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X-Ray Crystal Structure of the Dye 4-(*N*,*N*-Bis-(*β*-hydroxyethyl) amino) azobenzene

S. A. McIntosh,[a] H. S. Freeman[a]* & P. Singh[b]

[a]Department of Textile Engineering, Chemistry and Science,
[b]Department of Chemistry, North Carolina State University,
Raleigh, North Carolina 27695, USA

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ABSTRACT

*The crystal structure of 4-(*N,N*-bis-(β-hydroxyethyl)amino)azobenzene was determined through the use of X-ray diffractometer data. The structure was solved via direct methods and refined by least squares to* R = *0·0594 for a data set consisting of 1610 unique reflections. The azobenzene skeleton of the dye is essentially planar, with a dihedral angle of 10·3° between the planes defined by the two aromatic rings. The geometry about the azo linkage, and some key bond lengths of this dye, are compared to the corresponding values for some previously reported azobenzenes.*

INTRODUCTION

As part of a study designed to account for the effects of *ortho* substituents on the light-fastness of azo dyes, the photolytic properties of dyes **1a**–**f** were assessed.[1] The results of the study indicated that with the exception of the *ortho*-nitro dye, **1f**, photostability increased with increasing electron-withdrawing character of the *ortho* substituent. These results demonstrated that even though cyano- and nitro-substituents possess comparable electron-withdrawing properties, dye **1e** is light-fast while **1f** is not. Similar results had been reported previously.[2–4] It was also clear from our previous study[1] that the *ortho*-nitro group of **1f** inhibited light-induced *trans* → *cis*-isomerization, whereas the more light-fast dyes, **1a** and **1e**, readily undergo photoisomerization.

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* To whom correspondence should be addressed.

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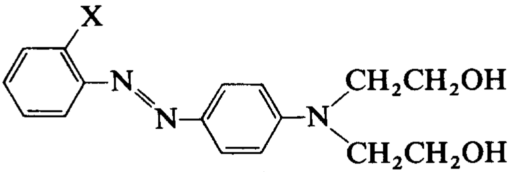

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		X			
a	CH_3	**c**	H	**e**	CN
b	OCH_3	**d**	Br	**f**	NO_2

In search of other factors contributing to the destabilizing effect of the *ortho*-nitro group, the crystal structures of dyes **1e** and **1f** were solved[5] and studied. The differences between the molecular conformations of these two dyes were significant, and were consistent with their photolytic behavior. The X-ray data confirmed the expected planar structure for **1e**, but revealed a strained aplanar structure for **1f**. However, the similarity of the key bond lengths of the two molecules was surprising.

To better assess the contribution of the *ortho*-nitro- and cyano-substituents to the resonance structure and ultimately the stability of dyes of type **1**, the crystal structure of dye **1c** has been determined.

EXPERIMENTAL

The dye was prepared[1] in our laboratory and purified by flash chromatography.[6] Crystals were generated through two methods:

(1) slow cooling of a solution of 100 mg of **1c** in 5 ml of methanol (MeOH), and
(2) slow evaporation of a solution of 50 mg of **1c** in 10 ml of toluene (PhMe).

Crystals grown from both systems were thick, yellow plates, and had a melting point of 135–137°C (uncorrected). A solution of the compound in acetone had a wavelength of maximum absorption (λ_{max}) of 413 nm and a molar extinction coefficient (ε_{max}) of 30 000 liter mol^{-1} cm^{-1}.

X-ray diffractometric data sets were collected on a Nicolet P3F diffractometer, with MoKα radiation (graphite monochromator, wavelength = 0·710 73 Å). Cell constants were measured for three separate crystals (Table 1). Crystals **A** and **B** were grown by slow cooling in MeOH, and crystal **C** was grown by slow evaporation of a solution of the dye in PhMe. The structure of dye **1c** was solved and refined from a data set created

TABLE 1
Cell Data for Crystals of **1c**

	A	**B**	**C**
Composition	$C_{16}H_{19}N_3O_2$	$C_{16}H_{19}N_3O_2$	$C_{16}H_{19}N_3O_2$
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)[a]	7·875 (3)	7·871 (6)	7·877 (3)
b (Å)[a]	9·439 (2)	9·408 (5)	9·440 (4)
c (Å)[a]	20·035 (5)	20·027 (11)	20·042 (9)
V (Å^3)	1 489	1 483	1 490
Z	4	4	4
Calculated density	1·27	1·28	1·27
Measured density	1·27	1·27	1·27
Number of reflections used for cell constant determination	25	17	25
$2\theta_{max}$	55	52	—

[a] Numbers in parentheses refer to the standard deviation of the last digit.

TABLE 2
Fractional Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å$^2 \times 10^3$) for Dye **1c**

	x	y	z	U[a]
C-1	5 829 (5)	−3 338 (3)	3 863 (2)	42 (1)
C-2	4 658 (5)	−3 267 (4)	3 359 (2)	46 (1)
C-3	4 531 (7)	−4 325 (4)	2 891 (2)	61 (2)
C-4	5 589 (8)	−5 479 (4)	2 935 (2)	67 (2)
C-5	6 774 (7)	−5 566 (4)	3 436 (2)	77 (2)
C-6	6 912 (6)	−4 491 (4)	3 900 (2)	61 (1)
N-1	6 127 (4)	−2 276 (3)	4 365 (1)	49 (1)
N-2	5 182 (4)	−1 205 (3)	4 310 (1)	45 (1)
C-7	5 425 (5)	−167 (3)	4 814 (1)	40 (1)
C-12	4 563 (6)	1 111 (4)	4 720 (2)	48 (1)
C-11	4 624 (5)	2 178 (3)	5 173 (2)	43 (1)
C-10	5 560 (5)	2 028 (3)	5 772 (1)	37 (1)
C-9	6 491 (5)	764 (4)	5 849 (2)	41 (1)
C-8	6 429 (5)	−303 (3)	5 379 (2)	40 (1)
N-3	5 559 (4)	3 066 (3)	6 251 (1)	38 (1)
C-15	4 455 (5)	4 307 (4)	6 198 (2)	43 (1)
C-16	5 220 (6)	5 526 (4)	5 822 (2)	52 (1)
O-2	6 541 (4)	6 177 (3)	6 186 (1)	75 (1)
C-13	6 650 (6)	2 952 (4)	6 845 (2)	44 (1)
C-14	5 876 (6)	2 111 (4)	7 416 (2)	50 (1)
O-1	4 429 (4)	2 808 (3)	7 658 (1)	71 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

by merging the individual data sets collected from crystals **A** and **B** (1610 unique reflections).

All calculations were performed with the SHELXTL crystallographic software package from Nicolet Instrument Corporation (Madison, Wisconsin, USA) on a Data General Micro-Eclipse Model 30 computer, with the exception of the interatomic distance calculations. The latter were performed with SADIAN.

RESULTS AND DISCUSSION

Table 1 contains the cell dimensions of dye **1c** that were determined by a least-squares fit. The final atomic and thermal parameters are given in Tables 2–6. The crystals exist in the orthorhombic space group $P2_12_12_1$. In order to facilitate refinement, two sets of data were collected on two different crystals (**A** and **B**) and then merged. The purpose was to average out any 'noise' present in the individual data sets. Cell constants were also measured

TABLE 3
Anisotropic Thermal Parameters (Å^2 × 10^3) for Dye **1c**

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C-1	47 (2)	39 (2)	39 (2)	−3 (1)	4 (2)	−6 (2)
C-2	51 (2)	41 (2)	46 (2)	1 (1)	5 (2)	10 (2)
C-3	75 (3)	63 (3)	44 (2)	−4 (2)	−4 (3)	−11 (3)
C-4	84 (4)	50 (2)	66 (2)	−25 (2)	17 (3)	−7 (3)
C-5	76 (4)	59 (3)	97 (3)	−23 (2)	−2 (3)	25 (3)
C-6	61 (3)	56 (2)	66 (2)	−7 (2)	−2 (2)	16 (3)
N-1	46 (2)	48 (2)	52 (2)	−4 (1)	−0 (2)	0 (2)
N-2	48 (2)	39 (1)	49 (1)	−3 (1)	−3 (2)	1 (2)
C-7	44 (2)	39 (2)	38 (2)	−6 (1)	1 (2)	−4 (2)
C-12	53 (2)	48 (2)	43 (2)	−4 (2)	−13 (2)	8 (2)
C-11	50 (2)	31 (2)	48 (2)	2 (1)	−13 (2)	2 (2)
C-10	38 (2)	37 (2)	36 (1)	2 (1)	−1 (2)	−5 (2)
C-9	45 (2)	43 (2)	36 (2)	5 (1)	−8 (2)	4 (2)
C-8	46 (2)	35 (2)	39 (2)	3 (1)	2 (2)	4 (2)
N-3	48 (2)	31 (1)	36 (1)	−3 (1)	0 (2)	−4 (2)
C-15	41 (2)	39 (2)	48 (2)	−6 (2)	0 (2)	0 (2)
C-16	66 (3)	37 (2)	52 (2)	0 (2)	1 (2)	−2 (2)
O-2	72 (2)	69 (2)	83 (2)	−27 (2)	16 (2)	−12 (2)
C-13	51 (2)	45 (2)	35 (2)	−4 (2)	−6 (2)	−3 (2)
C-14	59 (3)	52 (2)	39 (2)	2 (2)	2 (2)	−0 (2)
O-1	80 (2)	78 (2)	56 (1)	11 (1)	20 (2)	11 (2)

The anisotropic temperature factor exponent takes the form

$$-2\pi^2(h^2a^2 \times U_{11} + \cdots + 2hka \times b \times U_{12})$$

TABLE 4
Bond Lengths (Å) of Non-hydrogen Atoms, with ESD Values Given in Parentheses for Dye **1c**

C-1–C-2	1·368 (5)	C-1–C-6	1·385 (6)
C-1–N-1	1·439 (4)	C-2–C-3	1·375 (5)
C-3–C-4	1·374 (7)	C-4–C-5	1·373 (7)
C-5–C-6	1·380 (6)	N-1–N-2	1·260 (4)
N-2–C-7	1·420 (4)	C-7–C-12	1·397 (5)
C-7–C-8	1·387 (5)	C-12–C-11	1·356 (5)
C-11–C-10	1·416 (4)	C-10–C-9	1·409 (5)
C-10–N-3	1·372 (4)	C-9–C-8	1·379 (5)
N-3–C-15	1·462 (5)	N-3–C-13	1·471 (5)
C-15–C-16	1·501 (5)	C-16–O-2	1·411 (5)
C-13–C-14	1·520 (5)	C-14–O-1	1·402 (5)

on a crystal grown by slow evaporation from PhMe, in order to determine whether the crystallization conditions or the solvent influence molecular packing. However, since the cell constants are the same for the three crystals, these factors apparently had no effect on packing or molecular conformation.

Dye **1c** has an essentially planar azobenzene skeleton. Dihedral angles between selected planes appear in Table 7. The angle between the planes defined by the two aromatic rings (plane (1)–plane (2)) is 10·3°. As observed in dyes **1e** and **1f**, the hydroxyethyl groups of **1c** do not lie in the plane of the ring to which N-3 is attached. The molecular conformation is illustrated through the thermal ellipsoid plots in Figs 1 and 2, and the conformation and unit-cell packing are given in Fig. 3. In the cases of dyes **1c** and **1e** this

TABLE 5
Bond Angles (Degrees) for Dye **1c**

C-2–C-1–C-6	119·5 (3)	C-2–C-1–N-1	126·2 (3)
C-6–C-1–N-1	114·2 (3)	C-1–C-2–C-3	121·1 (4)
C-2–C-3–C-4	119·2 (4)	C-3–C-4–C-5	120·5 (4)
C-4–C-5–C-6	120·1 (4)	C-1–C-6–C-5	119·6 (4)
C-1–N-1–N-2	113·7 (3)	N-1–N-2–C-7	114·3 (3)
N-2–C-7–C-12	115·8 (3)	N-2–C-7–C-8	126·3 (3)
C-12–C-7–C-8	117·9 (3)	C-7–C-12–C-11	122·3 (3)
C-12–C-11–C-10	120·7 (3)	C-11–C-10–C-9	116·6 (3)
C-11–C-10–N-3	121·4 (3)	C-9–C-10–N-3	121·9 (3)
C-10–C-9–C-8	121·7 (3)	C-7–C-8–C-9	120·6 (3)
C-10–N-3–C-15	121·5 (3)	C-10–N-3–C-13	120·9 (3)
C-15–N-3–C-13	117·6 (3)	N-3–C-15–C-16	114·3 (3)
C-15–C-16–O-2	111·7 (3)	N-3–C-13–C-14	114·4 (3)
C-13–C-14–O-1	109·9 (3)		

TABLE 6
Hydrogen-Atom Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for Dye **1c**

	x	y	z	U
H-2	3 951 (46)	−2 552 (32)	3 272 (15)	50 (9)
H-3	3 570 (64)	−4 209 (42)	2 559 (19)	70 (13)
H-4	5 608 (61)	−6 240 (46)	2 609 (20)	78 (13)
H-5	7 440 (52)	−6 337 (37)	3 455 (16)	57 (10)
H-6	7 894 (58)	−4 581 (37)	4 249 (18)	82 (13)
H-8	4 078 (57)	1 218 (41)	4 312 (22)	75 (13)
H-9	3 837 (45)	3 021 (30)	5 131 (13)	42 (8)
H-11	7 128 (46)	618 (33)	6 216 (15)	42 (10)
H-12	7 110 (45)	−1 279 (34)	5 502 (15)	45 (9)
H-15A	3 363 (47)	4 021 (33)	5 999 (13)	33 (9)
H-15B	4 198 (44)	4 663 (31)	6 664 (15)	37 (9)
H-16A	4 352	6 215	5 734	123 (19)
H-16B	5 670	5 181	5 408	61 (11)
H-18	7 946	6 397	6 069	243 (30)
H-13A	7 742 (45)	2 503 (32)	6 712 (14)	34 (9)
H-13B	6 786 (39)	3 911 (29)	7 040 (12)	20 (7)
H-14A	6 829 (37)	2 010 (29)	7 761 (12)	28 (7)
H-14B	5 564 (50)	1 381 (38)	7 209 (16)	66 (11)
H-17	4 329	2 420	8 088	188 (24)

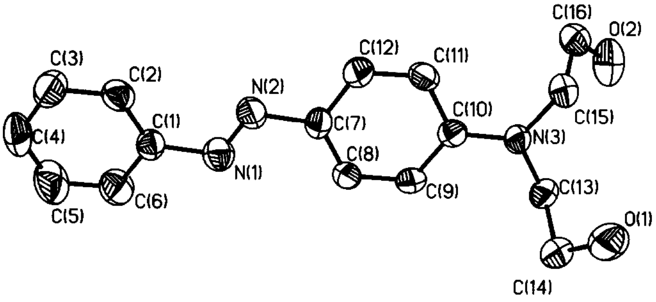


Fig. 1. Thermal ellipsoid plot of **1c** (view normal to molecular mean plane).

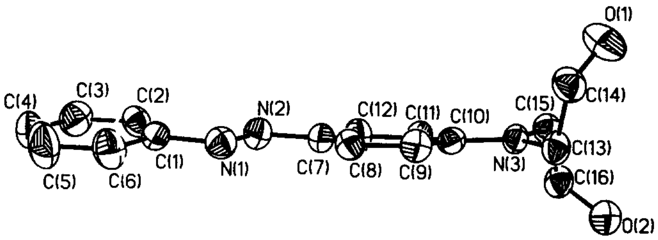


Fig. 2. Thermal ellipsoid plot of **1c** (view along molecular mean plane).

TABLE 7

Dihedral Angles (Degrees) between Planes for Dyes **1c**, **1e** and **1f**

Type	**1c**	**1e**	**1f**
Plane (1)[a]–plane (2)[b]	10·3	5·5	42·2
Plane (1)–plane (3)[c]	2·3	0·8	6·2
Plane (1)–plane (4)[d]	9·9	6·2	42·6
Plane (2)–plane (3)	9·6	4·7	38·4
Plane (2)–plane (4)	2·5	1·0	0·9
Plane (3)–plane (4)	8·7	5·5	38·8

[a] Plane (1) is defined by atoms C-1 to C-6.
[b] Plane (2) is defined by atoms C-7 to C-12.
[c] Plane (3) is defined by atoms C-1, C-2 and N-1.
[d] Plane (4) is defined by atoms C-7, C-8 and N-2.

means that, since the hydroxyalkyl chains are not in the plane formed by the azobenzene skeleton, these groups impart aplanarity to the overall molecule.

Table 8 contains distances between the planes defined by the aromatic rings and nitrogens N-1, N-2 and N-3 of dyes **1c**, **1e** and **1f**. These distances are under 0·2 Å for dyes **1c** and **1e**. Both of these azobenzenes have a planar chromophore, and N-1, N-2 and N-3 would be expected to lie within the plane defining the chromophore. For dye **1f**, which has an aplanar chromophore (dihedral angle for plane (1)–plane (2) is 47°), these distances are considerably larger. This indicates that the twist in the structure of **1f** occurs at the C-1–N-1 bond, and that N-1, N-2 and N-3 lie in the plane defined by C-7–C-12 but out of the plane defined by C-1–C-6.

Like dyes **1e** and **1f**, dye **1c** lacks inter- and intramolecular hydrogen bonding. The presence of two primary hydroxyl groups which reside on flexible alkyl chains would lead one to anticipate the existence of hydrogen bonding. However, none of the hydroxyl hydrogens lies closer than 2·5 Å to an oxygen located within or outside of the unit cell, with the obvious exception of the oxygen to which the hydrogen is bonded.

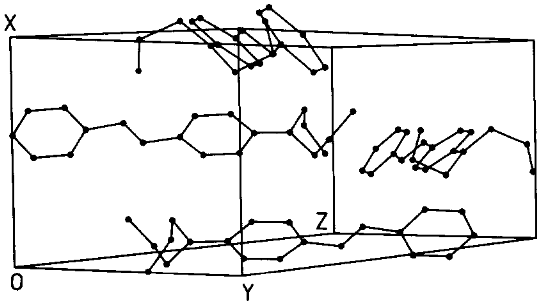
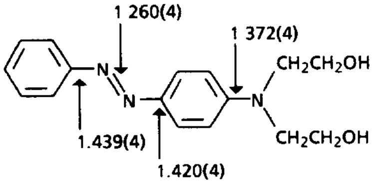


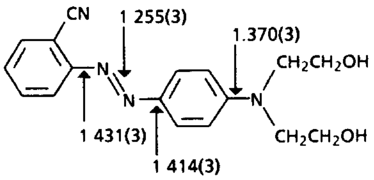
Fig. 3. Unit-cell packing diagram of **1c**.

TABLE 8
Distances between Key Nitrogens and Planes for Dyes **1c**, **1e** and **1f**

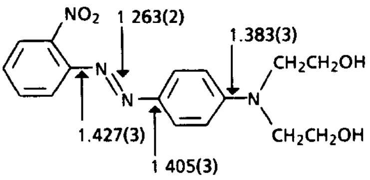
Dye	*Plane*	*Nitrogen*	*Distance (Å)*
1c	C-1–C-6	N-1	0·0392
1c	C-1–C-6	N-2	0·0837
1c	C-1–C-6	N-3	0·0768
1c	C-7–C-12	N-1	0·0478
1c	C-7–C-12	N-2	0·0864
1c	C-7–C-12	N-3	0·0898
1e	C-1–C-6	N-1	0·0083
1e	C-1–C-6	N-2	0·1670
1e	C-1–C-6	N-3	0·0507
1e	C-7–C-12	N-1	0·1093
1e	C-7–C-12	N-2	0·0283
1e	C-7–C-12	N-3	0·0653
1f	C-1–C-6	N-1	0·1368
1f	C-1–C-6	N-2	0·5808
1f	C-1–C-6	N-3	0·3155
1f	C-7–C-12	N-1	0·0032
1f	C-7–C-12	N-2	0·0228
1f	C-7–C-12	N-3	0·0304



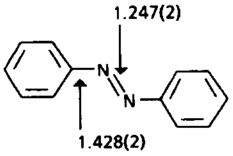
1c



1e



1f



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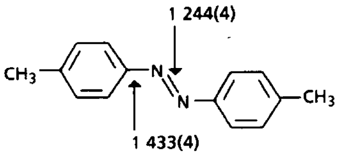

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Fig. 4. Comparison of selected bond lengths (Å) for some azobenzenes.

Comparison of the azo-(N-1–N-2)-linkage bond lengths and the lengths of the C-10–N-3 bond of dyes **1e, 1f** and **1c** shows no significant differences, after taking into account the associated standard deviations (Fig. 4). Since dye **1c** is a yellow-orange compound (λ_{max} 413 nm) while the other two are orange (**1e** 450 nm, **1f** 458 nm), this similarity in bond order is a surprising observation. The electron-withdrawing properties of cyano- and nitro-substituents, though responsible for the bathochromic shift observed when comparing the absorption spectra of dyes **1e** and **1f** to that of **1c**, do not alter the bond order of these dyes in the solid state to a level detectable by X-ray crystallography.

The bond lengths about the azo linkage for compound **1c** are also similar to those in azobenzene,[7] **2**, and 4,4′-azotoluene,[8] **3** (Fig. 4). In addition, examination of the azo linkage bond lengths of the compounds described in Fig. 4 suggests that the presence of the electron-donating dialkylamino group *para* to the azo group has little, if any, impact on the length of the C-1–N-1 bond of dyes **1c**, **1e** and **1f**.

CONCLUSIONS

As would be expected for a monoazo dye with no substituents *ortho* to the azo linkage, compound **1c** is a planar molecule. However, the C-1–N-1, N-1–N-2, N-2–C-7 and C-10–N-3 bond lengths are not significantly different from the corresponding bond lengths of dyes **1e** and **1f**. Comparison of the N-1–N-2 bond lengths of dyes **1c**, **1e** and **1f** with those of azobenzene and 4,4′-azotoluene indicates that the presence of an electron-donating dialkylamino group *para* to the azo linkage does not significantly affect the bond order of the C-1–N-1 linkage in the solid state. The fact that the absorption maximum of dye **1c** is appreciably different from the λ_{max} of dyes **1e** and **1f** suggests that changes in the conformation of *ortho*-substituted azobenzenes occur when they are dissolved in a solvent or polymer matrix.

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