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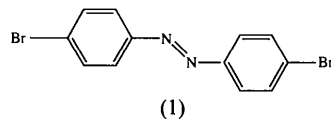
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A Novel Modification of *trans-p,p'*-Dibromoazobenzene

JUDITH A. K. HOWARD, ANDREI S. BATSANOV,
MARTIN R. BRYCE AND ANTONY CHESNEY

*Department of Chemistry, University of Durham,
Science Laboratories, South Road, Durham DH1 3LE,
England*

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, (1*b*), obtained by slow evaporation of a hexane/CH_2Cl_2 solution of (1), are isostructural with (2) and *p*-azotoluene (Brown, 1966*b*), 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 $0.8\,e\,\text{Å}^{-3}$ in the vicinity of the Br atom are apparently termination waves, other features are below $0.4\,e\,\text{Å}^{-3}$.

(1)

The molecule of (1) occupies a special position at the inversion centre (Fig. 1) and is essentially planar, similar to (1*a*) and (2), but not to the molecule of unsubstituted azobenzene which is twisted by 17° around the C—N bonds (Brown, 1966*a*; 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
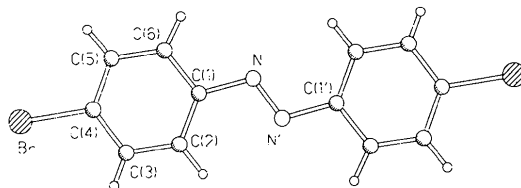

Fig. 1. Atomic numbering scheme for (1b); primed atoms are symmetrically related *via* an inversion centre.
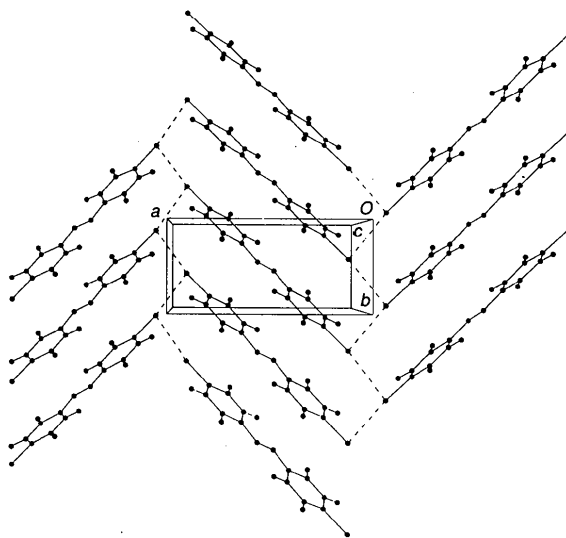

Fig. 2. Crystal packing in (1b), projected on the (001) plane; dashed lines show short Br···Br contacts.

rings. Each Br atom forms two Br···Br contacts of 3.54 Å, well under the doubled van der Waals radius of Br (1.85 Å) given by Bondi (1968), with C—Br···Br angles of 158 and 84°. According to the non-spherical representation of Nyburg & Faerman (1985), the van der Waals radius of the monocoordinate Br atom equals 1.54 Å along the continuation of the bond, and 1.84 Å in the perpendicular direction; therefore, the former contact should be regarded as normal, but the latter as significantly shortened.

Experimental

Crystal data

$C_{12}H_8Br_2N_2$
$M_r = 340.02$
Monoclinic
$P2_1/c$
$a = 10.1046$ (14) Å
$b = 4.7565$ (11) Å
$c = 11.677$ (3) Å
$\beta = 92.09$ (2)°
$V = 560.9$ (2) Å^3
$Z = 2$

$D_x = 2.013$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 13.5-15.0°$
$\mu = 7.179$ mm^{-1}
$T = 150$ (2) K
Pinakoid
$0.37 \times 0.25 \times 0.15$ mm
Brown

Data collection

Rigaku AFC-6S four-circle diffractometer
$2\theta/\omega$ scans
Absorption correction: empirical
$T_{min} = 0.4954$, $T_{max} = 1.0000$
1085 measured reflections
1015 independent reflections
791 observed reflections
$[I > 2\sigma(I)]$

$R_{int} = 0.0319$
$\theta_{max} = 27.22°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 6$
$l = -14 \rightarrow 14$
3 standard reflections monitored every 150 reflections
intensity variation: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0288$
wR(all reflections) = 0.0721
S(all reflections) = 1.092
1013 reflections
85 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0295P)^2 + 0.5761P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.004$
$\Delta\rho_{max} = 0.789$ e Å^{-3}
$\Delta\rho_{min} = -0.504$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Br	0.08500 (5)	0.08195 (10)	0.16769 (4)	0.0187 (2)
N	0.4564 (4)	0.9505 (9)	-0.0340 (3)	0.0207 (9)
C1	0.3758 (5)	0.7412 (10)	0.0222 (4)	0.0210 (10)
C2	0.3912 (5)	0.6513 (10)	0.1354 (4)	0.0190 (11)
C3	0.3063 (5)	0.4517 (11)	0.1781 (4)	0.0179 (10)
C4	0.2051 (4)	0.3465 (9)	0.1069 (4)	0.0142 (10)
C5	0.1879 (5)	0.4312 (11)	-0.0059 (4)	0.0202 (10)
C6	0.2744 (5)	0.6288 (11)	-0.0481 (4)	0.0231 (11)

Table 3. *Selected geometric parameters* (Å, °)

Br—C4	1.903 (4)	C2—C3	1.385 (6)
N—N^i	1.256 (7)	C3—C4	1.388 (6)
N—C1	1.457 (6)	C4—C5	1.383 (6)
C1—C2	1.393 (6)	C5—C6	1.387 (7)
C1—C6	1.395 (7)		
N^i—N—C1	111.2 (5)	C5—C4—C3	122.0 (4)
C2—C1—C6	119.6 (5)	C5—C4—Br	119.2 (3)
C2—C1—N	126.3 (4)	C3—C4—Br	118.8 (3)
C6—C1—N	114.0 (4)	C4—C5—C6	118.5 (4)
C3—C2—C1	120.2 (5)	C5—C6—C1	120.7 (4)
C2—C3—C4	118.9 (4)		

Symmetry codes: (i) $1 - x, 2 - y, -z$.

The low-temperature experiment was carried out using a Cryostream (Oxford Cryosystems) open-flow gas cryostat (Cosier & Glazer, 1986). The absorption correction (North, Phillips & Mathews, 1968) was based on 36 ψ scans of 1 reflection. The structure was solved by direct methods and refined by full-matrix least squares.

Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1989). Software used to prepare material for publication: *SHELXL93*.

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