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Structure of the Dye 2,6-Dichloro-4′-*N*,*N*-diethylaminoazobenzene

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SUMMARY

*The structure of 2,6-dichloro-4′-*N,N*-diethylaminoazobenzene has been determined from X-ray diffractometer data:* $C_{16}H_{17}Cl_2N_3$, *MW = 322·2, monoclinic,* $P2_1/n$, a = *11·160 (2),* b = *12·066 (2),* c = *13·633 (3) Å,* β = *116·46 (2)°,* V = *1643·5 Å*^{3}, Z = 4, D_c = *1·30 g cm*$^{-3}$, F(*000*) = *672,* λ(*MoK*α) = *0·71069 Å,* μ(*MoK*α) = *3·94 cm*$^{-1}$. *The structure was solved by direct methods and refined to* R = *0·073 for 1495 independent reflexions. The molecule is non-planar with a dihedral angle of 87·8° between the phenyl rings. The effects of substituents on the aromatic ring geometry are discussed. Significant molecular parameters are: N=N, 1·164 (9) Å; mean Cl—C, 1·741 (6) Å; mean C—N(azo), 1·487 (9) Å; N=N—C, 112·4 (2)° and 109·1 (2)°; N—C—C* (cis *relative to N=N), 125·5 (3)° and 122·4 (2)°; N—C—C* (trans *relative to N=N) 114·0 (3)° and 119·5 (3)°; mean C—C(Cl)—C, 122·3 (3)°.*

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1. INTRODUCTION

Dyes based on 4-aminoazobenzene, containing a donor–acceptor chromogen, are important in dyeing polyester fibres due to their desirable colour and satisfactory lightfastness properties. Notable examples of this class of dyes are CI Disperse Red 72 (CI 11114) and CI Disperse Blue 165 (CI 11077). Surprisingly few X-ray structural studies of these compounds have been reported and in general the influence of steric crowding on the structure and colour of the monoazo dyes has received little systematic investigation. As part of the X-ray structural studies of substituted azobenzene compounds[1] the crystal structure of 2,6-dichloro-4′-*N*,*N*-diethylaminobenzene (**I**) has now been determined and the effects of the substituents Cl, N=N, and $N(C_2H_5)_2$ on molecular conformation and aromatic ring geometry have been elucidated.

2. EXPERIMENTAL

Compound **I** was recrystallized from acetone as dark red plates ($\lambda_{max} = 387$ nm; ε(hexane) = 31·200; m.p. = 121 °C). Using a crystal mounted on a Picker FACS-1 four-circle computer-controlled diffractometer equipped with a scintillation counter and a pulse-height analyser, accurate cell dimensions and an orientation matrix were determined by a least-squares fit of χ, ϕ, ω and 2θ values of 12 independent reflexions.

2.1. Crystal data

$C_{16}H_{17}Cl_2N_3$, MW = 322·2, monoclinic, $P2_1/n$, $a = 11{\cdot}160$ (2), $b = 12{\cdot}066$ (2), $c = 13{\cdot}633$ (3)Å, $\beta = 116{\cdot}46$ (2)°, $V = 1643{\cdot}5$ Å^3, $Z = 4$, $D_0 = 1{\cdot}27$ g cm^{-3}, $D_c = 1{\cdot}30$ g cm^{-3}, $F(000) = 672$.

Intensity data were collected with a crystal of dimensions 0·5 × 0·4 × 0·1 mm mounted with c along the ϕ axis of the diffractometer using Zr-filtered MoKα radiation ($\lambda = 0{\cdot}710\,69$ Å). The moving-crystal moving-counter technique was used with a 2θ scan rate of 1 ° min^{-1} and a scan range of 2·0–2·5 ° in order to account properly for the separation of the Kα_1 and Kα_2 peaks at various 2θ values. Background counts of 10s were measured at each end of every 2θ scan. The net counts of three standard reflexions, monitored after every 50 reflexions, did not alter significantly

TABLE 1
Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å^2)
E.s.d. values are given in parentheses

Atom	*x*	*y*	*z*	B_{eq}[a]
Cl(1)	0·537 6 (2)	0·800 4 (2)	0·285 4 (2)	7·8 (1)
Cl(2)	0·261 6 (2)	0·419 3 (2)	0·139 1 (2)	8·5 (1)
N(1)	0·517 5 (6)	0·552 3 (5)	0·267 2 (4)	7·2 (2)
N(2)	0·532 5 (5)	0·529 5 (4)	0·354 9(4)	6·0 (2)
N(3)	1·008 2 (4)	0·309 4 (4)	0·629 8 (3)	5·1 (2)
C(1)	0·387 9 (5)	0·615 5 (5)	0·208 7 (4)	4·9 (2)
C(2)	0·390 3 (5)	0·730 7 (5)	0·205 5 (4)	5·3 (2)
C(3)	0·278 7 (6)	0·790 5 (5)	0·141 3 (5)	6·7 (3)
C(4)	0·160 5 (6)	0·735 7 (6)	0·076 6 (5)	7·4 (3)
C(5)	0·156 0 (6)	0·621 1 (6)	0·076 5 (5)	6·9 (3)
C(6)	0·269 4 (5)	0·564 2 (5)	0·143 0 (4)	5·5 (2)
C(7)	0·659 5 (4)	0·472 9 (4)	0·418 8 (4)	5·0 (2)
C(8)	0·754 4 (5)	0·447 1 (4)	0·382 1 (4)	5·3 (2)
C(9)	0·873 4 (5)	0·389 6 (4)	0·452 5 (4)	4·8 (2)
C(10)	0·893 6 (4)	0·362 3 (4)	0·559 6 (4)	4·1 (2)
C(11)	0·794 2 (5)	0·390 3 (4)	0·590 9 (4)	4·9 (2)
C(12)	0·679 3 (5)	0·442 6 (5)	0·521 5 (4)	5·7 (2)
C(13)	1·107 3 (5)	0·267 4 (5)	0·595 8 (5)	6·2 (3)
C(14)	1·071 3 (7)	0·153 0 (6)	0·546 2 (6)	7·3 (3)
C(15)	1·035 9 (6)	0·282 8 (5)	0·742 0 (4)	5·9 (2)
C(16)	1·115 9 (8)	0·373 3 (7)	0·822 0 (5)	8·7 (4)
H(3)	0·283	0·882	0·138	
H(4)	0·069	0·783	0·026	
H(5)	0·063	0·578	0·026	
H(8)	0·735	0·469	0·300	
H(9)	0·950	0·368	0·425	
H(11)	0·809	0·370	0·674	
H(12)	0·600	0·459	0·546	
H(131)	1·205	0·265	0·667	
H(132)	1·113	0·323	0·535	
H(141)	1·145	0·123	0·524	
H(142)	0·974	0·155	0·477	
H(143)	1·066	0·097	0·609	
H(151)	1·093	0·206	0·766	
H(152)	0·942	0·272	0·746	
H(161)	1·134	0·350	0·904	
H(162)	1·060	0·450	0·800	
H(163)	1·210	0·384	0·820	

[a] $B_{eq} = \frac{4}{3}\sum_i\sum_j B_{ij} a_i.a_j$ with $\sigma(B_{eq}) = \frac{4}{3}\sum_i\sum_j (a_i.a_j).\sigma(B_{ij})$. Each hydrogen atom has an assumed isotropic temperature factor $B = 5{\cdot}0$ Å^2.

TABLE 2

Anisotropic Thermal Parameters (Å^2) in the Form:

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

E.s.d. values are given in parentheses.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl(1)	6·45 (8)	7·48 (9)	7·61 (9)	−0·43 (7)	1·49 (7)	−0·83 (8)
Cl(2)	7·76 (9)	6·90 (9)	8·25 (10)	−1·03 (8)	1·32 (8)	1·80 (8)
N(1)	10·00 (34)	7·93 (31)	3·71 (20)	−0·10 (26)	3·10 (22)	3·15 (20)
N(2)	6·48 (24)	6·49 (25)	5·75 (22)	−0·62 (20)	3·42 (20)	−1·19 (20)
N(3)	4·05 (17)	5·72 (22)	4·82 (19)	1·40 (16)	1·45 (15)	0·28 (17)
C(1)	3·79 (20)	7·10 (30)	3·31 (19)	1·47 (19)	1·14 (16)	1·45 (19)
C(2)	5·43 (26)	6·40 (29)	3·89 (22)	0·73 (21)	1·80 (20)	−0·25 (20)
C(3)	7·64 (35)	6·32 (31)	5·42 (28)	2·70 (27)	2·15 (26)	0·63 (24)
C(4)	5·47 (29)	9·82 (44)	5·13 (28)	2·68 (28)	0·67 (23)	0·81 (28)
C(5)	5·37 (28)	8·85 (40)	5·26 (28)	0·79 (26)	1·23 (22)	1·16 (26)
C(6)	5·15 (24)	6·53 (30)	4·46 (23)	0·72 (22)	1·80 (19)	1·66 (22)
C(7)	3·09 (18)	3·81 (21)	6·61 (27)	0·29 (15)	0·82 (18)	−1·03 (19)
C(8)	6·47 (27)	4·36 (23)	3·31 (20)	−1·59 (20)	0·50 (19)	−1·15 (17)
C(9)	4·26 (21)	4·71 (23)	4·54 (22)	0·23 (17)	1·20 (18)	0·06 (18)
C(10)	3·60 (18)	3·41 (18)	4·30 (21)	0·03 (15)	1·00 (16)	−0·15 (16)
C(11)	4·44 (21)	5·46 (25)	5·19 (24)	0·83 (19)	2·41 (19)	−0·07 (20)
C(12)	4·72 (23)	6·52 (30)	5·20 (26)	0·94 (22)	1·55 (20)	0·18 (22)
C(13)	4·34 (24)	7·19 (33)	6·68 (30)	1·62 (23)	1·98 (23)	0·02 (26)
C(14)	8·27 (37)	7·18 (35)	7·80 (37)	2·30 (31)	4·80 (31)	−0·09 (30)
C(15)	6·62 (30)	6·84 (32)	4·24 (23)	2·07 (25)	2·34 (22)	1·58 (22)
C(16)	8·79 (43)	10·99 (52)	5·11 (31)	−0·32 (38)	1·97 (29)	−0·61 (33)

throughout the period of data collection. Out of the 2898 independent reflexions measured for $2\theta < 50°$, 1495 were observed with the $I > 2{\cdot}5\sigma$ limit ($\sigma = [N_s + (t_s/t_b)^2 N_b]^{1/2}$, where N_s is the total peak count during the time of scanning t_s, and t_b is the time spent measuring the N_b background counts). An arbitrary intensity of 0·5 of the observable limit was assigned to each of the non-significant reflexions ('unobserveds'). The intensities were corrected for Lorentz and polarization effects but not for absorption ($\mu(\text{MoK}\alpha) = 3{\cdot}94\,\text{cm}^{-1}$).

The structure was essentially 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 $R = 0{\cdot}096$. The H atoms were then introduced into the calculations at fixed positions on stereochemical

TABLE 3
Bond Distances (Å) and Angles (°)
E.s.d. values are given in parentheses

Bond distance		*Bond angle*	
Cl(1)—C(2)	1·732 (7)	Cl(1)—C(2)—C(1)	119·5 (3)
Cl(2)—C(6)	1·750 (6)	Cl(1)—C(2)—C(3)	119·0 (3)
Mean Cl—C	1·741 (6)	Cl(2)—C(6)—C(1)	119·5 (3)
		Cl(2)—C(6)—C(5)	117·5 (4)
N(1)—N(2)	1·164 (9)		
		N(1)—C(1)—C(2)	119·5 (3)
N(1)—C(1)	1·511 (10)	N(1)—C(1)—C(6)	122·4 (2)
N(2)—C(7)	1·462 (10)	N(1)—N(2)—C(7)	112·4 (2)
N(3)—C(10)	1·366 (9)	N(2)—N(1)—C(1)	109·1 (2)
N(3)—C(13)	1·467 (6)	N(2)—C(7)—C(8)	125·5 (3)
N(3)—C(15)	1·455 (9)	N(2)—C(7)—C(12)	114·0 (3)
Mean N—C	1·452 (9)	N(3)—C(10)—C(9)	120·1 (3)
		N(3)—C(10)—C(11)	121·5 (3)
C(1)—C(2)	1·391 (8)	N(3)—C(13)—C(14)	111·7 (2)
C(1)—C(6)	1·370 (9)	N(3)—C(15)—C(16)	112·2 (3)
C(2)—C(3)	1·366 (12)		
C(3)—C(4)	1·385 (11)	C(1)—C(2)—C(3)	121·5 (3)
C(4)—C(5)	1·384 (11)	C(1)—C(6)—C(5)	123·0 (3)
C(5)—C(6)	1·369 (12)	C(2)—C(1)—C(6)	117·2 (3)
		C(2)—C(3)—C(4)	119·6 (4)
C(7)—C(8)	1·393 (6)	C(3)—C(4)—C(5)	120·0 (4)
C(7)—C(12)	1·366 (10)	C(4)—C(5)—C(6)	118·6 (3)
C(8)—C(9)	1·425 (10)		
C(9)—C(10)	1·414 (9)	C(7)—C(8)—C(9)	119·7 (3)
C(10)—C(11)	1·396 (6)	C(7)—C(12)—C(11)	120·5 (3)
C(11)—C(12)	1·363 (11)	C(8)—C(9)—C(10)	118·8 (3)
		C(8)—C(7)—C(12)	120·5 (3)
C(13)—C(14)	1·511 (9)	C(9)—C(10)—C(11)	118·4 (3)
C(15)—C(16)	1·521 (10)	C(10)—C(11)—C(12)	122·0 (3)
		C(10)—N(3)—C(13)	122·8 (3)
		C(10)—N(3)—C(15)	122·3 (3)
		C(13)—N(3)—C(15)	114·8 (3)

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 converged to $R = 0{\cdot}073$ for the observed reflexions. The final shifts of the atomic parameters were negligible and all well below the corresponding σ. The final ΔF synthesis was featureless.

Positional and thermal parameters of the non-hydrogen atoms were refined with the least-squares program of Immirzi.[3] Atomic scattering factors were calculated according to ref. 4, using the values from the

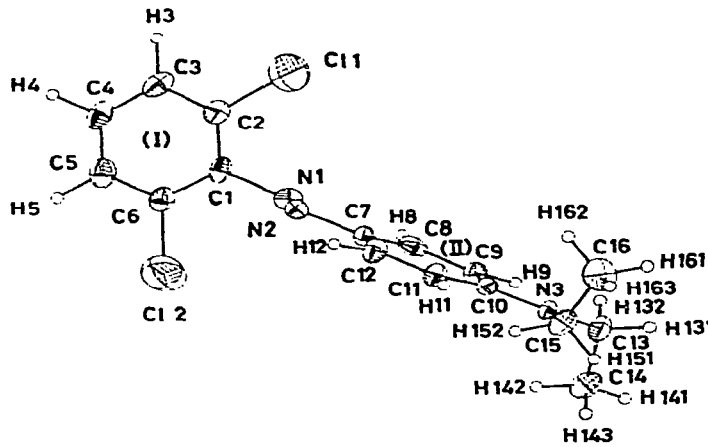


Fig. 1. The molecule of 2,6-dichloro-4′-*N*,*N*-diethylaminoazobenzene showing the atom labelling scheme and 30% probability thermal vibration ellipsoids.

parameters given by Moore.[5] The weighting scheme used was that of Cruickshank *et al.*:[6]

$$1/w = A + B|F_o| + C|F_o|^2$$

where $A = 2F_o(\text{min})$, $B = 1{\cdot}0$ and $C = 2/F_o(\text{max})$.

The final fractional coordinates and temperature factors are listed in Tables 1 and 2 and bond lengths and angles in Table 3. Figures 1 and 2 show views of **I**, together with the labelling scheme and the thermal vibration ellipsoids of the non-hydrogen atoms.[7] All calculations were performed on a Univac 1100/20 computer using a local program set. A list of structure factors may be obtained from the authors of this paper.

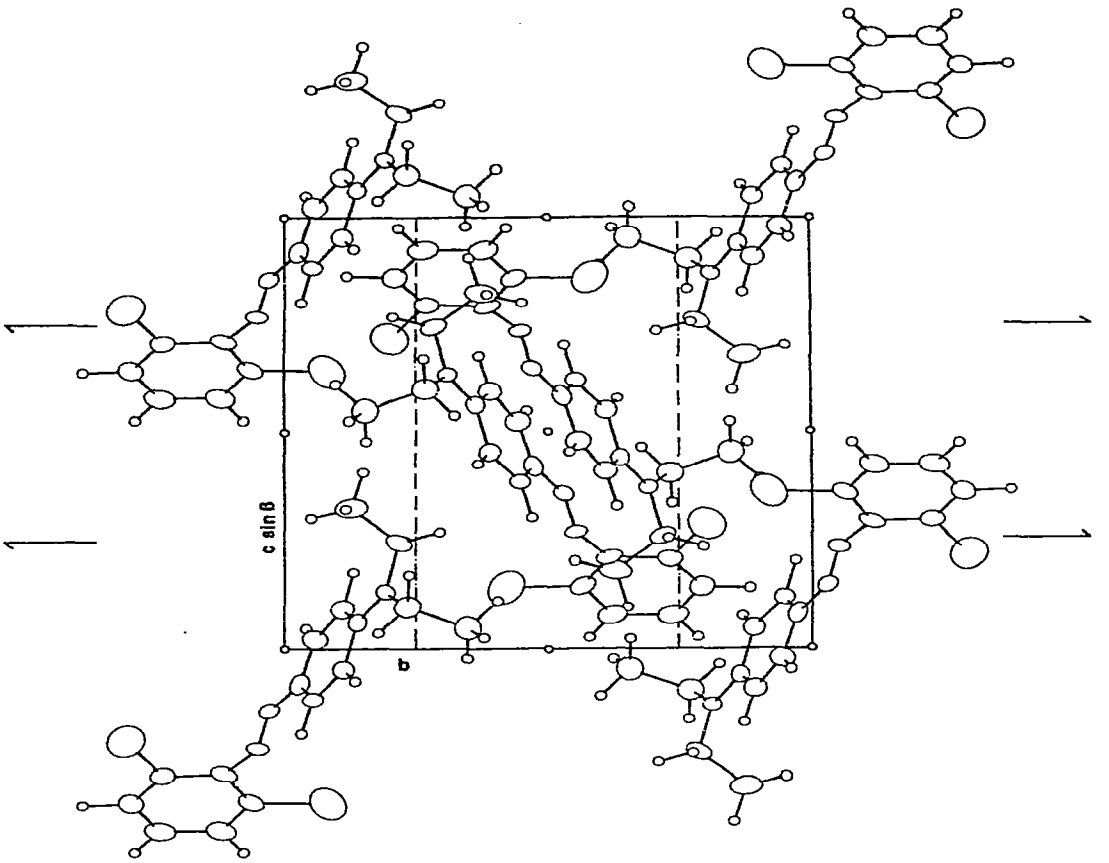


Fig. 2. Structure of 2,6-dichloro-4'-*N*,*N*-diethylaminoazobenzene viewed down the *a* axis.

3. DISCUSSION

Results of least-squares planes calculations (Table 4) show that the azobenzene skeleton of the asymmetrical structure of **I** deviates significantly from planarity with the azo group being approximately in the plane of the (diethylamino)benzene ring II. The dihedral angle between the two phenyl rings is 87·8°, which is not surprising in view of the observed $\lambda_{max} = 387$ nm. The loss of planarity of the molecule is caused by interaction of the lone pair electrons of the azo nitrogen atoms

TABLE 4
Planarity of Groups of Atoms in the Structure

Equations of the least-squares planes are expressed as

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

in the $a^*b\,c$ orthogonal axis system.

The distances of the atoms from the planes are in Å.

Plane (1)

$$0{\cdot}669x - 0{\cdot}034y - 0{\cdot}743z + 0{\cdot}094 = 0$$

C(1)	−0·001 (5)			C(2)	0·013 (6)
C(3)	−0·001 (7)			C(4)	−0·011 (7)
C(5)	0·003 (6)			C(6)	−0·001 (6)
Not defining plane:		Cl(1)	0·034 (2)	Cl(2)	0·050 (2)
		N(1)	0·244 (5)	N(2)	−0·807 (5)

Plane (2)

$$-0{\cdot}334x - 0{\cdot}890y - 0{\cdot}311z + 8{\cdot}238 = 0$$

C(7)	−0·039 (5)			C(8)	−0·052 (5)
C(9)	−0·004 (5)			C(10)	0·025 (5)
C(11)	0·040 (5)			C(12)	0·030 (6)
Not defining plane:		N(1)	−0·094 (6)	N(2)	−0·060 (5)
		N(3)	0·041 (5)	C(13)	0·182 (6)
		C(15)	0·025 (6)		

Plane (3)

$$0{\cdot}401x + 0{\cdot}869y + 0{\cdot}079z - 8{\cdot}418 = 0$$

N(3)	0·025 (4)	C(13)	−0·008 (6)
C(10)	−0·009 (7)	C(15)	−0·008 (5)

Plane (4)

$$-0{\cdot}554x - 0{\cdot}816y - 0{\cdot}163z + 8{\cdot}156 = 0$$

N(1)	−0·116 (6)			N(2)	0·137 (5)
C(1)	−0·018 (6)			C(7)	−0·003 (5)
Not defining plane:		C(2)	−1·172 (6)	C(6)	1·129 (6)
		C(8)	−0·387 (6)		
				C(12)	0·315 (6)

Dihedral angles (degrees) between planes:

Plane (1)–Plane (2)	87·8
Plane (1)–Plane (3)	79·6
Plane (1)–Plane (4)	102·8
Plane (2)–Plane (3)	21·4
Plane (2)–Plane (4)	15·8
Plane (3)–Plane (4)	19·3

with the two chlorine substituents of ring I in positions *ortho* to the azo group. This leads to the hypsochromic displacement of the first absorption band and to a decrease in intensity as compared with 4-*N*,*N*-diethylaminoazobenzene ($\lambda_{max} = 415$ nm, $\log \varepsilon = 4{\cdot}47$).[8] Similarly, chlorine substitution in the 2- and 2,6-positions in 4-nitro-4'-*N*-ethyl-4'-*N*-cyanoethylaminoazobenzene ($\lambda_{max} = 453$ nm, $\varepsilon = 44{\cdot}000$ in MeOH) modifies $\lambda_{max}(\varepsilon)$ from 475 nm (40·000) to 417 nm (31·000), respectively,[9] clearly indicating the effect of steric hindrance due to *ortho* disubstituted benzene rings.

The observed angle between the aromatic rings of **I** exceeds that of other azobenzene compounds described previously (Table 5), yet is very close to that of one of the polymorphs of 2,2',4,4',6,6'-hexanitroazobenzene (**II**).[10] It is quite noticeable that this compound also exhibits another conformation which, while non-planar, contains parallel phenyl rings. Steric crowding in **II** is relieved by a multiplicity of contributions, amongst which are bond angle distortions, considerable out-of-plane rotation of the *ortho* nitro groups (by twists of 29–86°), displacement of the azo nitrogen atoms from the benzene rings to which they are attached and rotation of the azo group by about 45° with respect to the aromatic plane. A similar out-of-plane displacement has been found in **I** for N(1) with respect to the C(1–6) plane (Table 4). Rotation of the azo group out of this plane is even more pronounced (102·8°) than in the hexanitroazobenzene. In the case of one Cl atom in the *ortho* position, as in *trans*-2,2'-dichloroazobenzene, the angle of twist is only 12·8°.[11] In the absence of *ortho* substituents in ring C(7–12) of **I** the dihedral angle with the plane through C(1), N(1), N(2) and C(7) amounts to 15·8°. Although the diethylamino group as a whole is not planar the dihedral angle between the plane defined by C(10), N(3), C(13) and C(15) and the ring to which it is attached is only 21·4°.

The conformation of **I** (Fig. 1) is such that N(2) is oriented *anti* with respect to C(2) with an N(2)...C(2) distance of 3·111 (9) Å. With the exception of the N=N bond length and the mean N=N—C bond angle, the other values for the azo group in the molecule are in good agreement with the corresponding values found in earlier reported azo compounds (see Table 5). The N=N bond distance of 1·164 (9)Å is very much shorter than usual values (1·20–1·28 Å with an average value of 1·248 Å[12]) and the mean N=N—C bond angle of 110·8 (2)° is slightly smaller than the common value (about 112°). This indicates a genuine effect which is in keeping with zwitterionic resonance forms such as those shown in

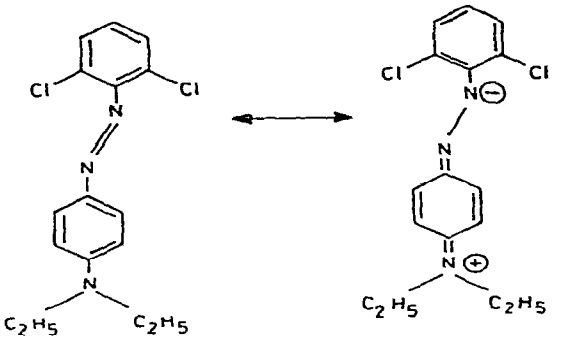
TABLE 5

Comparison of the Mean Bond Lengths (Å) and Angles (°) and the Dihedral Angle (°) Between Two Phenyl Rings (ϕ_{ph}) and Distance (Δ_{ph}, Å) Between the Aromatic Planes in Some Azo Compounds

Compound	*N=N*	*N—C*	*N=N—C*	*N—C—C* (*cis*)[a]	*N—C—C* (*trans*)[a]	ϕ_{ph}	Δ_{ph}	*Reference*
2,6-Dichloro-4′-*N*,*N*-diethylaminoazobenzene	1·164 (9)	1·487 (10)	110·8 (2)	124·0 (3)	116·8 (3)	87·8	—	This work
2-Bromo-4-cyano-4′-*N*,*N*-diethylaminoazobenzene	1·264 (6)	1·410 (7)	114·4 (2)	124·3 (3)	117·6 (2)	2·2	0·08	1
trans-2,2′-Dichloroazobenzene	1·254 (10)	1·432 (10)	112·8 (7)	125·0 (7)	116·4 (7)	0·0	0·17	11
trans-*p*,*p*′-Dichloroazobenzene	1·252 (5)	1·443 (5)	112·6 (4)	125·9 (4)	114·2 (4)	0·0	0	16
trans-*p*,*p*′-Dibromoazobenzene	1·276 (14)	1·428 (16)	112·2 (12)	125·6 (21)	114·7 (16)	0·0	0	25
cis-Azobenzene	1·253 (4)	1·449 (4)	121·9 (3)	122·5 (3)	117·3 (3)	64·0	—	26
trans-*p*-Azotoluene[b]	1·244 (n.d.)[c]	1·433 (n.d.)	113·8 (n.d.)	128·8 (n.d.)	112·6 (n.d.)	0·0	0·08	27
trans-Azobenzene[b]	1·243 (3)	1·433 (3)	113·6 (2)	124·1 (2)	115·5 (2)	55·5	—	28
trans-4,4′-Azodiphenetole	1·255 (10)	1·426 (10)	114·3 (8)	125·3 (8)	115·7 (8)	2·0	0·15	29
trans-2,2′,4,4′,6,6′-Hexanitroazobenzene								
Form I	1·244 (5)	1·426 (5)	112·0 (4)	125·0 (4)	118·0 (4)	0·0	1·36	10
Form II	1·243 (5)	1·434 (5)	112·0 (4)	125·0 (4)	119·0 (4)	81	—	
trans-2,2′-Azo-*p*-cymene	1·246 (4)	1·423 (3)	115·1 (2)	123·4 (2)	115·9 (2)	0·0	0	30
trans-*o*-Aminoazotoluene	1·258 (4)	1·408 (4)	115·5 (3)	124·6 (3)	116·6 (3)	9·2	[d]	14
trans-Azobenzene-2-sulphenyl cyanide	1·22 (2)	1·44 (2)	112·0 (n.d.)	131·0 (n.d.)	115·0 (n.d.)	8·0	—	31
trans-Azobenzene-4-dimethylamino-2′-carboxylic acid	1·269 (10)	1·403 (10)	115·6 (—)	124·5 (—)	116·6 (—)	12·0	—	32
Methyl Orange.H_2O.EtOH	1·244 (6)	1·423 (6)	113·8 (4)	125·9 (4)	115·4 (4)	10·0	[d]	13
4-(4′-Ethoxyphenylazo)phenyl valerate	1·239 (7)	1·412 (0)	115·7 (5)	124·6 (6)	117·8 (6)	4·8	0·10	33

N-*p*-Methoxybenzylidene-*p*-phenylazoaniline	1·22 (5)	1·44 (4)	114 (3)	124·5 (30)	114·5 (30)	3·0	[d]	34
2,4-Diaminoazobenzene.HCl.$2H_2O$[e]	1·313 (4) 1·314 (3)	1·362 (4) 1·363 (4)	121·1 (3) 121·5 (3)	125·0 (3) 124·2 (3)	115·9 (3) 116·9 (3)	0·0	<0·10	35
trans-4,4′-Azopyridine-*N*-oxide	1·228 (15)	1·419 (12)	113·3 (6)	125·2 (6)	116·9 (6)	—	—	36
4-Phenylazobenzene	1·232 (5)	1·455 (5)	111·6 (3)	126·4 (3)	113·2 (3)	3·0, 3·0	<0·05	37
6-(p-Hydroxyphenylazo)uracil	1·265 (5)	1·406 (5)	113·8 (2)	122·5 (2)	117·5 (2)	—	—	38
p-Chlorobenzene-*trans*-diazo-imidoglyoxynitrile	1·264 (10)	1·447 (10)	112·9 (7)	124·4 (6)	113·9 (7)	10·0	—	17
2,2′,4,4′,6,6′-Hexa-*t*-butylazobenzene	1·257 (7)	1·460 (7)	113·5 (4)	112·0 (4)	126·8 (4)	68·7	—	39
2,2′,4,4′,6,6′-Hexa-isopropylazobenzene	1·253 (6)	1·454 (6)	113·2 (4)	122·3 (4)	114·0 (4)	76·2	—	40
2,2′,4,4′,6,6′-Hexa-methylazobenzene	1·217 (3)	1·442 (3)	116·7 (2)	127·5 (2)	112·5 (2)	0	0·0	41
6,6′-Dibromo-2,2′,4,4′-tetra-*t*-butylazobenzene	1·253 (6)	1·427 (6)	113·6 (3)	123·2 (3)	118·1 (3)	92·7	—	42
2′-Acetamido-2-chloro-4′-diethylamino-4-mesylazobenzene	1·279 (4)	1·408 (4)	115·1 (3)	126·5 (3)	115·4 (3)	5·0	—	43
2-Chloro-4′-diethylamino-4-mesyl-2′-propion-amidoazobenzene	1·276 (7)	1·387 (7)	114·8 (5)	127·0 (5)	115·6 (5)	10·6	—	43

[a] *Cis* and *trans* relative to N=N.
[b] Disordered.
[c] n.d., not determined.
[d] Azobenzene part of molecule planar to within about 0·3 Å.
[e] Protonated azobenzene cation.



Scheme 1

Scheme 1, which make a smaller contribution than in more coplanar azobenzene derivatives. It is also of interest that the N(2)–C(7) bond is considerably shorter than the corresponding N(1)–C(1) bond length (1·462 (10) Å vs 1·511 (10) Å, respectively). This is not uncommon for aminoazobenzene structures such as **I**, sodium 4′-dimethylamino-azobenzene-4-sulphonate (Methyl Orange)[13] and *trans*-*o*-aminoazo-toluene,[14] where the C—N bond at the NR_2 side is shorter by about 0·029 Å than the corresponding bond towards the other phenyl ring. The value of ΔR(CN) in **I** is within the established limits (<0·06 Å) usually observed for azo tautomers.[12] Whereas conjugating terminal substituents tend to shorten the CN bond of an azo group and increase the N—N distance, interruption of conjugation, as in **I**, leads to a N=N distance below the normally observed range and a C—N bond distance exceeding the usual values (1·37–1·49 Å).[12] In the case of other highly non-planar azobenzene derivatives no similar azo bond shortening is observed (Table 5). As a result of the non-planarity of the molecule of **I** we notice a considerable variation in N—C—C(*cis*) and N—C—C(*trans*) bond angles at the two aromatic rings. In accordance with the out-of-plane rotation around N(1)—C(1) the difference between these bond angles reduces from 11·5° for ring II to 2·9° for ring I.

The mean Cl—C length of 1·741 (6) Å is in good agreement with those of 1·742 (4) Å found in 1-(2,6-dichlorobenzyl)-6-hydroxy-1,4,5,6-tetra-hydronicotinamide dihydrate,[15] 1·747 (10) Å in *trans*-2,2′-dichloro-azobenzene,[11] 1·737 (5) Å in *trans*-*p*,*p*′-dichloroazobenzene[16] and 1·735 (7) Å in *p*-chlorobenzene *trans*-diazoimidoglyoxynitrile.[17] The bond lengths and angles in the $N(C_2H_5)_2$ moiety are unexceptional and close to those of the dye 2-bromo-4-cyano-4′-*N*,*N*-diethylaminoazo-

benzene **III**.[1] The N(3)—C(10) bond length of 1·366 (9) Å is significantly shorter than the ordinary single N—C(sp^2) bond length. Such a shortening is observed in various aromatic amines, e.g. **III**,[1] 4-nitroaniline,[18] Methyl Orange,[13] 2-amino-3-methylbenzoic acid,[19] *p*-aminoacetophenone[20] and 2',3-dimethyl-4-aminoazobenzene.[14]

In accordance with the well-known effects of substituents on aromatic ring geometry,[21–23] the C(3)—C(4)—C(5) angle (120·0 (4)°) is significantly larger than the C(2)—C(1)—C(6) angle (117·2 (3)°) at the N=N end. It is interesting to note that the value of the former angle is the same as that suggested by Domenicano *et al.*,[23] whereas the latter angle is significantly smaller than the value of 120·0° suggested by the same authors. The difference may be attributed to complications arising from the presence of electron-withdrawing Cl atoms in the *ortho* positions. A similar decrease in the expected value (120·0°) of the C(2)—C(1)—C(6) angle (117·7 (2)°) occurs in **III**,[1] which has an electron-withdrawing Br atom in the *ortho* position. The C(9)—C(10)—C(11) angle (118·4 (3)°) at the $N(C_2H_5)_2$ end of the molecule is also smaller than the C(8)—C(7)—C(12) angle (120·5 (3)°) at the N=N end, in line with the observation by Domenicano *et al.*[21–23] The C(1)—C(2)—C(3) and C(1)—C(6)—C(5) angles have also been affected by the presence of the Cl substituents so that they are larger (121·5 (3)° and 123·0 (3)°) than 120°, in line with earlier observations on electron-withdrawing substituents.[1,15,24] The fact that the C(2)—C(3) (1·366 (12) Å) and the C(5)—C(6) (1·369 (12) Å) bond distances are shorter than C(3)—C(4) (1·385 (11) Å) and C(4)—C(5) (1·384 (11) Å), respectively, is also consistent with earlier observations.[21–23]

The mode of packing of the molecules in the crystal is shown in Fig. 2. With the exception of the C(8)...H(151) and N(2)...H(12) contact distances of 2·57 Å and 2·41 Å, respectively, which are below the sum of the van der Waals radii, all the other shortest intermolecular contacts in the structure (Cl...Cl, >4·0 Å; Cl...C, 3·57 Å; Cl...N, >3·8 Å; Cl...H, 2·76 Å; C...C, 3·56 Å; C...N, 3·48 Å; N...N, >3·60 Å; H...H, 2·25 Å) conform to normal van der Waals interactions.

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REFERENCES

1. K. A. Woode, J. C. J. Bart and M. Calcaterra, *Dyes and Pigments*, **2**, 271 (1981).
2. G. Germain, P. Main and M. M. Woolfson, *Acta Cryst.*, **A27**, 368 (1971).
3. A. Immirzi, *Ric. Sci.*, **37**, 743 (1967).
4. V. Vand, P. E. Eiland and R. Pepinsky, *Acta Cryst.*, **19**, 303 (1957).
5. F. H. Moore, *Acta Cryst.*, **16**, 1169 (1963).
6. D. W. J. Cruickshank, D. E. Pilling, A. Bujosa, F. M. Lovell and M. R. Truter, *Computing methods and the phase problem in X-ray crystal analysis*, p. 32. Oxford, Pergamon Press (1961).
7. C. K. Johnson. *ORTEP Report* ORNL-3794. Tennessee, Oak Ridge National Laboratory (1965).
8. E. Sawicki, *J. Org. Chem.*, **22**, 915 (1957).
9. G. Hallas, *J. Soc. Dyers Colour.*, **95**, 285 (1979).
10. E. J. Graeber and B. Morosin, *Acta Cryst.*, **B30**, 310 (1974).
11. M. Komeyama, S. Yamamoto, N. Nishimura and S. Hasegawa, *Bull. Chem. Soc. Japan*, **46**, 2606 (1973).
12. J. Kelemen, G. Kormány and G. Rihs, *Dyes and Pigments*, **3**, 249 (1982).
13. A. W. Hanson, *Acta Cryst.*, **B29**, 454 (1973).
14. S. Kurosaki, S. Kashino and M. Haisa, *Acta Cryst.*, **B32**, 3160 (1976).
15. H. Hope, *Acta Cryst.*, **B25**, 78 (1969).
16. H. Hope and D. Victor, *Acta Cryst.*, **B25**, 1849 (1969).
17. H. H. Erichsen and C. Rømming, *Acta Chem. Scand.*, **22**, 1430 (1968).
18. N. Trueblood, E. Goldish and J. Donohue, *Acta Cryst.*, **14**, 1009 (1961).
19. G. M. Brown and R. E. Marsh, *Acta Cryst.*, **16**, 191 (1963).
20. M. Haisa, S. Kashino, T. Yuasa and K. Akigawa, *Acta Cryst.*, **B32**, 1326 (1976).
21. A. Domenicano, A. Vaciago and C. A. Coulson, *Acta Cryst.*, **B31**, 221 (1975).
22. A. Domenicano, A. Vaciago and C. A. Coulson, *Acta Cryst.*, **B31**, 1630 (1975).
23. A. Domenicano, P. Mazzeo and A. Vaciago, *Tetrahedron Lett.*, 1029 (1976).
24. O. L. Carter, A. J. McPhail and G. A. Sim, *J. Chem. Soc. A*, 822 (1966).
25. A. G. Amit and H. Hope, *Acta Chem. Scand.*, **20**, 835 (1966).
26. A. Mostad and C. Rømming, *Acta Chem. Scand.*, **25**, 3561 (1971).
27. C. J. Brown, *Acta Cryst.*, **21**, 153 (1966).
28. C. J. Brown, *Acta Cryst.*, **21**, 146 (1966).
29. J. L. Galigné, *Acta Cryst.*, **B26**, 1977 (1970).
30. J. B. Wetherington, K. D. R. Holmes and J. W. Moncrief, *Acta Cryst.*, **B30**, 246 (1974).
31. K. K. Kakati and B. Chaudhuri, *Acta Cryst.*, **B24**, 1645 (1968).
32. D. Moreiras, J. Solans, X. Solans, C. Miratvitlles, G. Germain and J. P. Declercq, *Cryst. Struct. Comm.*, **9**, 921 (1980).
33. J. S. Prasad, *Acta Cryst.*, **B35**, 1407 (1979).
34. G. V. Vani and K. Vijayan, *Acta Cryst.*, **B33**, 2236 (1977).

35. D. Moreiras, J. Solans, X. Solans, C. Miratvitlles, G. Germain and J. P. Declercq, *Acta Cryst.*, **B37**, 737 (1981).
36. E. L. Eichhorn, *Acta Cryst.*, **12**, 746 (1959).
37. R. D. Gilardi and I. L. Karle, *Acta Cryst.*, **B28**, 1635 (1972).
38. C. L. Coulter and N. R. Cozzarelli, *Acta Cryst.*, **B30**, 2176 (1974).
39. Y. Le Page, E. J. Gabe, Y. Wang, L. R. C. Barclay and H. L. Holm, *Acta Cryst.*, **B36**, 2846 (1980).
40. Y. Le Page, E. J. Gabe, L. R. C. Barclay and J. M. Dust, *Acta Cryst.*, **B37**, 976 (1981).
41. E. J. Gabe, Y. Wang, L. R. C. Barclay and J. M. Dust, *Acta Cryst.*, **B37**, 978 (1981).
42. E. J. Gabe, Y. Wang and Y. Le Page, *Acta Cryst.*, **B37**, 980 (1981).
43. R. P. Gruska, M. H. P. Ardebili, D. Boccio and J. G. White, *Acta Cryst.*, **B36**, 3203 (1980).