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X-Ray Crystal Structure of the Dye 2,4,6-Tricyano-4′-*N*,*N*-diethylaminoazobenzene

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SUMMARY

*The crystal structure and molecular conformation of 2,4,6-tricyano-4′-*N,N*-diethylaminoazobenzene* ($C_{19}H_{16}N_6$, *mol. wt. 328·4 a.m.u.) has been determined from X-ray diffraction data: monoclinic* $P2_1/c$, $a = 9{\cdot}302(7)$ *Å*, $b = 8{\cdot}733(5)$ *Å*, $c = 20{\cdot}98(1)$ *Å*, $\beta = 94{\cdot}93(6)°$, $V = 1699(2)$ *Å*^{3}, $Z = 4$, $D_c = 1{\cdot}284$ *gcm*$^{-3}$, $F(000) = 688$, $\lambda(MoK\alpha) = 0{\cdot}710\,69$ *Å*, $\mu(MoK\alpha) = 0{\cdot}76$ *cm*$^{-1}$. *The structure was solved by MULTAN and refined by full-matrix least-squares to* $R = 0{\cdot}050$ *for 1358 independent observed reflections. The azobenzene skeleton is planar to within 0·12 Å. Most significant bonding data are: N=N, 1·286(4) Å; mean C—N (azo) 1·383(4) Å; mean C—C (cyano) 1·439(5) Å; mean C≡N 1·146(5) Å; N=N—C, 112·8(2)° and 115·9(2)°; N—C—C (cis relative to N=N) 127·6(2)° and 124·3(2)°; N—C—C* (trans) *115·2(2)° and 117·7(2)°.*

1. INTRODUCTION

It has been noticed before[1] that steric interference in azobenzene derivatives can be relieved by 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 offsetting of parallel

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phenyl rings. *Ortho* disubstitution is usually considered to induce overall non-planar molecular conformations,[2] as indeed has been observed for 2,6-dichloro-4′-*N*,*N*-diethylaminoazobenzene[1] and 2,2′,4,4′,6,6′-hexanitroazobenzene.[3] Yet, in the latter case, the existence of a second polymorphic form with planar molecular conformation indicates that a suitable combination of the aforementioned factors may accommodate non-bonded interactions in an alternative way. Knowledge of steric complications is particularly useful in relation to the prediction and understanding of the long-wave π–π^* bands that determine the visible

TABLE 1
Final Fractional Coordinates for Non-hydrogen Atoms[a]
Standard deviations are in parentheses

Atom	*x*	*y*	*z*
C(1)	0·571 2 (4)	−0·064 3 (4)	0·420 2 (2)
C(2)	0·496 5 (4)	−0·007 6 (4)	0·363 9 (2)
C(3)	0·404 6 (4)	−0·097 7 (4)	0·325 2 (2)
C(4)	0·382 0 (4)	−0·249 9 (4)	0·342 2 (2)
C(5)	0·450 5 (4)	−0·308 7 (4)	0·398 2 (2)
C(6)	0·545 2 (4)	−0·218 5 (4)	0·436 9 (2)
C(7)	0·831 5 (4)	0·075 7 (4)	0·535 8 (2)
C(8)	0·849 5 (4)	0·231 6 (4)	0·521 7 (2)
C(9)	0·952 5 (4)	0·315 4 (4)	0·555 8 (2)
C(10)	1·043 7 (4)	0·251 9 (4)	0·606 8 (2)
C(11)	1·016 6 (4)	0·097 1 (4)	0·623 2 (2)
C(12)	0·915 1 (4)	0·014 4 (4)	0·587 6 (2)
C(13)	0·286 0 (4)	−0·343 9 (4)	0·301 7 (2)
C(14)	0·517 9 (4)	0·149 5 (4)	0·345 5 (2)
C(15)	0·615 8 (4)	−0·291 0 (4)	0·492 6 (2)
C(16)	1·184 5 (4)	0·490 3 (4)	0·617 0 (2)
C(17)	1·094 6 (5)	0·613 0 (5)	0·644 2 (2)
C(18)	1·232 5 (4)	0·278 5 (4)	0·696 5 (2)
C(19)	1·150 5 (4)	0·295 7 (5)	0·755 3 (2)
N(1)	0·663 2 (3)	0·040 0 (3)	0·453 3 (1)
N(2)	0·735 0 (3)	−0·019 7 (3)	0·502 2 (1)
N(3)	1·151 7 (3)	0·333 8 (3)	0·637 8 (1)
N(4)	0·211 4 (4)	−0·418 8 (4)	0·268 3 (2)
N(5)	0·530 3 (4)	0·271 7 (4)	0·326 8 (2)
N(6)	0·663 3 (4)	−0·367 9 (4)	0·533 4 (2)

[a] Atom labelling as in Fig. 1.

absorption spectra, even though it appears that energy parameters are more crucial in colour prediction than structural details.[4]

In the present paper we examine the crystal structure of the *ortho* disubstituted disperse dye 2,4,6-tricyano-4'-N,N-diethylaminoazobenzene (**I**) and discuss the effects of the rod-shaped substituents on the molecular conformation and geometry of the phenyl and azo groups. As is well known, monoazo disperse dyes, such as **I**, find application in polyester and nylon transfer printing.[5] It is perhaps appropriate to point out here that evidence is accumulating that differing fibre affinities of dispersed phase dyes cannot be rationalized in terms of conformational and structural properties.[6-8]

2. EXPERIMENTAL

Compound **I**, prepared by Griffiths and Roozpeikar,[9] was recrystallized from ethanol as deep green trapezoids ($\lambda_{max} = 562$ nm; $\log \varepsilon$(ethanol) = 4·67; m.p. = 198–200 °C). Cell parameters ($a = 9{\cdot}302(7)$ Å, $b = 8{\cdot}733(5)$ Å,

TABLE 2
Positional and Thermal Parameters for Hydrogen Atoms[a]

Atom	*x*	*y*	*z*	*B* (Å²)
H(3)	0·356 (3)	−0·061 (4)	0·283 (1)	4·1 (8)
H(5)	0·435 (4)	−0·417 (4)	0·409 (2)	5·4 (9)
H(8)	0·787 (4)	0·274 (4)	0·487 (2)	5·4 (9)
H(9)	0·961 (4)	0·424 (4)	0·543 (2)	5·8 (9)
H(11)	1·075 (4)	0·044 (4)	0·660 (2)	4·5 (8)
H(12)	0·898 (3)	−0·086 (3)	0·597 (1)	3·2 (7)
H(161)	1·174 (4)	0·492 (4)	0·564 (2)	5·0 (8)
H(162)	1·284 (3)	0·505 (4)	0·630 (1)	3·6 (7)
H(181)	1·322 (4)	0·333 (4)	0·702 (2)	5·3 (9)
H(182)	1·255 (3)	0·171 (4)	0·691 (2)	4·2 (8)
H(171)	1·119 (4)	0·715 (4)	0·630 (2)	5·9 (9)
H(172)	1·108 (4)	0·609 (4)	0·689 (2)	5·7 (9)
H(173)	0·989 (5)	0·608 (5)	0·630 (2)	7·6 (11)
H(191)	1·204 (4)	0·251 (4)	0·794 (2)	5·2 (9)
H(192)	1·052 (4)	0·240 (5)	0·752 (2)	7·2 (11)
H(193)	1·124 (4)	0·401 (5)	0·764 (2)	7·1 (11)

[a] Atom labelling as in Fig. 1.

TABLE 3

Anisotropic Thermal Parameters of Non-hydrogen Atoms ($Å^2$)[a] 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}
C(1)	2·97 (16)	3·53 (15)	3·14 (16)	−0·16 (28)	1·17 (26)	−0·47 (25)
C(2)	3·22 (16)	3·01 (14)	3·02 (16)	−0·67 (28)	−0·06 (26)	−0·25 (24)
C(3)	4·01 (18)	3·63 (15)	2·90 (16)	0·25 (30)	0·08 (27)	0·56 (25)
C(4)	3·14 (17)	3·35 (15)	3·70 (17)	−0·95 (29)	−0·08 (27)	−1·41 (26)
C(5)	3·75 (18)	3·18 (15)	3·66 (17)	−0·49 (29)	0·95 (29)	−0·59 (25)
C(6)	3·67 (17)	3·07 (14)	2·72 (15)	0·39 (28)	1·42 (27)	0·01 (24)
C(7)	3·74 (17)	2·80 (14)	2·64 (15)	−0·30 (28)	−0·16 (26)	0·50 (23)
C(8)	4·27 (19)	3·20 (15)	3·19 (16)	−0·51 (30)	−1·37 (28)	1·21 (25)
C(9)	4·91 (20)	3·43 (16)	3·52 (17)	−1·32 (31)	−0·98 (31)	2·40 (26)
C(10)	3·11 (17)	3·59 (15)	2·88 (15)	−0·93 (28)	0·65 (26)	−0·86 (25)
C(11)	4·06 (18)	2·77 (14)	3·08 (16)	−0·20 (28)	−0·85 (28)	0·57 (24)
C(12)	4·38 (18)	2·54 (14)	3·86 (18)	−0·59 (29)	−0·57 (30)	1·28 (25)
C(13)	4·41 (20)	3·49 (16)	4·38 (19)	0·39 (32)	−0·57 (32)	−0·16 (28)
C(14)	4·26 (19)	3·90 (16)	3·15 (17)	−0·77 (31)	−1·67 (28)	0·28 (27)
C(15)	5·43 (21)	3·45 (16)	3·49 (18)	−0·72 (33)	−0·80 (32)	0·88 (27)
C(16)	3·70 (19)	3·30 (16)	5·21 (21)	−1·17 (31)	0·32 (31)	−1·01 (29)
C(17)	6·53 (26)	4·20 (19)	5·81 (23)	2·25 (39)	1·33 (40)	−0·48 (34)
C(18)	3·44 (18)	4·52 (18)	3·51 (17)	0·19 (32)	−0·84 (29)	−0·45 (29)
C(19)	5·39 (23)	5·35 (21)	3·34 (18)	0·19 (37)	0·80 (33)	0·20 (31)
N(1)	3·40 (14)	3·14 (12)	3·19 (13)	−0·18 (23)	−0·61 (22)	0·04 (20)
N(2)	3·71 (14)	2·96 (12)	3·06 (13)	−0·11 (24)	−0·26 (22)	0·31 (20)
N(3)	3·80 (15)	3·38 (13)	3·37 (14)	−0·99 (24)	0·01 (23)	−0·34 (21)
N(4)	7·29 (23)	4·58 (17)	6·70 (22)	−1·47 (34)	−4·27 (36)	−1·77 (31)
N(5)	6·46 (20)	3·99 (15)	5·88 (19)	−2·12 (31)	−2·51 (32)	2·63 (28)
N(6)	8·14 (24)	4·25 (16)	4·87 (18)	−1·80 (34)	−2·63 (33)	2·78 (27)

[a] Atom labelling as in Fig. 1.

$c = 20·98(1)$ Å, $\beta = 94·93(6)°$; space-group, $P2_1/c$, $Z = 4$) were determined from 12 reflections measured on a Picker FACS-1 four-circle diffractometer with a crystal mounted with the *a*-axis approximately along the instrumental phi-axis. Intensity data (1811 total independent reflections of which the 1358 considered were observed with $I > 2·5\sigma(I)$) were collected in the $3° < 2\theta < 45°$ interval using a crystal of dimensions 0·4 mm × 0·4 mm × 0·5 mm and Mo$K\alpha$ radiation. Standard reflections, monitored regularly, did not vary during data collection. Lorentz and polarization corrections were applied. The heavy atom skeleton of the

TABLE 4
Bond Distances and Angles of Non-hydrogen Atoms[a]
E.s.d. values are given in parentheses

Type	*Length (Å)*	*Type*	*Angle (°)*
C(1)—C(2)	1·408 (5)	C(1)–C(2)–C(3)	122·1 (2)
C(2)—C(3)	1·375 (5)	C(1)–C(2)–C(14)	119·3 (2)
C(3)—C(4)	1·397 (5)	C(1)–C(6)–C(5)	120·5 (2)
C(4)—C(5)	1·386 (5)	C(1)–C(6)–C(15)	122·9 (2)
C(5)—C(6)	1·390 (5)	C(1)–N(1)–N(2)	112·8 (2)
C(6)—C(1)	1·417 (5)	C(2)–C(1)–C(6)	117·3 (2)
		C(2)–C(1)–N(1)	115·2 (2)
C(7)—C(8)	1·406 (5)	C(2)–C(3)–C(4)	119·6 (2)
C(8)—C(9)	1·358 (5)	C(2)–C(14)–N(5)	175·3 (2)
C(9)—C(10)	1·420 (5)	C(3)–C(2)–C(14)	118·6 (2)
C(10)—C(11)	1·422 (5)	C(3)–C(4)–C(5)	120·0 (2)
C(11)—C(12)	1·360 (5)	C(3)–C(4)–C(13)	119·5 (2)
C(12)—C(7)	1·387 (5)	C(4)–C(5)–C(6)	120·4 (2)
		C(4)–C(13)–N(4)	178·5 (2)
C(2)—C(14)	1·444 (5)	C(5)–C(4)–C(13)	120·4 (2)
C(4)—C(13)	1·436 (5)	C(5)–C(6)–C(15)	116·6 (2)
C(6)—C(15)	1·438 (5)	C(6)–C(1)–N(1)	127·6 (2)
C(16)—C(17)	1·503 (6)	C(6)–C(15)–N(6)	170·1 (2)
C(18)—C(19)	1·513 (5)	C(7)–C(8)–C(9)	120·2 (2)
		C(7)–C(12)–C(11)	122·7 (2)
C(13)—N(4)	1·147 (5)	C(7)–N(2)–N(1)	115·9 (2)
C(14)—N(5)	1·146 (5)	C(8)–C(7)–C(12)	118·0 (2)
C(15)—N(6)	1·146 (5)	C(8)–C(7)–N(2)	124·3 (2)
C(1)—N(1)	1·392 (4)	C(8)–C(9)–C(10)	122·3 (2)
C(7)—N(2)	1·374 (4)	C(9)–C(10)–C(11)	116·5 (2)
C(10)—N(3)	1·352 (4)	C(9)–C(10)–N(3)	121·8 (2)
C(16)—N(3)	1·475 (5)	C(10)–C(11)–C(12)	120·1 (2)
C(18)—N(3)	1·468 (4)	C(10)–N(3)–C(16)	120·8 (2)
		C(10)–N(3)–C(18)	122·3 (2)
N(1)—N(2)	1·286 (4)	C(11)–C(10)–N(3)	121·8 (2)
		C(12)–C(7)–N(2)	117·7 (2)
		C(16)–N(3)–C(18)	116·7 (2)
		C(17)–C(16)–N(3)	114·3 (3)
		C(19)–C(18)–N(3)	113·2 (3)

[a] Atom labelling as in Fig. 1.

TABLE 5
Bond Distances (Å) Involving Hydrogen Atoms[a]
E.s.d. values are given in parentheses

Type	*Length (Å)*	*Type*	*Length (Å)*
C(3)—H(3)	1·01 (3)	C(17)—H(171)	0·97 (4)
C(5)—H(5)	0·99 (4)	C(17)—H(172)	0·94 (4)
C(8)—H(8)	0·97 (4)	C(17)—H(173)	1·00 (4)
C(9)—H(9)	1·00 (4)	C(18)—H(181)	0·96 (4)
C(11)—H(11)	1·01 (3)	C(18)—H(182)	0·97 (3)
C(12)—H(12)	0·92 (3)	C(19)—H(191)	0·99 (4)
C(16)—H(161)	1·11 (3)	C(19)—H(192)	1·03 (4)
C(16)—H(162)	0·95 (3)	C(19)—H(193)	0·97 (4)

[a] Atom labelling as in Fig. 1.

structure was readily determined by means of MULTAN-78; hydrogen atoms were placed in agreement with a $\Delta\rho$ synthesis. Refinement (anisotropic for C, N; isotropic for H) converged to $R = 0{\cdot}050$ when the final shifts of the atomic parameters were negligible and the final $\Delta\rho$ map featureless ($<0{\cdot}1\,e\,Å^{-3}$). Scattering factors were taken from ref. 10 and the weighting scheme followed our usual procedures.[11] Final co-ordinates and thermal parameters are listed in Tables 1–3 and bond data in Tables 4–6. Figures 1 and 2 show views of the molecule and crystal packing arrangement, as drawn by the PLUTO program.[12] A list of structure factors may be obtained from the authors of this paper.

TABLE 6
Main Non-bonded Distances (Å) and Torsional Angles[a]
E.s.d. values are given in parentheses

Type	*Length (Å)*	*Type*	*Angle (°)*
N(2)—N(6)	3·192 (5)	C(2)–C(1)–N(1)–N(2)	176·3 (4)
N(2)—C(15)	2·617 (5)	C(6)–C(1)–N(1)–N(2)	−3·7 (3)
N(1)—C(14)	2·713 (5)	C(8)–C(7)–N(2)–N(1)	−3·3 (3)
N(1)—H(8)	2·42 (4)	C(12)–C(7)–N(2)–N(1)	177·6 (4)
H(9)—H(161)	2·08 (5)	C(9)–C(10)–N(3)–C(18)	−170·6 (4)
H(11)—H(182)	2·07 (5)	C(11)–C(10)–N(3)–C(16)	−175·6 (4)
		C(10)–N(3)–C(16)–C(17)	−85·2 (3)
		C(10)–N(3)–C(18)–C(19)	77·2 (3)

[a] Atom labelling as in Fig. 1.

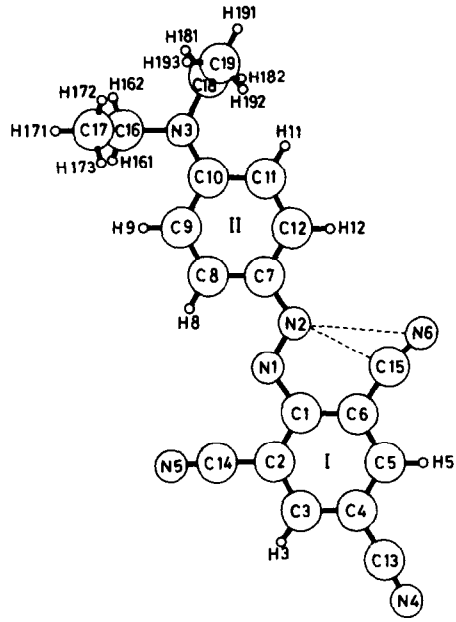


Fig. 1. View of 2,4,6-tricyano-4'-*N*,*N*-diethylaminoazobenzene onto the C(7)–C(12) plane showing the atom-labelling scheme.

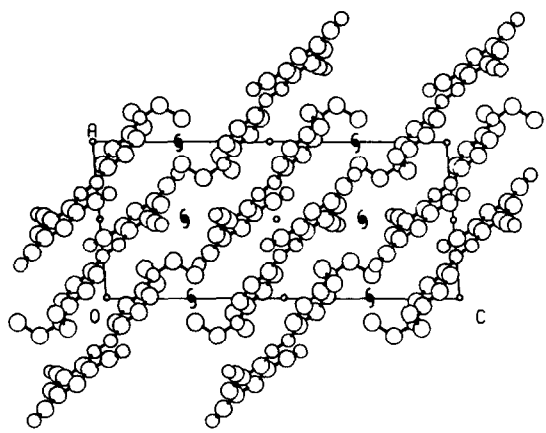


Fig. 2. Crystal structure of 2,4,6-tricyano-4'-*N*,*N*-diethylaminoazobenzene viewed down the crystallographic *b*-axis.

3. RESULTS AND DISCUSSION

In 2-cyano-4-bromo-4′-*N*,*N*-diethylaminoazobenzene (**II**)[13] the molecular structure conforms to N(2) being oriented *anti* with respect to the cyano substituted C(2) atom. While this minimizes repulsive interaction between the electron lone pair at N(1) and the electron cloud of the 2-CN group, the *ortho* disubstituted cyano derivative **I** suffers from more severe repulsion between the sp^2 electrons on N(2) and the 6-CN group, as is obvious from the short N(2)—N(6) and N(2)—C(15) contacts of 3·192(5) Å and 2·617(5) Å, respectively (compare with the 2·51 Å N—H non-bonded distance in **II**, and the C(6)–C(15)–N(6) angle of 189·9(2)°, with the cyano substituent being bent away from N(2) (Fig. 1). Interaction between the 6-CN substituent and the N(2) electron pair is further accommodated by bending out of the phenyl plane (Table 7) and by an increased distortion of the N(1)–C(1)–C(6) bond angle (127·6(2)° in **I** as compared with 125·9(4)° in **II**). On the other hand, no appreciable bond angle variations occur for the 2-CN substituent in **I** and **II** (C(2)–C(1)–N(1) of 115·2(2)° and 116·8(5)°, respectively; C(2)–C(14)–N(5) of 184·7(2)° and 184·0(4)°, respectively), confirming the weak interaction between the parallel oriented sp^2 protrusion at N(1) and the rod-like substituent at C(2). It is noticeable that the N(2)—C(15) non-bonded contact is only 0·1 Å shorter than the N(1)—C(14) distance. On the whole, the results are in keeping with the previously reported absorption characteristics of **I**. Absence of severe steric interactions accounts for the large extinction coefficient, in accordance with the deductions of Griffiths and Roozpeikar.[9]

As in the case of the (2-CN, 4-Br) analogue (**II**), the molecular skeleton of **I** is therefore almost planar (Table 7) with C(10) showing the largest deviation (0·12 Å or 25σ) from planarity and a dihedral angle of 7·8(1)° between the phenyl rings (3·3° in **II**). Whereas in **II** the ethyl groups are rotated in the same direction around N(3)–C(10), leading to absence of symmetry in the diethylamino group (as in 6′-acetamido-6-bromo-2-cyano-4′-diethylamino-4-nitroazobenzene),[7] the NEt_2 moiety of **I** has approximate *m* symmetry, as previously noticed for 2-bromo-4-cyano-4′-*N*,*N*-diethylaminoazobenzene (**III**).[11] Packing requirements probably play a role in this respect. Although the diethylamino group as a whole is not planar (similar to other cases[1]), the C(16)–N(3)–C(18) moiety is almost coplanar with the skeleton (Table 7).

The bond data for the azo group are as follows (for comparison

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 $(b–c)$ plane and z along the c-axis. The distance of the atoms to the plane are in Å units (e.s.d. 0·005 Å).

Plane (1)

$$0{\cdot}806\,0x - 0{\cdot}288\,9y - 0{\cdot}516\,6z + 0{\cdot}680\,9 = 0$$

C(1)	0·010	C(2)	−0·008		
C(3)	0·002	C(4)	0·009		
C(5)	−0·011	C(6)	0·001		
Not defining plane		C(13)	0·020	N(1)	0·034
		C(14)	−0·020	N(2)	0·127
		C(15)	0·035	N(6)	0·088

Plane (2)

$$0{\cdot}729\,9x - 0{\cdot}271\,7y - 0{\cdot}627\,3z + 2{\cdot}253\,8 = 0$$

C(7)	0·026	C(8)	−0·019		
C(9)	−0·008	C(10)	0·029		
C(11)	−0·023	C(12)	−0·005		
Not defining plane		N(1)	0·153	C(16)	0·273
		N(2)	0·008	C(18)	−0·040
		N(3)	0·123		

Plane (3)

$$0{\cdot}723\,7x - 0{\cdot}389\,9y - 0{\cdot}569\,5z + 1{\cdot}790\,0 = 0$$

C(10)	−0·015	C(16)	−0·013
N(3)	0·026	C(18)	−0·013
Not defining plane		C(17)	−1·393
		C(19)	−1·397

Dihedral angles between planes:

Plane (1)–Plane (2)	7·8 (1)°
Plane (2)–Plane (3)	7·6 (2)°

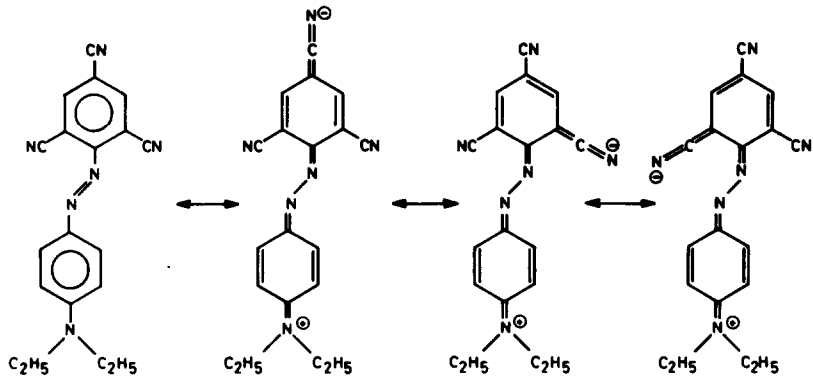
values of **II** are in parentheses): N=N 1·286(4) Å (1·290(8) Å); N—C 1·392(4) Å and 1·374(4) Å (1·394(8) and 1·365(8) Å); N=N—C 112·8(2)° and 115·9(2)° (113·6(4)° and 115·3(4)°); N—C—C(*cis*) 127·6(2)° and 124·3(2)° (125·9(4)° and 126·7(4)°); N—C—C(*trans*) 115·2(2)° and 117·7(2)° (116·8(5)° and 116·1(4)°). As expected, the value of ΔR(CN) in **I** is within the established limits (< 0·06 Å) commonly observed for azo tautomers.[14] Both the N=N and C—N bond lengths are at the extremes

of the usual ranges for azo dyes, namely 1·20–1·28 Å and 1·37–1·49 Å, respectively,[14] and may be compared with the values of 1·247(2)° and 1·428(2) Å in azobenzene.[15] It is also of interest to notice the 1·330(7) Å N—N bond length in the quinone hydrazone tautomer of 2-amino-3-hydroxy-6-phenylazopyridine[16] and the value of 1·412(10) Å for the single bond distance between sp^2 nitrogens in benzalazine.[17] On the whole, our results denote considerable electron delocalization in the molecule, in line with the presence of three *ortho* and *para* electron-withdrawing groups in ring I and the electron-donor in ring II. Bond orders of 1·80 and 1·35–1·45 v.u. may be assigned to the N=N and C—N(azo) bonds.[18] The N—C—C(*cis*) and N—C—C(*trans*) bond angles differ by as much as 12·4° and 6·7° for rings I and II, respectively. Even greater differences have been observed in various other azobenzene derivatives (cf. Table 5 of ref. 1 and refs 7, 8). The N—C bond length towards the tricyanobenzene moiety 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**,[13] **III**,[11] sodium 4′-dimethylaminoazobenzene-4-sulphonate (Methyl Orange),[19] 2′-acetamido-2-chloro-4′-diethylamino-4-mesylazobenzene,[6] 2-chloro-4′-diethylamino-4-mesyl-2′-propionamidoazobenzene,[6] 6-bromo-2-cyano-4′-diethylamino-4-nitro-6′-propionamidoazobenzene,[8] and trans-*o*-aminoazotoluene,[20] where on average the C—N bond on the NR_2 side is shorter by about 0·03 Å than the corresponding bond towards the other phenyl ring, close to the present findings.

In keeping with the substituent effects on aromatic ring geometry,[21–23] the endocyclic angles (average 120·9°) involved in CN substitution, are larger than the C(2)–C(1)–C(6) angle (117·3(2)°) with azo group attachment. The former value is close to the standard value of 121·8°,[23] whereas the latter is significantly smaller than the suggested 120·0° for azo monosubstitution. The C(9)–C(10)–C(11) angle of 116·5(2)° is considerably smaller than the C(8)–C(7)–C(12) angle (118·0(2)°) at the N=N end and also less than the average value (117·2°) at $N(CH_3)_2$ substitution sites.[24] Noteworthy also is the stretching of the N(3)–C(10) bond from 1·326(8) Å (1·7 v.u.) in **II** to 1·352(4) Å (1·55 v.u.) in **I**, close to the values of 1·364(7) Å in **III** and 1·354(7) Å in 6′-acetamido-6-bromo-2-cyano-4′-diethylamino-4-nitrobenzene (ABRCA).[7]

In spite of the considerable bond angle distortions in the aromatic rings (117·3–122·1° in ring I and 116·5–122·7° in ring II) the average C–C–C bond angle conforms to the standard value (120°). The aromatic bond

lengths, which vary from 1·375(5)–1·417(5) Å in ring I to 1·358(5)–1·422(5) Å in ring II (mean values of 1·396 and 1·392 Å, respectively) denote contributions of the low-energy resonance forms (Scheme 1):



Scheme 1

This scheme is in good accordance with the previous considerations about the N—N and N—C bond lengths.

The bond distances of the diethylamino substituent are standard. The dimensions of the carbonitrile groups (average C—C and C—N bond lengths of 1·439(5) and 1·146(5) Å, respectively) are close to those observed in $C_6(CN)_6$ (1·435(2) and 1·143(5) Å, respectively),[25] in some tetrachlorodicyanobenzene derivatives (1·441(3) and 1·130 Å)[26] and more reasonable than the reported values of 1·493(8) and 1·025(8) Å in ABRCA.[7] The average C—H bond length of 0·99(4) Å is not significantly different from the mean value (0·95(2) Å) usually determined by refinement of X-ray diffraction data.[27] The hydrogen atoms of C(17) and C(19) are in a *staggered* position.

The packing arrangement of 2,4,6-tricyano-4'-*N*,*N*-diethylaminoazobenzene is shown in Fig. 2. Apart from a short N(6)--H(5) $(1-x, -1-y, 1-z)$ distance of 2·45 Å all other minimum intermolecular contacts (in Å) in the structure (N—N, 3·65; C--C, 3·44; C--N, 3·35; C--H, 3·15; N--H, 2·74; H--H, 2·43) conform to normal Van der Waals interactions. As shown in Fig. 3, which allows a view of the crystal structure of **I** perpendicular to the molecular plane, the molecules are disposed on top of each other in an antiparallel fashion with a displacement which avoids superposition of the phenyl rings.

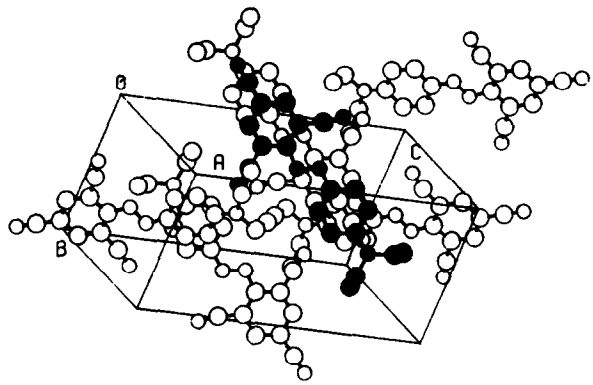


Fig. 3. Packing arrangement of 2,4,6-tricyano-4'-*N*,*N*-diethylaminoazobenzene viewed down the molecular plane (●).

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