

trans-4-Bromo-*ONN*-azoxybenzene at 100 K

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Received 6 February 2004

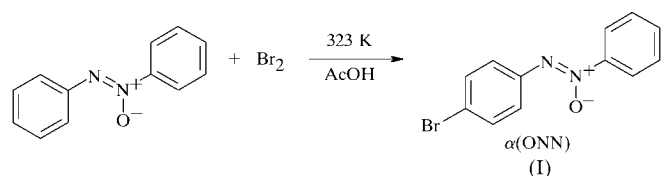
Accepted 25 March 2004

Online 30 April 2004

The crystal structure of the α isomer of *trans*-4-bromoazoxybenzene [systematic name: *trans*-1-(bromophenyl)-2-phenyldiazene 2-oxide], $C_{12}H_9BrN_2O$, has been determined by X-ray diffraction. The geometries of the two molecules in the asymmetric unit are slightly different and are within ~ 0.02 Å for bond lengths, $\sim 2^\circ$ for angles and $\sim 3^\circ$ for torsion angles. The azoxy bridges in both molecules have the typical geometry observed for *trans*-azoxybenzenes. The crystal network contains two types of planar molecules arranged in columns. The torsion angles along the Ar–N bonds are only $7(2)^\circ$, on either side of the azoxy group.

Comment

The commonly used methods for the preparation of unsymmetrical azoxybenzenes suffer from a lack of selectivity. Condensation and oxidation reactions provide, in every case, mixtures of isomers differing in the position of the O atom with respect to the substituents bound to the benzene rings. It has been claimed (Angeli & Valori, 1912) that bromination of azoxybenzene provides only one isomer, *viz.* the title compound α -4-bromoazoxybenzene, (I); this result was important evidence for the unsymmetrical structure of the azoxy bridge. Since then, the reaction has played an important role in mechanistic investigations of the Wallach rearrangement, since it was the only tool for recognizing the distribution of tracers with ^{15}N - and ^{14}C -labelled substrates (Shemyakin *et al.*, 1958; Behr & Hendley, 1966). We now confirm the Angeli & Valori (1912) statement; bromination of azoxybenzene



occurs with difficulty but selectively; another (β) isomer is not formed at all. α -4-Bromoazoxybenzene seems to be a good

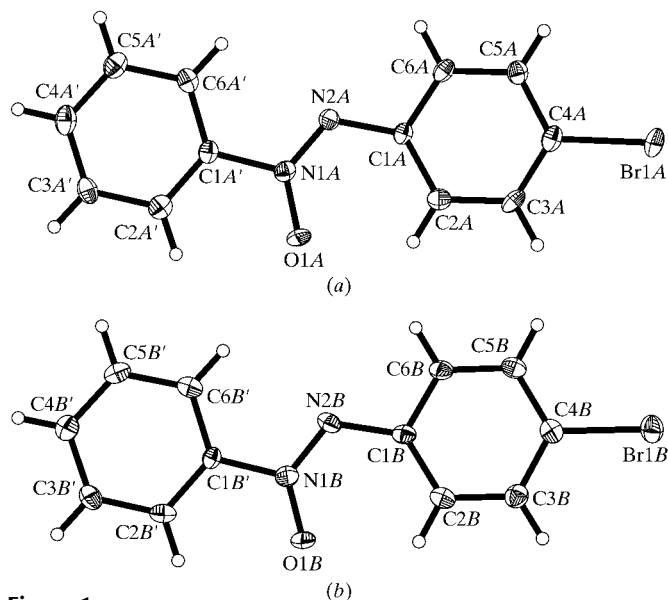


Figure 1

The molecular structures of (a) molecule A and (b) molecule B of *trans*-4-bromoazoxybenzene. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.

model compound for investigations of the structure of the azoxy bridge.

There are two independent molecules of the title compound in the unit cell (A and B; Fig. 1). The geometries of the molecules are similar; differences do not exceed 0.02 Å for bond lengths (*e.g.* N1A–C1A' and N1B–C1B'), 2° for valence angles (*e.g.* O1A–N1A–C1A' and O1B–N1B–C1B') and 3° for torsion angles (*e.g.* N1A–N2A–C1A–C2A and N1B–N2B–C1B–C2B; Table 1). Both molecules are almost planar; this is the preferential conformation of the azoxybenzene molecules. However, the rotation energy barrier is only 13 kJ mol $^{-1}$ on the unoxidized side and 23 kJ mol $^{-1}$ on the other (Tsuji *et al.*, 2000). In solution, the rotation is fast enough to make the C atoms at, for example, the C2A- and C6A-atom positions magnetically equivalent (Domański & Kyzioł, 2001). The twist angles along the C_{aryl} –N bonds are $-7.3(4)$ and $5.9(5)^\circ$ for A, and $5.2(4)$ and $-8.7(5)^\circ$ for B. The planarity of the molecules can also be described by the dihedral angles of three planar fragments, *viz.* the benzene ring, I, connected to the oxidized N atom (N1A and N1B), the azoxy group, II, and the other benzene ring, III. The dihedral angles between these groups are $7.7(5)$ (I/II), $5.2(6)$ (II/III) and $2.5(2)^\circ$ (I/III) for A, and $6.2(5)$, $7.3(5)$ and $1.7(2)^\circ$ for B. Atom C1A (or C1B) lies in plane II. The C–N bond lengths on the oxidized side of the bridge are ~ 0.03 (for A) and 0.07 Å (for B) longer than the C–N bond lengths on the unoxidized side. The valence angles of the bridge are typical for trigonal hybridization of the C and N atoms. Some deviations are observed for both molecules in the C–C–N angles on the unoxidized side of the azoxy group, as a result of steric hindrance around the azoxy group. Analogously, the N–N–O valence angles are widened to nearly 130° in order to keep atom O1A (O1B) far from the H atom bound to atom C2A

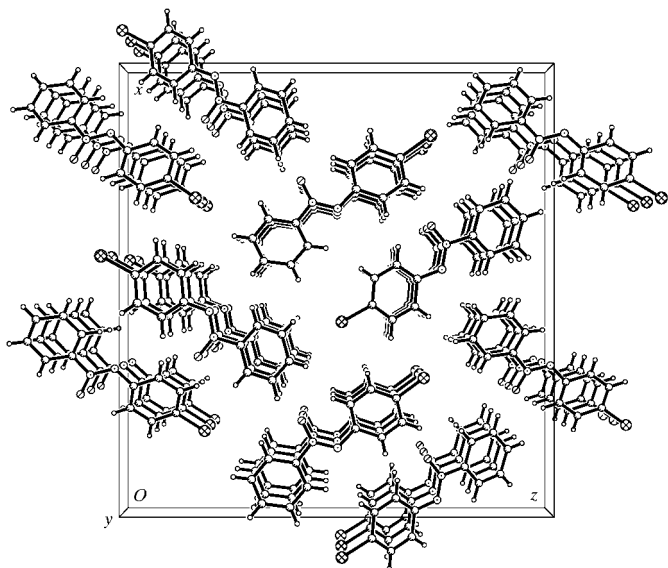


Figure 2
The columns formed in the *ac* plane by molecules of *trans*-4-bromo-*ONN*-azoxybenzene.

(C2B). The non-valence O...H distances are 2.34 (to H2') and 2.15 (2) Å (to H2) in *A*, and 2.38 (to H22') and 2.19 Å (to H22) in *B* (Table 2). These distances are shorter than the sum of the van der Waals radii (2.6 Å) given by Pauling (1967). These features are typical of those reported for the molecular structures of *trans*-azoxybenzenes (Krigbaum & Barber, 1971; Krigbaum & Taga, 1974; Hoesch & Weber, 1977; Ejsmont *et al.*, 2000, 2002; Domański *et al.*, 2001). All atoms bonded to atom N1A (N1B) are coplanar to within 0.017 (5) Å for C1A' and 0.038 (6) Å for C1B'. The C—Br bond lengths are comparable to that found in 4,4'-dibromoazobenzene (Howard *et al.*, 1994).

It is well known that isomerization of *cis*-azoxybenzenes occurs with great ease, *e.g.* *cis*-4-methylazoxybenzenes are spontaneously transformed into the *trans* isomers in the dark at room temperature (Webb & Jaffé, 1964). This fact should be easily explicable if the N—N bond order is significantly lower than it is in azobenzenes. Such a difference should be reflected in the N—N bond lengths, but the estimation of this distance appears to be difficult. Symmetrically 4,4'-disubstituted azoxybenzenes have been examined several times: the reported N—N distances lie in the range 1.155 (6)–1.276 (6) Å (Krigbaum & Barber, 1971; Sciau *et al.*, 1988), indicating high bond order, but the large differences make a comparison with azobenzenes unreliable. The results of measurements are influenced by the orientational disorder in the crystal networks, but librations within the azoxy bridge may also play a role, as observed in the case of *trans*-stilbenes. In mono-substituted azoxybenzenes, the N—N bond lengths do not differ significantly from those observed in molecules *A* and *B* (*e.g.* Ejsmont *et al.*, 2002). However, repeated measurements at room temperature gave lower values [1.221 (6) and 1.248 (5) Å] for 4-bromo-*NNO*-azoxybenzene. The apparent shortening of the N—N bond at higher temperature probably

results from molecular motions. Restricted rotation along the Ar—N bond in the crystal network may cause torsion vibrations within the azoxy group. In the crystal network, the molecules of compound (I) are arranged in columns (Fig. 2). The distance between neighbouring molecules in the column is 3.939 (4) Å. Strong intermolecular interactions were not found in the crystals, and this fact may influence the planar conformation of *trans*-4-bromoazoxybenzene molecules.

Experimental

Elemental bromine (2.14 ml, 0.04 mol) was added slowly to a stirred solution of azoxybenzene (3.96 g, 0.02 mol) in acetic acid (50 ml). The mixture was stirred for 4 h at 323 K and left to stand overnight at room temperature. The solution was poured into cold water (250 ml). Sodium hydrogen sulfite (40% aqueous solution) was added dropwise until the colour changed from brown. A yellow precipitate was collected by filtration and crystallized twice from methanol. 4-Bromo-*ONN*-azoxybenzene (3.88 g, 70%) was obtained as colourless needles (m.p. 346–347 K) suitable for X-ray diffraction studies. MS, *m/z* (int.): 278 (49), 276 (M^+ , 50), 249 (6), 247 (6), 169 (38), 157 (23), 155 (24), 145 (8), 143 (8), 91 (22), 90 (29), 77 (100); IR (KBr, cm^{-1}): 1480, 1324 (stretching vibrations of the azoxy group); ^1H NMR (CDCl_3): δ 8.23–8.32 (*m*, 2H, aromatic H atoms of the monosubstituted ring), 8.07 ($d^3J = 8.5$ Hz, 2H, 3,5-H atoms), 7.58 ($d^3J = 8.5$ Hz, 2H, 2,6-H atoms), 7.24–7.49 (*m*, 3H, remaining aromatic H atoms); ^{13}C NMR (DMSO- d_6): δ 147.6 (C1'), 142.5 (C1), 132.4 (C2', C6'), 131.9 (C3, C5), 129.3 (C3', C5'), 127.0 (C2, C6), 122.3 (C4), 122.0 (C4').

Crystal data

$\text{C}_{12}\text{H}_9\text{BrN}_2\text{O}$	Mo $K\alpha$ radiation
$M_r = 277.12$	Cell parameters from 11 971 reflections
Orthorhombic, $Pna2_1$	$\theta = 3.4$ – 25.0°
$a = 23.987$ (2) Å	$\mu = 3.77$ mm^{-1}
$b = 3.9394$ (5) Å	$T = 90.0$ (1) K
$c = 22.965$ (2) Å	Prisms, yellow
$V = 2170.1$ (4) Å 3	0.40 × 0.25 × 0.13 mm
$Z = 8$	
$D_x = 1.696$ Mg m^{-3}	

Data collection

Oxford Diffraction Xcalibur diffractometer	3634 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.054$
Absorption correction: empirical (CrysAlis RED; Oxford Diffraction, 2002)	$\theta_{\text{max}} = 25.0^\circ$
$T_{\text{min}} = 0.336$, $T_{\text{max}} = 0.613$	$h = -28 \rightarrow 28$
11 971 measured reflections	$k = -4 \rightarrow 3$
3773 independent reflections	$l = -27 \rightarrow 27$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.027$	$\Delta\rho_{\text{max}} = 0.49$ e \AA^{-3}
$wR(F^2) = 0.062$	$\Delta\rho_{\text{min}} = -0.50$ e \AA^{-3}
$S = 1.04$	Absolute structure: Flack (1983), 1806 Friedel pairs
3773 reflections	Flack parameter = -0.004 (7)
289 parameters	
H-atom parameters constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0385P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1

Selected geometric parameters (Å, °).

Br1A—C4A	1.899 (3)	Br1B—C4B	1.892 (3)
O1A—N1A	1.258 (4)	O1B—N1B	1.250 (4)
N1A—N2A	1.274 (4)	N1B—N2B	1.290 (4)
N1A—C1A'	1.475 (4)	N1B—C1B'	1.455 (4)
N2A—C1A	1.409 (4)	N2B—C1B	1.421 (5)
O1A—N1A—N2A	127.7 (3)	O1B—N1B—N2B	127.5 (3)
O1A—N1A—C1A'	116.1 (3)	O1B—N1B—C1B'	117.9 (3)
N2A—N1A—C1A'	116.1 (3)	N2B—N1B—C1B'	114.6 (3)
N1A—N2A—C1A	119.5 (3)	N1B—N2B—C1B	119.4 (3)
C2A—C1A—N2A	129.5 (3)	C2B—C1B—N2B	130.0 (3)
C6A—C1A—N2A	112.2 (3)	C6B—C1B—N2B	111.2 (3)
C2A'—C1A'—N1A	117.1 (3)	C2B'—C1B'—N1B	117.5 (3)
C6A'—C1A'—N1A	120.3 (3)	C6B'—C1B'—N1B	121.1 (3)
N1A—N2A—C1A—C2A	5.9 (5)	N1B—N2B—C1B—C2B	−8.7 (5)
N1A—N2A—C1A—C6A	−174.6 (3)	N1B—N2B—C1B—C6B	172.5 (3)
O1A—N1A—C1A'—C2A'	−8.0 (4)	O1B—N1B—C1B'—C2B'	6.7 (4)

Table 2

Intramolecular hydrogen-bonding and short-contact geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C2A—H2A'...O1A	0.93	2.15	2.718 (4)	119
C2A'—H2A'...O1A	0.93	2.34	2.661 (4)	100
C2B—H2B'...O1B	0.93	2.19	2.747 (4)	118
C2B'—H2B'...O1B	0.93	2.38	2.688 (5)	99

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97*

(Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1208). Services for accessing these data are described at the back of the journal.

References

- Angeli, A. & Valori, B. (1912). *Atti Accad. Nat. Lincei*, **21**, 155–163.
- Behr, L. C. & Hendley, E. C. (1966). *J. Org. Chem.* **31**, 2715–2716.
- Domański, A. A., Ejsmont, K., Kyzioł, J. B. & Zaleski, J. (2001). *Acta Cryst.* **C57**, 467–470.
- Domański, A. A. & Kyzioł, J. B. (2001). *Pol. J. Chem.* **75**, 1839–1846.
- Ejsmont, K., Broda, M., Domański, A. A., Kyzioł, J. B. & Zaleski, J. (2002). *Acta Cryst.* **C58**, o545–o548.
- Ejsmont, K., Domański, A. A., Kyzioł, J. B. & Zaleski, J. (2000). *Acta Cryst.* **C56**, 697–699.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Hoesch, L. & Weber, H. P. (1977). *Helv. Chim. Acta*, **60**, 3015–3024.
- Howard, J. A. K., Batsanov, A. S., Bryce, M. R. & Chesney, A. (1994). *Acta Cryst.* **C50**, 1818–1819.
- Krigbaum, W. R. & Barber, P. G. (1971). *Acta Cryst.* **B27**, 1884–1891.
- Krigbaum, W. R. & Taga, T. (1974). *Mol. Cryst. Liq. Cryst.* **28**, 85–98.
- Oxford Diffraction (2002). *CrysAlis CCD* and *CrysAlis RED*. Version 1.170. Oxford Diffraction, Wrocław, Poland.
- Pauling, L. C. (1967). *The Chemical Bond*, p. 152. Ithaca, NY: Cornell University Press.
- Sciau, P. P., Lapasset, J. & Moret, J. (1988). *Acta Cryst.* **C44**, 1089–1092.
- Sheldrick, G. M. (1990). *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXS97*. University of Göttingen, Germany.
- Shemyakin, M. M., Meimind, V. I. & Vaychunayte, B. K. (1958). *Zh. Obshch. Khim.* **28**, 1708–1709.
- Tsuji, T., Takashima, H., Takeuchi, H., Egawa, T. & Konaka, S. (2000). *J. Mol. Struct.* **554**, 203–210.
- Webb, D. L. & Jaffé, H. H. (1964). *J. Am. Chem. Soc.* **86**, 2419–2421.