Dyes and Pigments 5 (1984) 401–413

X-ray Crystal Structure of the Dye 2-Cyano-4-bromo-4′-*N*,*N*-Diethylaminoazobenzene

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(Received: 28 June, 1983)

SUMMARY

The crystal structure and molecular conformation of 2-cyano-4-bromo-4′-N,N-diethylaminoazobenzene ($C_{17}H_{17}N_4Br$, *mol. wt.* = 357·2 *a.m.u*) *has been determined from X-ray diffraction data: triclinic,* $P\bar{1}$ (*No.* 2), $a = 10{\cdot}132(11)$ Å, $b = 12{\cdot}216(16)$ Å, $c = 6{\cdot}966(11)$ Å, $\alpha = 104{\cdot}21(9)^\circ$, $\beta = 92{\cdot}67(12)^\circ$, $\gamma = 97{\cdot}22(7)^\circ$, $V = 826{\cdot}5(9)$ Å^3, $Z = 2$, $D_c = 1{\cdot}436\ \mathrm{g\,cm^{-3}}$, $F(000) = 378$, $\lambda(MoK\alpha) = 0{\cdot}71069$ Å, $\mu(MoK\alpha) = 26{\cdot}0\ \mathrm{cm^{-1}}$. *The structure was solved by the multiple solution direct method and refined by full-matrix least-squares to* $R = 0{\cdot}059$ *for 1538 independent observed reflections. The azobenzene skeleton is planar to within 0·06 Å. Most significant bonding data are: N═N, 1·290(8) Å; Br—C, 1·866(6) Å; mean C—N (azo) 1·380(8) Å; N═N—C, 113·6(4) and 115·3(4)°; N—C—C (cis relative to N═N) 125·9(4)° and 126·7(4)°; N—C—C (trans) 116·8°(5)° and 116·1(4)°.*

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Dyes and Pigments 0143-7208/84/$03·00

1. INTRODUCTION

The technical interest in azo-dyes has led to considerable efforts to determine their crystal and molecular structures. Up to now about 20 variously substituted single azobenzene derivatives have been fully structurally refined.[1,2] In these compounds steric interference is relieved in various ways by a combination of contributions, such as bond angle distortions, rotation of the azo group and aromatic rings and their substituents, displacement of the azo-nitrogen atoms from the benzene ring planes and offset of parallel phenyl rings. In some cases[3] the molecule crystallizes in various polymorphic forms with quite different molecular shape, showing the existence of various energy minima in conformational space. On the whole, *a priori* determination of the energetically most

TABLE 1
Final Fractional Coordinates for Non-hydrogen Atoms[a]

Atom	*x*	*y*	*z*
Br	0·205 79 (9)	0·153 76 (7)	0·059 35 (13)
N(1)	0·206 6 (5)	−0·150 7 (5)	−0·770 8 (8)
N(2)	0·304 5 (5)	−0·127 1 (4)	−0·872 7 (8)
N(3)	0·335 3 (5)	−0·407 8 (5)	−1·623 0 (8)
N(4)	−0·071 3 (6)	−0·272 9 (6)	−0·576 8 (11)
C(1)	0·213 5 (6)	−0·077 2 (5)	−0·581 5 (10)
C(2)	0·113 1 (6)	−0·101 0 (5)	−0·457 9 (10)
C(3)	0·111 9 (6)	−0·031 9 (6)	−0·270 3 (10)
C(4)	0·210 7 (6)	0·061 4 (6)	−0·196 2 (10)
C(5)	0·310 9 (7)	0·083 7 (6)	−0·317 7 (11)
C(6)	0·311 0 (7)	0·016 4 (6)	−0·503 2 (12)
C(7)	0·302 5 (6)	−0·198 4 (5)	−1·057 7 (9)
C(8)	0·207 8 (6)	−0·293 5 (6)	−1·143 1 (10)
C(9)	0·216 4 (6)	−0·361 2 (5)	−1·324 5 (10)
C(10)	0·325 1 (5)	−0·341 0 (5)	−1·444 4 (10)
C(11)	0·417 6 (6)	−0·242 6 (5)	−1·356 6 (10)
C(12)	0·410 5 (6)	−0·175 1 (5)	−1·170 9 (10)
C(13)	0·011 3 (6)	−0·199 3 (6)	−0·530 2 (11)
C(14)	0·255 2 (7)	−0·519 9 (6)	−1·700 7 (11)
C(15)	0·135 3 (8)	−0·515 2 (7)	−1·833 5 (13)
C(16)	0·432 3 (7)	−0·373 8 (6)	−1·754 1 (11)
C(17)	0·567 4 (8)	−0·407 1 (7)	−1·722 1 (13)

[a] Atom labelling as in Fig. 1. Standard deviations in parentheses.

convenient way to relieve non-bonded interactions in these relatively simple molecules is not straightforward, as is convincingly illustrated by the bonding data collected in Table 5 of ref. (1).

In the present work we describe the crystal structure of the disperse dye 2-cyano-4-bromo-4'-*N*,*N*-diethylaminoazobenzene (I) and discuss the effects of the substituents on the molecular conformation and geometry of the phenyl and azo groups. Monoazo disperse dyes, such as (I), are particularly suitable for application to polyester and nylon by means of transfer printing.[4]

2. EXPERIMENTAL

Compound (I), prepared by Griffiths *et al.*,[5] was recrystallized from acetone as dark red needles ($\lambda_{max} = 448$ nm; ε(hexane) = 41·500; m.p. = 146 °C). Cell parameters ($a = 10·132(11)$ Å, $b = 12·216(16)$ Å, $c = 6·966(11)$ Å, $\alpha = 104·21(9)°$, $\beta = 92·67(12)°$, $\gamma = 97·22(7)°$; space-group

TABLE 2

Positional and Thermal Parameters for Hydrogen Atoms[a]

Atom	*x*	*y*	*z*	$B(Å^2)$[b]
H(3)	0·046 (7)	−0·049 (6)	−0·183 (11)	7·9 (19)
H(5)	0·371 (6)	0·139 (5)	−0·263 (9)	5·1 (13)
H(6)	0·387 (6)	0·036 (5)	−0·582 (9)	5·7 (14)
H(8)	0·137 (7)	−0·317 (6)	−1·067 (10)	6·9 (17)
H(9)	0·160 (6)	−0·425 (5)	−1·383 (9)	5·4 (14)
H(11)	0·489 (5)	−0·225 (5)	−1·414 (8)	4·3 (12)
H(12)	0·469 (6)	−0·107 (5)	−1·140 (9)	6·4 (16)
H(141)	0·311 (7)	−0·573 (6)	−1·800 (11)	7·7 (18)
H(142)	0·266 (8)	−0·546 (7)	−1·599 (12)	9·5 (21)
H(151)	0·097 (6)	−0·591 (5)	−1·869 (9)	7·2 (17)
H(152)	0·165 (6)	−0·506 (5)	−1·954 (9)	11·1 (26)
H(153)	0·086 (7)	−0·471 (6)	−1·768 (10)	5·5 (14)
H(161)	0·396 (9)	−0·400 (8)	−1·885 (14)	5·3 (13)
H(162)	0·438 (6)	−0·285 (5)	−1·748 (9)	5·6 (14)
H(171)	0·625 (11)	−0·403 (9)	−1·851 (15)	13·7 (30)
H(172)	0·555 (7)	−0·486 (5)	−1·742 (9)	6·2 (15)
H(173)	0·598 (7)	−0·378 (6)	−1·588 (10)	7·0 (17)

[a] Atom labelling as in Fig. 1. Standard deviations in parentheses.

[b] Isotropic thermal parameter.

TABLE 3

Anisotropic Thermal Parameters of Non-hydrogen Atoms (Å^2)[a]

The parameters appear in the equation of the form:

$$\exp - 1/4(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl).$$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	6·93 (4)	6·57 (4)	7·66 (4)	−0·32 (6)	3·69 (7)	1·14 (7)
N(1)	4·0 (2)	5·4 (3)	6·4 (3)	1·2 (4)	1·8 (4)	4·3 (4)
N(2)	4·4 (2)	4·9 (2)	6·2 (3)	1·4 (4)	1·5 (4)	3·7 (4)
N(3)	4·6 (2)	5·6 (3)	4·9 (3)	−1·9 (4)	1·0 (4)	1·8 (4)
N(4)	4·8 (3)	8·6 (4)	9·3 (4)	−2·2 (5)	0·5 (6)	3·5 (7)
C(1)	4·5 (3)	4·6 (3)	5·4 (3)	1·4 (5)	0·6 (5)	3·7 (5)
C(2)	3·5 (2)	4·7 (3)	6·0 (3)	1·9 (4)	1·7 (4)	4·7 (5)
C(3)	4·2 (3)	5·5 (3)	5·8 (3)	0·9 (5)	2·4 (5)	3·2 (5)
C(4)	4·4 (3)	5·6 (3)	5·8 (3)	0·4 (5)	1·9 (5)	3·2 (5)
C(5)	5·7 (4)	5·3 (3)	7·1 (4)	−1·5 (5)	3·3 (6)	2·2 (6)
C(6)	5·5 (3)	4·7 (3)	8·2 (4)	−0·7 (5)	4·7 (6)	4·1 (6)
C(7)	4·3 (3)	3·9 (2)	5·5 (3)	0·9 (4)	0·5 (5)	2·9 (5)
C(8)	4·6 (3)	5·4 (3)	5·5 (3)	−1·0 (5)	0·6 (5)	4·4 (5)
C(9)	4·7 (3)	4·4 (3)	6·0 (3)	−1·3 (5)	−0·1 (5)	3·9 (5)
C(10)	3·2 (2)	4·6 (3)	5·7 (3)	1·1 (4)	0·3 (4)	4·8 (5)
C(11)	4·4 (3)	4·6 (3)	6·0 (3)	−1·6 (4)	3·1 (5)	2·8 (5)
C(12)	4·8 (3)	4·6 (3)	6·3 (4)	−1·8 (5)	1·7 (5)	3·1 (5)
C(13)	2·9 (2)	6·9 (4)	7·1 (4)	−0·1 (5)	−0·2 (5)	4·4 (6)
C(14)	5·1 (3)	5·5 (3)	6·7 (4)	−1·1 (5)	−1·2 (6)	3·1 (6)
C(15)	6·2 (4)	7·9 (5)	8·1 (5)	−1·6 (7)	−0·5 (7)	3·2 (8)
C(16)	5·1 (3)	6·0 (3)	5·9 (4)	0·1 (5)	1·0 (5)	3·9 (6)
C(17)	6·7 (4)	7·2 (4)	8·3 (5)	5·1 (7)	1·6 (7)	3·9 (7)

[a] Figures in parentheses are e.s.d.

$P\bar{1}$, $Z = 2$) were determined from 12 reflections measured on a Picker FACS-1 four-circle diffractometer with a crystal mounted with the *c*-axis approximately along the phi-axis of the instrument. Intensity data (2912 total independent reflections of which 1538 considered observed with $I \geq 2{\cdot}5\sigma(I)$) were collected in the $3° < 2\theta < 50°$ interval using a red prismatic crystal of dimensions 0·6 × 0·5 × 0·4 mm and Mo*Kα* radiation. Standard reflections, monitored after every 50 observations, did not vary during data collection. Lorentz and polarization corrections were applied. The heavy atom skeleton of the structure was solved by means of MULTAN-78; hydrogen atoms were placed in agreement with a ΔF synthesis. Refinement (anisotropic for Br, C, N; isotropic for H)

TABLE 4
Bond Distances and Angles of Non-hydrogen Atoms[a]

Type	*Length (Å)*	*Type*	*Angle (degrees)*
Br—C(4)	1·866 (6)	Br—C(4)—C(3)	120·0 (4)
N(1)—N(2)	1·290 (8)	Br—C(4)—C(5)	121·5 (4)
N(1)—C(1)	1·394 (8)	N(1)—C(1)—C(2)	116·8 (5)
N(2)—C(7)	1·365 (8)	N(1)—C(1)—C(6)	125·9 (4)
N(3)—C(10)	1·326 (8)	N(1)—N(2)—C(7)	115·3 (4)
N(3)—C(14)	1·464 (8)	N(2)—N(1)—C(1)	113·6 (4)
N(3)—C(16)	1·463 (9)	N(2)—C(7)—C(8)	126·7 (4)
N(4)—C(13)	1·121 (9)	N(2)—C(7)—C(12)	116·1 (4)
		N(3)—C(10)—C(9)	122·7 (4)
C(1)—C(2)	1·411 (9)	N(3)—C(10)—C(11)	123·1 (4)
C(2)—C(3)	1·372 (9)	N(3)—C(14)—C(15)	112·3 (5)
C(3)—C(4)	1·394 (8)	N(3)—C(16)—C(17)	113·9 (5)
C(4)—C(5)	1·395 (11)	N(4)—C(13)—C(2)	176·0 (4)
C(5)—C(6)	1·351 (10)		
C(6)—C(1)	1·393 (8)	C(1)—C(2)—C(3)	120·3 (4)
C(2)—C(13)	1·450 (8)	C(1)—C(6)—C(5)	122·4 (5)
		C(2)—C(1)—C(6)	117·3 (5)
C(7)—C(8)	1·396 (8)	C(2)—C(3)—C(4)	121·0 (5)
C(8)—C(9)	1·343 (9)	C(3)—C(4)—C(5)	118·5 (5)
C(9)—C(10)	1·446 (9)	C(4)—C(5)—C(6)	120·4 (5)
C(10)—C(11)	1·414 (8)	C(1)—C(2)—C(13)	119·5 (5)
C(11)—C(12)	1·363 (9)	C(3)—C(2)—C(13)	120·2 (4)
C(12)—C(7)	1·419 (9)	C(7)—C(8)—C(9)	122·5 (4)
C(14)—C(15)	1·508 (12)	C(7)—C(12)—C(11)	120·3 (4)
C(16)—C(17)	1·499 (12)	C(8)—C(7)—C(12)	117·2 (5)
		C(8)—C(9)—C(10)	122·2 (4)
		C(9)—C(10)—C(11)	114·2 (5)
		C(10)—C(11)—C(12)	123·7 (4)
		C(10)—N(3)—C(14)	123·5 (4)
		C(10)—N(3)—C(16)	121·0 (4)
		C(14)—N(3)—C(16)	115·5 (4)

[a] Atom labelling as in Fig. 1. Figures in parentheses are e.s.d.

converged to $R = 0{\cdot}059$ when the final shifts of the atomic parameters were negligible and well below the corresponding σ. The final ΔF map was featureless ($< 0{\cdot}1$ e/Å^3). Scattering factors were taken from a recent compilation[6] and the weighting scheme used followed our usual procedures.[7] The final coordinates and thermal parameters are listed in Tables 1–3 and bond data in Tables 4–6. Figures 1 and 2 show views of the

TABLE 5
Bond Distance and Angles Involving Hydrogen Atoms[a]

Type	*Length (Å)*	*Type*	*Angle (degrees)*
C(3)—H(3)	0·96 (8)	C(2)—C(3)—H(3)	121 (3)
C(5)—H(5)	0·85 (5)	C(4)—C(3)—H(3)	118 (3)
C(6)—H(6)	1·01 (7)	C(4)—C(5)—H(5)	115 (3)
C(8)—H(8)	0·97 (7)	C(6)—C(5)—H(5)	125 (3)
C(9)—H(9)	0·90 (5)	C(5)—C(6)—H(6)	116 (3)
C(11)—H(11)	0·88 (6)	C(1)—C(6)—H(6)	121 (3)
C(12)—H(12)	0·93 (6)	C(7)—C(8)—H(8)	120 (3)
C(14)—H(141)	1·06 (7)	C(9)—C(8)—H(8)	117 (3)
C(14)—H(142)	0·90 (9)	C(8)—C(9)—H(9)	125 (3)
C(15)—H(151)	0·92 (7)	C(10)—C(9)—H(9)	113 (3)
C(15)—H(152)	0·93 (10)	C(10)—C(11)—H(11)	121 (3)
C(15)—H(153)	0·85 (6)	C(12)—C(11)—H(11)	115 (3)
C(16)—H(161)	0·93 (6)	C(11)—C(12)—H(12)	115 (3)
C(16)—H(162)	1·07 (6)	C(7)—C(12)—H(12)	124 (3)
C(17)—H(171)	1·10 (11)	N(3)—C(14)—H(141)	109 (4)
C(17)—H(172)	0·93 (7)	N(3)—C(14)—H(142)	109 (5)
C(17)—H(173)	0·94 (7)	C(15)—C(14)—H(141)	102 (4)
		C(15)—C(14)—H(142)	108 (5)
		C(14)—C(15)—H(151)	102 (4)
		C(14)—C(15)—H(152)	108 (5)
		C(14)—C(15)—H(153)	109 (4)
		N(3)—C(16)—H(161)	109 (3)
		N(3)—C(16)—H(162)	111 (3)
		C(17)—C(16)—H(161)	113 (3)
		C(17)—C(16)—H(162)	112 (3)
		C(16)—C(17)—H(171)	110 (5)
		C(16)—C(17)—H(172)	107 (4)
		C(16)—C(17)—H(173)	109 (4)

[a] Atom labelling as in Fig. 1. Figures in parentheses are e.s.d.

molecule as drawn by means of the PLUTO program[8] (a list of structure factors may be obtained from the authors of this paper).

3. RESULTS AND DISCUSSION

The conformation of the molecule (Fig. 1) is such that N(2) is oriented *anti* with respect to C(2) carrying the CN substituent, minimizing the repulsive interaction between the electron lone pair at N(1) and the

TABLE 6
Main Non-bonded Distances (Å) and Torsional Angles[a]

Type	*Length (Å)*	*Type*	*Length (Å)*
N(1)—C(13)	2·753 (8)	H(9)—H(142)	2·04 (10)
N(2)—H(6)	2·51 (6)	H(11)—H(162)	2·27 (8)
N(1)—H(8)	2·51 (6)		
Type	*Angle (degrees)*	*Type*	*Angle (degrees)*
C(2)—C(1)—N(1)—N(2)	177·2 (1)	C(9)—C(10)—N(3)—C(16)	−169·0 (1)
C(6)—C(1)—N(1)—N(2)	−2·2 (1)	C(11)—C(10)—N(3)—C(14)	−168·6 (1)
C(8)—C(7)—N(2)—N(1)	1·3 (1)	C(10)—N(3)—C(14)—C(15)	−97·5 (1)
C(12)—C(7)—N(2)—N(1)	178·9 (1)	C(10)—N(3)—C(16)—C(17)	−87·3 (1)

[a] Atom labelling as in Fig. 1. Figures in parentheses are e.s.d.

electron cloud of the cyano-group. The corresponding *syn* conformation would have led to severe repulsion between CN and the lone pair on N(2). The situation is analogous to that found for 2-bromo-4-cyano-4′-*N*,*N*-diethylaminoazobenzene (II).[7] It is of interest to notice a decrease in the C(2)—C(1)—N(1) bond angle (from 119·2 to 116·8°) as a result of the variation in substitutional pattern from (II) (2Br, 4CN) to (I) (2CN, 4Br), indicating the smaller interaction (or probably even the absence of any

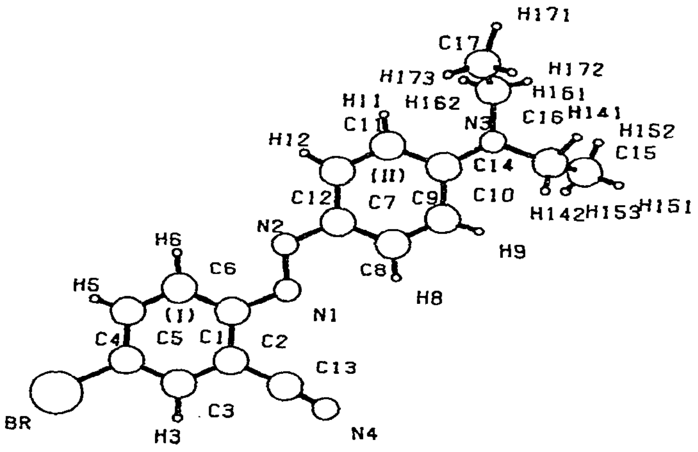


Fig. 1. View of 2-cyano-4-bromo-4′-*N*,*N*-diethylaminoazobenzene on to the molecular plane, showing the atom-labelling scheme.

TABLE 7

Planarity of Groups of Atoms in the Structure

Equations of the least-squares planes are expressed as $Px + Qy + Rz - S = 0$ with reference to an orthogonal system of axes with x along the a^* axis, y in the $(b\text{–}c)$ plane and z along the c axis. The distances of the atoms to the plane are in Å units.

Plane (1)					
		$0{\cdot}6469x - 0{\cdot}5822y + 0{\cdot}4926z = 0{\cdot}0831$			
C(1)	−0·006	C(2)	0·008		
C(3)	−0·004	C(4)	−0·002		
C(5)	0·004	C(6)	−0·001		
Not defining plane:		Br	−0·022	N(1)	−0·009
		N(2)	0·038	N(4)	0·049
		C(13)	0·040		
Plane (2)					
		$0{\cdot}6208x - 0{\cdot}5685y + 0{\cdot}5398z = -0{\cdot}3051$			
C(7)	0·001	C(8)	−0·004		
C(9)	−0·003	C(10)	0·013		
C(11)	−0·017	C(12)	0·009		
Not defining plane:		N(1)	0·057	C(14)	0·295
		N(3)	0·025	H(141)	0·75
		C(16)	−0·200	H(142)	0·74
		N(2)	0·044	H(161)	−0·66
				H(162)	−0·97
Plane (3)					
		$0{\cdot}7588x - 0{\cdot}4306y + 0{\cdot}4887z = 0{\cdot}1556$			
N(3)	−0·009	C(14)	0·003		
C(10)	0·003	C(16)	0·003		
Not defining plane:		C(9)	−0·241	C(11)	0·225
		C(15)	−1·379	C(17)	1·377

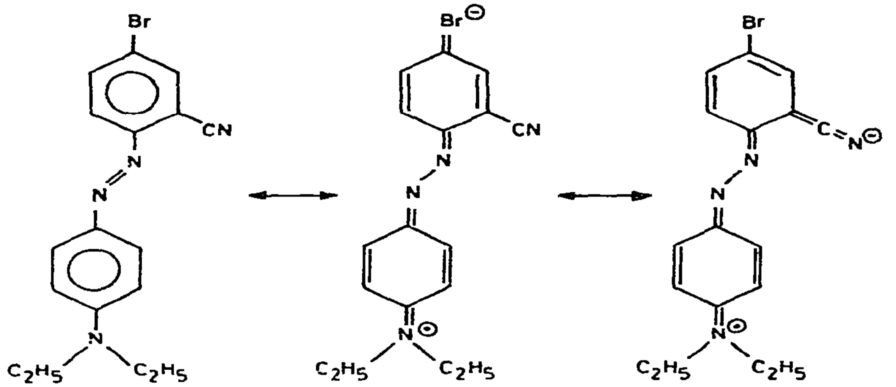
Dihedral angles (degrees) between planes:
Plane (1)–Plane (2) 3·3
Plane (2)–Plane (3) 11·6

such interaction) of the 2-cyano substituent with the electron lone pair at N(1) as compared with 2-Br and the relief of the corresponding interaction between H(6) and the N(2) electron pair. In this respect it is also quite significant that the N(1)—C(1)—C(6) and N(2)—C(7)—C(8) bond angles in (**I**) are equal within the limits of accuracy; the N(2)—H(6) and N(1)—H(8) non-bonded distances amount to 2·51 Å each. On the whole, the results are in accordance with the fact that the absorption characteristics of (I) and (II) are virtually identical.

As in the case of the (2Br, 4CN) analogue (II), the molecular skeleton of (I) is essentially planar (Table 7) with C(10) showing the largest deviation (0·06 Å) from planarity and a dihedral angle of 3·3 ° between the phenyl rings (2·1 ° in II)) with an average step height of about 0·20 Å. Whereas in (I) the ethyl groups are rotated around N(3)—C(10) in the same direction, leading to absence of symmetry (cf. Table 7 and Fig. 1), the NEt_2 moiety of (II) has ethyl groups on either side of a mirror plane. The difference is likely to be connected with packing requirements. Although the diethylamino-group as a whole is not planar (similar to other cases[1]), the N(3)—C(14)—C(16) moiety is almost coplanar with the skeleton (Table 7).

The bond data for the azo-group are as follows (for comparison values of (II) are given in parentheses): N=N 1·290(8) Å (1·264(6) Å); N—C 1·394(8) and 1·365(8) Å (1·421(7) and 1·399(7) Å); N=N—C 113·6(4) and 115·3(4)° (113·0(2) and 115·7(2)°); N—C—C(*cis*) 125·9(4) and 126·7(4)° (123·1(2) and 125·4(3)°); N—C—C(*trans*) 116·8(5) and 116·1(4)° (119·2(2) and 116·0(2)°). The value of ΔR(CN) in (I) is within the established limits (<0·06 Å) usually observed for azo-tautomers.[2] Both the N=N and C—N bond lengths are at the extremes of usual ranges, reportedly 1·20–1·28 Å and 1·37–1·49 Å, respectively.[2] This indicates considerable electron delocalization in the molecule. Bond orders of 1·75 and 1·4–1·3 v.u. may be assigned to the N=N and C—N(azo) bonds.[9] The N—C—C(*cis*) and N—C—C(*trans*) bond angles differ by as much as 9·1 and 10·6 ° for rings I and II, respectively. Even greater differences have been observed in other azobenzene derivatives (cf. Table 5 of ref. 1). The N—C bond length towards the bromocyanobenzene ring is significantly longer than towards the diethylaminophenyl group. This is a common feature in aminoazobenzene structures, such as 2,6-dichloro-4'-*N*,*N*-diethylaminoazobenzene,[1] (II),[7] sodium-4'-dimethylaminoazobenzene-4-sulphonate (Methyl Orange),[10] 2'-acetamido-2-chloro-4'-diethylamino-4-mesylazobenzene,[11] 2-chloro-4'-diethylamino-4-mesyl-2'-propionamidoazobenzene,[11] and *trans*-*o*-aminoazotoluene,[12] where on average the C—N bond at the NR_2 side is shorter by about 0·03 Å than the corresponding bond towards the other phenyl ring, exactly as observed in the present case.

In keeping with the substituent effects on aromatic ring geometry,[13–15] the C(1)—C(2)—C(3) angle (120·3(4)°) involved in CN substitution, is



Scheme 1.

larger than the C(2)—C(1)—C(6) angle (117·3(5)°) with azo-group attachment. The former value is close to the standard value of 121·8°,[15] whereas the latter is significantly smaller than the suggested 120·0° for azo mono-substitution. As in (**II**), this may be due to the disturbing influence of the Br atom in the ring. Quite noticeably, the bond angle distributions in ring I in the two bromocyanoazobenzene derivatives (**I**) and (**II**) vary, mainly at the side of the Br substituent (118·5(5)° and 123·0(2)°, respectively). No ready explanation is available for this detail. The C(9)—C(10)—C(11) angle of 114·2(5)° is quite noteworthy, being considerably smaller than the C(8)—C(7)—C(12) angle ((117·2(5)°) at the N=N end and also less than the average value (117·2°) at $N(CH_3)_2$ substitution sites. Deserving further note, is the shortening of the N(3)—C(10) bond from 1·364(7) Å in (**II**) to 1·326(8) Å (1·7 v.u.) in the present case. It is felt that these facts are not unrelated.

In spite of the considerable bond angle distortions in the aromatic rings (117·3–122·4° in ring I and 114·2–123·7° in ring II) the average C—C—C bond angle conforms to the standard value (120°). As to the aromatic bond lengths, which vary from 1·351(10)–1·411(9) Å in ring I to 1·343(9)–1·446(9) Å in ring II with mean values of 1·386 and 1·397 Å, respectively, we notice a pattern which suggests contributions of the canonical forms shown in Scheme 1. This scheme is in good accordance with the previous statements regarding N—N and N—C bond lengths.

The Br—C(4) bond length of 1·866(6) Å is significantly shorter than those of 1·914(6) Å in *o*-bromobenzene-*anti*-diazocyanide,[16] 1·904(5) Å in (**II**) and 6,6′-dibromo-2,2′,4,4′-tetra-*tert*-butylazobenzene,[17] 1·902(8) Å in *p*-bromodiazoaminobenzene,[18] and 1·891(13) Å in *trans*-4,4′-dibromo-

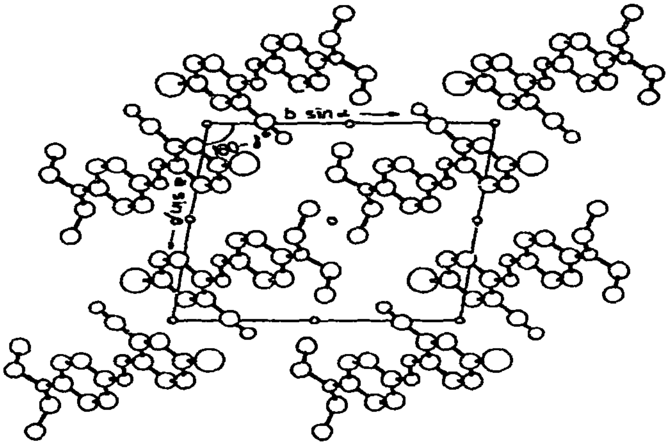


Fig. 2. Crystal structure of 2-cyano-4-bromo-4'-*N,N*-diethylaminoazobenzene viewed down the crystallographic *c* axis.

azobenzene,[19] but close to the values of 1·880(4) Å reported for hexabromobenzene[20] and 1·883(8) Å in *o*-dibromobenzene.[21]

Apart from the aforementioned short N(3)—C(10) link, the bond distances of the diethylamino-substituent are standard (cf. ref. 1). The dimensions of the carbonitrile group are not significantly different from those observed in $C_6(CN)_6$.[22] The average C—H bond length of 0·95 Å is identical to the mean value usually observed by refinement of X-ray diffraction data.[23] The hydrogen atoms of C(15) and C(17) are in *staggered* positions.

The packing arrangement of 2-cyano-4-bromo-4'-*N,N*-diethylaminoazobenzene is shown in Fig. 2. All short intermolecular contacts (in Å) in the structure (Br—C, 3·66; Br—N, 3·82; Br—H, 3·26; N—N, >3·60; C—C, 3·53; C—N, 3·68; C—H, 2·84; N—H, 2·77; H—H, 2·45) conform to normal van der Waals interactions.

It is of interest to compare the crystal structures of (I) and (II) ($P\bar{1}$, $Z = 2$; $a = 13{\cdot}162(5)$ Å, $b = 7{\cdot}516(3)$ Å, $c = 8{\cdot}496(4)$ Å, $\alpha = 101{\cdot}63(4)°$, $\beta = 95{\cdot}79(4)°$, $\gamma = 91{\cdot}49(4)°$), which differ only in the position (*ortho* and *para*) of the Br and CN substituents. As may be seen from Fig. 2 for (I) and Fig. 2 of ref. 7 for (II), the packing schemes of the two isomers both consist of diagonally oriented strings of molecules. Whereas on the one hand the diethylamino-groups are interlocked in a similar fashion around a centre of symmetry, also the mutual dispositions of Br and CN substituents in the molecules composing the string (arranged around

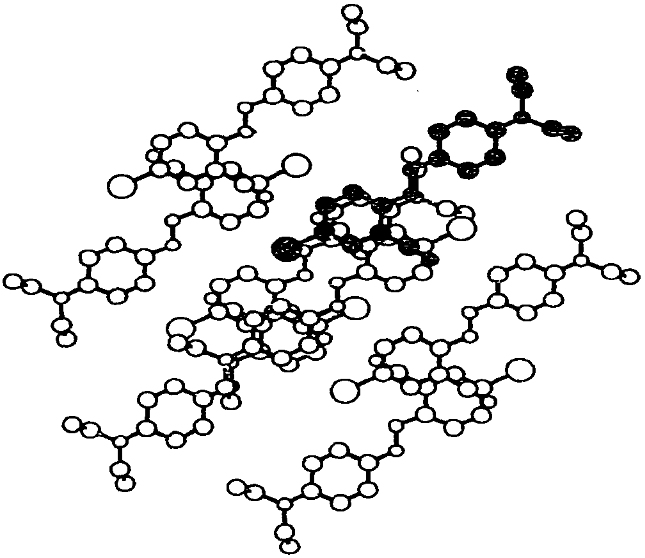


Fig. 3. Packing arrangement of 2-cyano-4-bromo-4'-*N*,*N*-diethylaminoazobenzene viewed down the molecular plane.

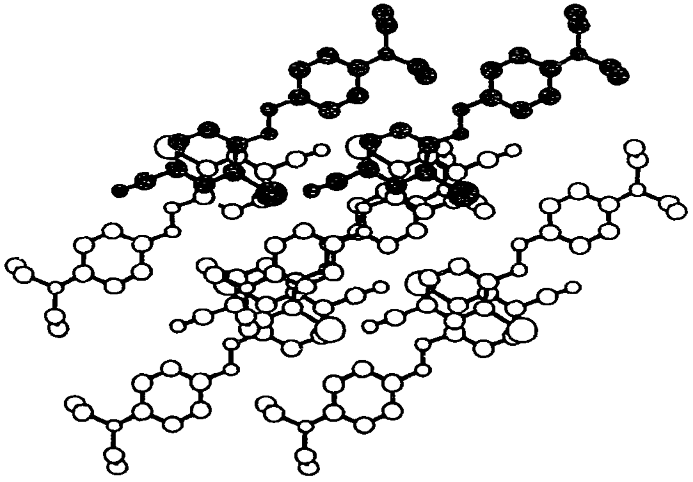


Fig. 4. Packing arrangement of 2-bromo-4-cyano-4'-*N*,*N*-diethylaminoazobenzene viewed down the molecular plane.

another symmetry centre) are alike. A view of structures (I) and (II), seen perpendicular to the molecular planes (Figs. 3 and 4), shows the close analogy in packing schemes but also indicates differences in overlap of structural moieties. As shown by the unit-cell values (826·5 Å^3 in (I) and 818·1 Å^3 in (II)), packing of the molecules of (II) is more efficient.

ACKNOWLEDGEMENT

Thanks are due to Dr J. Griffiths (Department of Colour Chemistry and Dyeing, The University, Leeds) for providing the crystals.

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