C(35)	0.1923 (8)	0.1603 (3)	0.8910 (7)	6.9 (2)

Table 2. Selected geometric parameters (Å, °)

Br(1)—C(1)	1.897 (7)	C(8)—C(9)	1.38 (1)
Br(2)—C(21)	1.893 (7)	C(8)—C(13)	1.40 (1)
N(1)—C(4)	1.401 (8)	C(9)—C(10)	1.37 (1)
N(1)—C(7)	1.239 (9)	C(10)—C(11)	1.43 (1)
N(2)—C(11)	1.356 (9)	C(11)—C(12)	1.396 (9)
N(2)—C(14)	1.45 (1)	C(12)—C(13)	1.36 (1)
N(2)—C(15)	1.441 (9)	C(21)—C(22)	1.367 (9)
N(3)—C(24)	1.409 (8)	C(21)—C(26)	1.38 (1)
N(3)—C(27)	1.262 (8)	C(22)—C(23)	1.362 (9)
N(4)—C(31)	1.375 (9)	C(23)—C(24)	1.382 (9)
N(4)—C(34)	1.44 (1)	C(24)—C(25)	1.39 (1)
N(4)—C(35)	1.43 (1)	C(25)—C(26)	1.37 (1)
C(1)—C(2)	1.368 (9)	C(27)—C(28)	1.47 (1)
C(1)—C(6)	1.392 (9)	C(28)—C(29)	1.385 (9)
C(2)—C(3)	1.356 (9)	C(28)—C(33)	1.375 (9)
C(3)—C(4)	1.404 (9)	C(29)—C(30)	1.37 (1)
C(4)—C(5)	1.382 (9)	C(30)—C(31)	1.393 (9)
C(5)—C(6)	1.36 (1)	C(31)—C(32)	1.408 (9)
C(7)—C(8)	1.46 (1)	C(32)—C(33)	1.36 (1)
C(4)—N(1)—C(7)	121.1 (7)	N(1)—C(7)—C(8)	124.3 (7)
C(11)—N(2)—C(14)	120.5 (7)	C(4)—C(7)—C(8)	155.7 (6)
C(11)—N(2)—C(15)	122.1 (7)	C(7)—C(8)—C(9)	123.3 (7)
C(14)—N(2)—C(15)	117.4 (7)	C(7)—C(8)—C(13)	120.3 (7)
C(24)—N(3)—C(27)	119.7 (6)	C(9)—C(8)—C(13)	116.4 (7)
C(31)—N(4)—C(34)	121.6 (6)	C(8)—C(9)—C(10)	122.6 (7)
C(31)—N(4)—C(35)	121.9 (7)	C(9)—C(10)—C(11)	120.9 (7)
C(34)—N(4)—C(35)	116.1 (7)	N(2)—C(11)—C(10)	121.8 (7)
Br(1)—C(1)—C(2)	121.5 (6)	N(2)—C(11)—C(12)	122.2 (7)
Br(1)—C(1)—C(6)	119.1 (6)	C(10)—C(11)—C(12)	116.0 (7)
C(2)—C(1)—C(6)	119.4 (7)	C(11)—C(12)—C(13)	121.7 (7)
C(1)—C(2)—C(3)	120.9 (7)	C(8)—C(13)—C(12)	122.4 (7)
C(2)—C(3)—C(4)	121.1 (7)	Br(2)—C(21)—C(22)	120.9 (6)
N(1)—C(4)—C(3)	115.6 (6)	Br(2)—C(21)—C(26)	119.4 (6)
N(1)—C(4)—C(5)	127.7 (7)	C(22)—C(21)—C(26)	119.7 (7)
N(1)—C(4)—C(7)	27.5 (3)	C(21)—C(22)—C(23)	120.6 (7)
C(3)—C(4)—C(5)	116.7 (6)	C(22)—C(23)—C(24)	121.6 (6)
C(3)—C(4)—C(7)	143.0 (6)	N(3)—C(24)—C(23)	117.9 (6)
C(5)—C(4)—C(7)	100.2 (5)	N(3)—C(24)—C(25)	125.1 (7)
C(4)—C(5)—C(6)	122.6 (7)	C(23)—C(24)—C(25)	116.9 (7)
C(1)—C(6)—C(5)	119.2 (7)	C(24)—C(25)—C(26)	121.8 (7)
N(1)—C(7)—C(4)	31.4 (4)	C(21)—C(26)—C(25)	119.5 (7)
N(3)—C(27)—C(28)	124.4 (7)	N(4)—C(31)—C(30)	121.6 (7)
C(27)—C(28)—C(29)	122.7 (7)	N(4)—C(31)—C(32)	121.5 (7)
C(27)—C(28)—C(33)	119.7 (7)	C(30)—C(31)—C(32)	116.9 (7)
C(29)—C(28)—C(33)	117.5 (7)	C(31)—C(32)—C(33)	120.7 (6)
C(28)—C(29)—C(30)	121.3 (7)	C(28)—C(33)—C(32)	122.2 (7)
C(29)—C(30)—C(31)	121.2 (7)		

Table 3. Intermolecular distances (Å)

Br(1)···N(3^i)	3.371 (9)	A···B
Br(1)···C(23^i)	3.544 (8)	A···B
Br(1)···H(141^{ii})	3.001 (8)	A···A
Br(1)···H(23^i)	3.111 (8)	A···B
Br(1)···H(3^{iii})	3.282 (8)	A···A

Br(2)···C(4^{iv})	3.427 (9)	A···A
Br(2)···C(5^{iv})	3.696 (9)	B···A
Br(2)···H(23^v)	3.392 (8)	B···B
Br(2)···H(6^{vi})	3.183 (8)	B···A
N(1)···H(152^{vii})	3.191 (7)	A···A
N(2)···H(30^{viii})	3.139 (9)	A···B
N(3)···C(3^{ix})	3.566 (11)	B···A
N(3)···H(3^{ix})	2.965 (7)	B···A
N(3)···H(13^{vi})	3.076 (8)	B···A

Symmetry codes: (i) $-x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $-1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $-1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (v) $x, -\frac{1}{2} - y, z - \frac{1}{2}$; (vi) $-1 - x, -y, 1 - z$; (vii) $-1 - x, -y, -z$; (viii) $x - 1, y, z - 1$; (ix) $-x, -y, 1 - z$.

The cell dimensions were determined from the setting angles of 25 reflections in the range $9 < \theta < 14°$ and refined after setting of 25 reflections in the range $16 < \theta < 22°$. Data collection was carried out by the *NEEDLE* method (Enraf–Nonius, 1990) in which each collection was carried out at an azimuthal angle (ψ) calculated to minimize absorption by minimizing the path of X-rays through the crystal. Lorentz and polarization corrections were applied to the data. The structure was determined by direct methods using *SHELXS*86 (Sheldrick, 1985) and refined by least-squares methods using anisotropic displacement parameters for all non-H atoms. All H atoms were included in calculated positions.

Computations were carried out on a MicroVAX using *SHELXS*86 (Sheldrick, 1985) and *MolEN* (Fair, 1990). Diagrams were drawn with *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data and torsion angles have been deposited with the IUCr (Reference: HU1034). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Novel Modification of *trans-p,p'*-Dibromoazobenzene

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Abstract

The X-ray crystal structure of the second polymorphic modification of the title compound, $C_{12}H_8Br_2N_2$, was studied at 150 K, revealing essentially the same molecular geometry but different crystal packing, similar to that in the chloro and methyl analogues.

Comment

The crystal structure of *trans-p,p'*-dibromoazobenzene, (1), studied by Amit & Hope (1966), appeared to be entirely different from that of *trans-p,p'*-dichloroazobenzene, (2) (Hope & Victor, 1969), notwithstanding the structural similarity between Cl and Br (see Table 1). We report here another polymorphic modification of (1), obtained as a by-product during our studies of thionitroso compounds. Dark-yellow crystals, (1b), obtained by slow evaporation of a hexane/CH_2Cl_2 solution of (1), are isostructural with (2) and *p*-azotoluene (Brown, 1966b), but unlike the latter, exhibit no signs of disorder. In the residual elec-
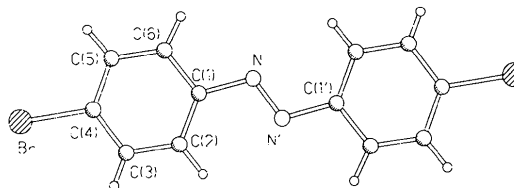
Table 1. *Unit-cell parameters* (Å, °) *of compounds* $(RC_6H_4N{=})_2$

In all cases, space group $P2_1/c$, $Z = 2$.

Compound	R	a	b	c	β	Reference
(1a)	Br	4.01	5.88	24.69	92.6	Amit & Hope (1966)
(1b)	Br	10.105	4.757	11.677	92.09	This work
(2)	Cl	9.817	4.708	11.710	91.12	Hope & Victor (1969)
(3)	Me	9.713	4.850	11.914	91.0	Brown (1966a)

tron density map, the two highest peaks of 0.8 e Å^{-3} in the vicinity of the Br atom are apparently termination waves, other features are below 0.4 e Å^{-3}.

(1)
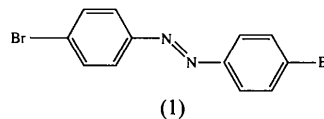
The molecule of (1) occupies a special position at the inversion centre (Fig. 1) and is essentially planar, similar to (1a) and (2), but not to the molecule of unsubstituted azobenzene which is twisted by 17° around the C—N bonds (Brown, 1966a; Bouwstra, Schouten & Kroon, 1983). Parallel molecules of (1) form stacks along the *y* direction (Fig. 2), with an interplanar separation of 3.45 Å; the azo moieties overlap with the benzene

Fig. 1. Atomic numbering scheme for (1b); primed atoms are symmetrically related *via* an inversion centre.
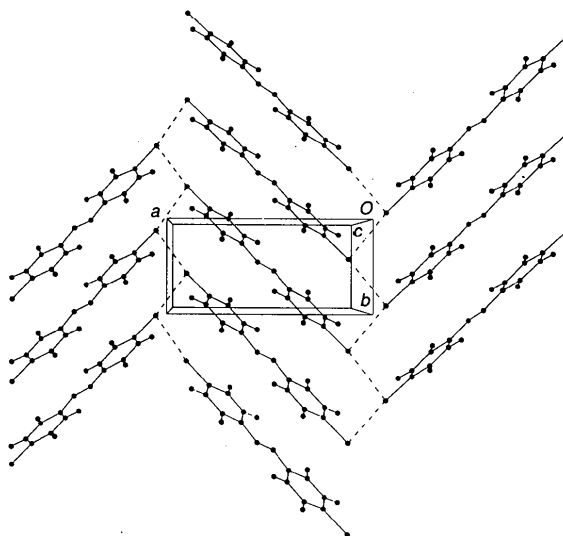

Fig. 2. Crystal packing in (1b), projected on the (001) plane; dashed lines show short Br···Br contacts.