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X-RAY CRYSTAL STRUCTURE OF THE DYE 2-BROMO-4-CYANO-4′-*N*,*N*-DIETHYLAMINOAZOBENZENE

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SUMMARY

*The crystal structure of 2-bromo-4-cyano-4′-*N,N*-diethylaminoazobenzene has been determined from X-ray diffraction data* $C_{17}H_{17}N_4Br$, *mol. wt* $= 357{\cdot}1$. *Triclinic,* $P\bar{1}$ *(No 2),* $a = 13{\cdot}162(5)$ Å, $b = 7{\cdot}516(3)$ Å, $c = 8{\cdot}496(4)$ Å, $\alpha = 101{\cdot}63(4)^\circ$, $\beta = 95{\cdot}79(4)^\circ$, $\gamma = 91{\cdot}49(4)^\circ$, $V = 818{\cdot}10$ Å^3, $Z = 2$, $D_c = 1{\cdot}45\,g\,cm^{-3}$, $F(000) = 378$, $\lambda(Mo_{K\alpha}) = 0{\cdot}7107$ Å, $\mu(Mo_{K\alpha}) = 26{\cdot}70\,cm^{-1}$. *The structure was solved by direct methods and refined by full-matrix least-squares to* $R = 0{\cdot}053$ *for 2081 independent reflexions. The molecule possesses an essentially planar azobenzene skeleton. The effects of substituents on the geometry of the azo group are discussed Significant molecular parameters are* N═N, *1·264(6) Å, Br—C, 1·904(5) Å, mean N—C, 1·410(7) Å, N═N—C, 115·7(2)° and 113·0(2)°, N—C—C* (cis *relative to N═N*), *125·4(3)° and 123·1(2)°, C—C(Br)—C, 123·0(2)°*

1 INTRODUCTION

In spite of the fact that aromatic azo compounds are of considerable technical interest, rather few X-ray structural studies have been done. The present work on the crystal structure of the title compound, a potential azo dye for polyesters, was therefore undertaken not only to provide some of this much needed information but also to elucidate the effects of the substituents Br, CN and $N(C_2H_5)_2$ on the geometry of the phenyl and azo groups.

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2. EXPERIMENTAL

2-Bromo-4-cyano-4′-*N*,*N*-diethylaminoazobenzene (*I*) was recrystallized from acetone as dark red needles (λ_{max} = 454 nm; ε(hexane) = 42,650, m.p. = 149 °C). Cell parameters were determined by least-squares from 12 reflexions measured on a Picker FACS-1 four-circle computer-controlled diffractometer equipped with a scintillation counter and a pulse-height analyzer Intensity data were collected with a crystal of dimensions 0 5 × 0 3 × 0·1 mm (Zr-filtered $Mo_{K\alpha}$ radiation) using the procedure described by Bart *et al*[1] The net counts of three standard reflexions,

TABLE I

FRACTIONAL COORDINATES FIGURES IN PARENTHESES ARE E S DS

Atom	x/a	y/b	z/c
Br	0 20506(5)	−0 17502(7)	0 49179(7)
N(1)	0 1946(3)	0 1717(6)	0 3578(5)
N(2)	0 1891(3)	0 3113(6)	0 2963(5)
N(3)	0 3737(4)	0 3271(6)	−0 2649(5)
N(4)	−0 0573(5)	0 2191(8)	1 0214(7)
C(1)	0 1432(4)	0 1874(6)	0 4989(6)
C(2)	0 1396(4)	0 0416(6)	0 5749(6)
C(3)	0 0902(4)	0 0444(7)	0 7109(6)
C(4)	0 0421(4)	0 2019(7)	0 7727(6)
C(5)	0 0456(5)	0 3541(7)	0 7020(7)
C(6)	0 0949(4)	0 3462(7)	0 5666(6)
C(7)	0 2373(4)	0 3031(7)	0 1558(6)
C(8)	0 2834(4)	0 1505(7)	0 0743(7)
C(9)	0 3297(4)	0 1600(7)	−0 0626(6)
C(10)	0 3297(4)	0 3192(7)	−0 1277(6)
C(11)	0 2809(4)	0 4700(7)	−0 0440(7)
C(12)	0 2359(4)	0 4603(7)	0 0918(7)
C(13)	−0 0128(5)	0 2094(8)	0 9133(7)
C(14)	0 4327(5)	0 1775(8)	−0 3417(7)
C(15)	0 5375(6)	0 1712(11)	−0 2573(10)
C(16)	0 3700(5)	0 4895(8)	−0 3361(7)
C(17)	0 4547(6)	0 6316(10)	−0 2602(10)
H(3)	0 088	−0 074	0 767
H(5)	0 008	0 476	0 753
H(6)	0 097	0 464	0 510
H(8)	0 282	0 024	0 119
H(9)	0 367	0 042	−0 123
H(11)	0 281	0 596	−0 088
H(12)	0 197	0 576	0 151
H(141)	0 441	0 193	−0 465
H(142)	0 391	0 051	−0 345
H(151)	0 578	0 059	−0 318
H(152)	0 532	0 156	−0 133
H(153)	0 581	0 298	−0 253
H(161)	0 296	0 548	−0 319
H(162)	0 377	0 448	−0 464
H(171)	0 447	0 748	−0 318
H(172)	0 528	0 576	−0 277
H(173)	0 447	0 676	−0 133

monitored after every 50 reflexions, did not alter significantly throughout the period of data collection. A total of 3278 independent reflexions were measured (up to $2\theta = 50°$) of which 2081 were judged to be observed with $I \geq 2{\cdot}5\sigma$. The intensities were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods using the program MULTAN,[2] the remaining non-hydrogen atoms being obtained from a subsequent Fourier synthesis. Fully anisotropic refinement of all the non-hydrogen atoms gave $R = 0{\cdot}065$. The H atoms were then introduced into the calculations at fixed positions, on stereochemical grounds (C—H, 1 08 Å) and in agreement with a ΔF synthesis. The B value of each H atom was set at 5 0 Å^2 Refinement then converged to $R = 0\ 053$ for the 2081 observed reflexions. The final shifts of the atomic parameters were negligible and all well below the corresponding σ. The final ΔF synthesis was also featureless

The positional and thermal parameters of the non-hydrogen atoms were refined with the least-squares program of Immirzi.[3] Scattering factors were calculated from the expression of Vand *et al*[4] using the values for the parameters given by Moore[5] The weighting scheme used was that of Cruickshank *et al*:[6] $1/w = A + B|F_0| + C|F_0|^2$, where $A = 2F_0(\text{min})$, $B = 1\ 0$ and $C = 2/F_0(\text{max})$. The final coordinates and anisotropic thermal parameters are listed in Tables 1 and 2 and the bond lengths and

TABLE 2

ANISOTROPIC THERMAL PARAMETERS (Å^2) THE PARAMETERS APPEAR IN THE EQUATION OF THE FORM $\exp[-1/4(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$[a] FIGURES IN PARENTHESES ARE E S DS

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	5 77(3)	3 58(2)	5 63(3)	0 84(2)	1 52(2)	1 41(2)
N(1)	4 44(19)	3 76(18)	3 49(18)	−0 01(15)	1 05(15)	1 12(14)
N(2)	5 16(21)	3·91(18)	3 56(18)	0 29(16)	1 14(16)	1 67(15)
N(3)	5 35(22)	3 90(19)	3 69(19)	−0 27(16)	1 26(16)	0 89(15)
N(4)	9 58(38)	5 97(28)	5 86(29)	2 18(26)	4 04(27)	2 84(23)
C(1)	3 63(30)	3 42(20)	3 65(21)	0 01(16)	0 39(16)	1 08(16)
C(2)	3 17(19)	3 36(19)	3 98(21)	0 20(15)	0 56(16)	1 21(16)
C(3)	4 29(23)	3 52(21)	3 98(23)	0 02(17)	0 40(18)	1 43(17)
C(4)	4 06(22)	4 22(22)	3 45(21)	0 18(17)	0 95(17)	1 33(17)
C(5)	5 70(28)	3 72(22)	4 33(24)	0 62(19)	1 43(21)	1-34(19)
C(6)	5 06(25)	3 50(21)	4 09(23)	0 19(18)	1 47(19)	1 50(17)
C(7)	4 05(22)	3 79(21)	3 66(21)	0 05(17)	0 88(17)	1 17(17)
C(8)	5 05(25)	3 43(21)	4 53(24)	0 68(18)	1 42(22)	1 52(18)
C(9)	4 90(25)	3 47(21)	3 87(23)	0 33(18)	1 35(19)	0 85(17)
C(10)	3 97(21)	3 69(20)	3 21(20)	−0 30(16)	0 68(16)	0 91(16)
C(11)	5 22(26)	3 59(22)	4 72(25)	0 24(18)	1 69(20)	1 65(19)
C(12)	5 43(27)	2 67(23)	4 46(25)	0 82(19)	1 63(20)	1 40(18)
C(13)	6 39(31)	4 17(24)	4 58(26)	0 74(21)	1 68(22)	1 61(20)
C(14)	6 49(32)	4 40(25)	4 17(25)	−0 18(22)	1 97(23)	0 25(20)
C(15)	6 53(38)	6 79(39)	7 91(45)	0 79(30)	2 37(33)	−0 87(34)
C(16)	6 14(31)	5 33(28)	4 35(26)	−0 05(23)	1·26(22)	1 80(22)
C(17)	8 00(42)	5 08(31)	7 58(42)	−1 15(29)	1 87(33)	2 06(29)

[a] Each hydrogen atom has an assumed isotropic temperature factor $B = 5\ 0$ Å^2

TABLE 3
BOND DISTANCES AND ANGLES FIGURES IN PARENTHESES ARE E.S DS

Bond	*Distance* (Å)	*Bonds*	*Angle* (*degrees*)
Br—C(1)	1 904(5)	Br—C(2)—C(3)	117 2(3)
N(1)—N(2)	1 264(6)	Br—C(2)—C(1)	119 8(3)
N(1)—C(1)	1 421(7)	N(1)-C(1)—C(2)	119 2(2)
N(2)—C(7)	1 399(7)	N(1)—C(1)—C(6)	123 1(2)
N(3)—C(10)	1 364(7)	N(1)—N(2)—C(7)	115 7(2)
N(3)—C(14)	1 465(8)	N(2)—N(1)—C(1)	113 0(2)
N(3)—C(16)	1 467(8)	N(2)—C(7)—C(8)	125 4(3)
N(4)—C(13)	1 130(9)	N(2)—C(7)—C(12)	116 0(2)
		N(3)—C(10)—C(9)	121 8(2)
		N(3)—C(10)—C(11)	121 5(2)
		N(3)—C(14)—C(15)	114 0(3)
C(2)—C(3)	1 379(7)	N(3)—C(16)—C(17)	112 9(3)
C(1)—C(2)	1 381(7)	N(4)—C(13)—C(4)	177 9(3)
C(3)—C(4)	1 391(7)	C(1)—C(2)—C(3)	123 0(2)
C(4)—C(5)	1 397(7)	C(1)—C(6)—C(5)	120 9(2)
C(5)—C(6)	1 368(8)	C(2)—C(1)—C(6)	117 7(2)
C(4)—C(13)	1 450(8)	C(2)—C(3)—C(4)	117 8(2)
C(1)—C(6)	1 413(7)	C(3)—C(4)—C(5)	121 3(2)
		C(3)—C(4)—C(13)	119 7(3)
		C(4)—C(5)—C(6)	119 4(3)
C(7)—C(8)	1 402(7)	C(5)—C(4)—C(13)	119 1(3)
C(7)—C(12)	1 396(7)		
C(8)—C(9)	1 379(8)	C(7)—C(8)—C(9)	120 0(3)
C(9)—C(10)	1 416(7)	C(7)—C(12)—C(11)	121 6(3)
C(11)—C(12)	1 363(8)	C(8)—C(7)—C(12)	118 6(2)
C(10)—C(11)	1 416(7)	C(8)—C(9)—C(10)	121 9(2)
		C(9)—C(10)—C(11)	116 7(2)
C(14)—C(15)	1 495(10)	C(10)—C(11)—C(12)	121 2(3)
C(16)—C(17)	1 522(10)		
		C(10)—N(3)—C(14)	121 1(2)
		C(10)—N(3)—C(16)	121 8(2)
		C(14)—N(3)—C(16)	116 9(3)

angles in Table 3 Figures 1 and 2 show views of the molecule as drawn by means of the ORTEP program [7]†

3 DISCUSSION

The conformation of the molecule (Fig 1) is such that N(2) is oriented *anti* with respect to C(2) with an N(2)   C(2) distance of 3 51 Å In this *anti* conformation, there is the least repulsive interaction between the electron cloud of Br and the lone pair on N(1). The corresponding *syn* conformation will lead to severe repulsion between the electron cloud of Br and the lone pair on N(2). Results of least-squares planes calculations (Table 3) show that the title compound possesses an essentially

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† A list of structure factors may be obtained from the authors of this paper

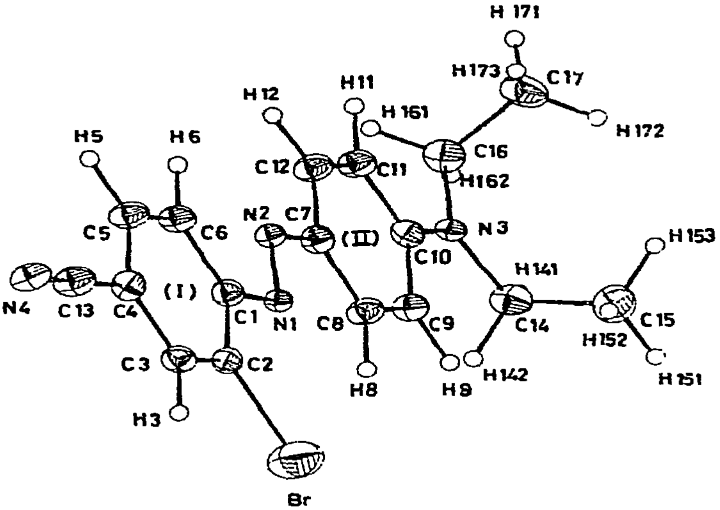


Fig 1 The molecule of 2-bromo-4-cyano-4'-*N*,*N*-diethylaminoazobenzene, showing the atom-labelling scheme and 30% probability thermal vibration ellipsoids

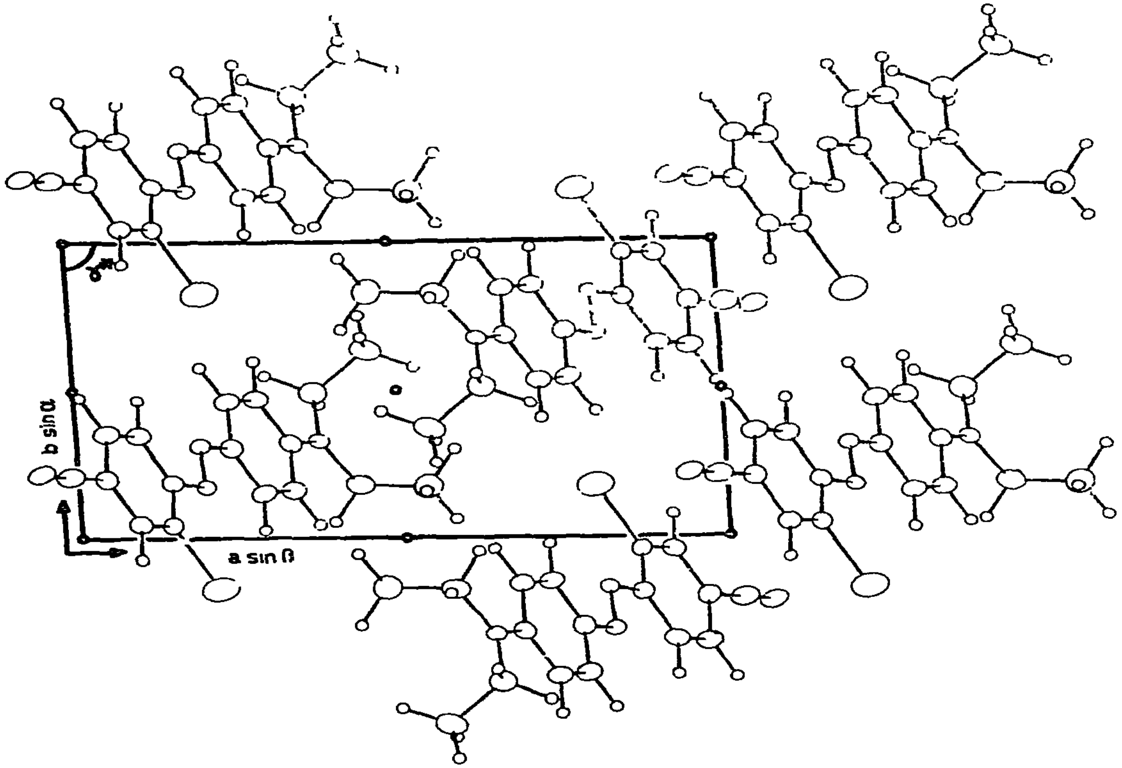


Fig 2 Structure of 2-bromo-4-cyano-4'-*N*,*N*-diethylaminoazobenzene viewed down the *c* axis

planar azobenzene skeleton with N(1) showing the largest deviation (0 092 Å) from planarity and a dihedral angle of 2 1° between the two phenyl rings. The diethylamino group is not planar but the N(3)—C(14)—C(16) moiety is almost coplanar with the skeleton (Table 4) The geometry of the azo group in the molecule is quite similar to those reported earlier. Thus the values obtained for the N(1)—N(2) and the mean N—C distances, the N(1)—N(2)—C(7), N(1)—C(1)—C(2), N(1)—C(1)—C(6), N(2)—C(7)—C(8) and N(2)—C(7)—C(12) bond angles are in good agreement with the corresponding values found in *cis*-azobenzene[8] and in other azobenzene derivatives such as *trans*-4,4'-dibromoazobenzene,[9] *trans*-4,4'-dichloroazobenzene,[10] *trans*-2,2'-dichloroazobenzene,[11] *trans*-4,4'-azodiphenetole,[12] *trans*-2,2',4,4',6,6'-hexanitroazobenzene,[13] *trans*-*o*-aminoazotoluene[14] and *trans*-2,2'-azo-*p*-cymene [15]

In accordance with the well-known effects of substituents on aromatic ring geometry,[16-18] the C(3)—C(4)—C(5) angle (121 3°) at the C=N end of the molecule is larger than the C(2)—C(1)—C(6) angle (117 7°) at the N=N end. It is

TABLE 4

PLANARITY OF GROUPS OF ATOMS IN THE STRUCTURE

Equations of the least-squares planes are expressed as

$$Px + Qy + Rz - S = 0$$

with x, y z being fractional coordinates The distances of the atoms from the planes are in Å

Plane (1)

$$-0\ 782x - 0\ 233y - 0\ 578z + 3\ 630 = 0$$

C(1)	0 007(5)	C(2)	−0 004(5)		
C(3)	−0 004(5)	C(4)	0 010(5)		
C(5)	−0 007(6)	C(6)	−0 001(5)		
Not defining plane		Br	−0 023(1)	N(1)	0 026(4)
		N(2)	0 087(4)	N(4)	0 084(6)
		C(13)	0 042(6)		

Plane (2)

$$-0\ 802x - 0\ 211y - 0\ 558z + 3\ 483 = 0$$

C(7)	−0 012(5)	C(8)	0 011(6)		
C(9)	−0 005(5)	C(10)	−0 001(5)		
C(11)	0 000(6)	C(12)	0 006(6)		
Not defining plane		N(1)	−0 092(4)	N(2)	−0 015(4)
		N(3)	0 012(5)	C(14)	−0 124(6)
		C(16)	0 072(6)		

Plane (3)

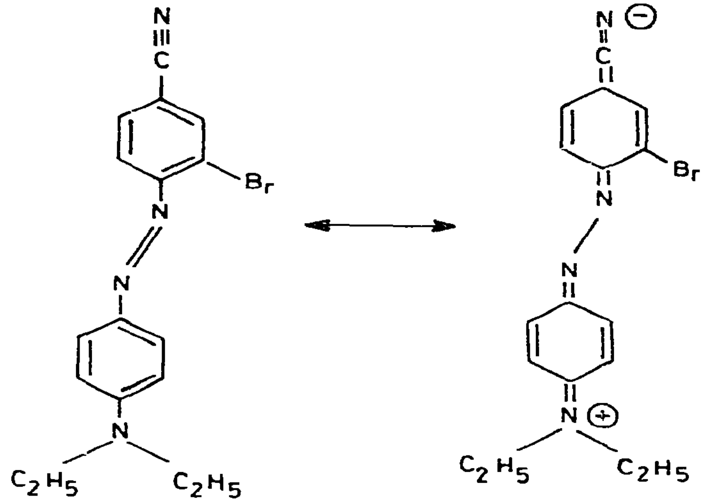
$$0\ 250x + 0\ 088y - 0\ 964z - 4\ 084 = 0$$

N(3)	−0 444(4)	C(14)	0 299(6)		
C(15)	−0 064(8)	C(16)	0 238(6)		
C(17)	−0 030(8)				
Not defining plane		C(9)	−2 379(5)	C(10)	−1 738(5)
		C(11)	−2 504(6)		

Dihedral angles (degrees) between planes

Plane (1)–Plane (2)	2 1
Plane (2)–Plane (3)	71 4

interesting to note that the value of the former angle is very similar to that of 121·8° suggested by Domenicano *et al.*,[18] whereas the latter angle is significantly smaller than the value of 120·0° suggested by the same authors. This difference may be attributed to complications arising from the presence of the Br atom in the *ortho* position The C(9)—C(10)—C(11) angle (116·7°) at the $N(C_2H_5)_2$ end of the molecule is also smaller than C(8)—C(7)—C(12) (118·6°) at the N═N end, in line with the observation by Domenicano and coworkers. In keeping with the general trend, the C(1)—C(2)—C(3) angle has also been affected by the presence of the electron-withdrawing Br substituent so that it is significantly larger (123 0°) than all the endocyclic bond angles. The fact that the C(2)—C(3) bond length is shorter than C(3)—C(4) is also consistent with the observation by Domenicano and coworkers The corresponding C—C bond lengths in ring (II) (Fig. 1) are, in general, very similar because, unlike ring (I), this is to a good approximation a symmetrically *para*-disubstituted ring. The above observations are also in keeping with the main canonical forms of the molecule.



The Br—C(2) bond length of 1 904 Å is in good agreement with those of 1·902 Å found in *p*-bromodiazoaminobenzene[19] and 1 891 Å in *trans*-4,4′-dibromoazobenzene.[9] The N(4)—C(13), C(4)—C(13) bond distances and the bond lengths and angles in the $N(C_2H_5)_2$ group are unexceptional

The packing scheme is indicated in Fig 2 With the exception of the edge-on N(4) · H(3) contact distance of 2 35 Å, which is below the sum of the van der Waals radii, all the other short intermolecular contacts in the structure (Br · C, 3·63 Å, Br N, 3 87 Å, Br· ·H, 2 99 Å; C· ·C, 3 51 Å, H H, 2·35 Å) conform to normal van der Waals interactions.

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