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X-Ray Crystal Structure of Disperse Red 167*

Harold S. Freeman,[a]‡ James C. Posey, Jr[a] & Phirtu Singh[b]

Departments of [a]Textile Engineering, Chemistry, and Science, and [b]Chemistry,
North Carolina State University, Raleigh, North Carolina 27695-8301, USA

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ABSTRACT

X-ray diffractometer data have been used to determine the crystal structure of CI Disperse Red 167, an important automotive disperse dye. The structure was solved by direct methods and refined by least squares to $R = 0{\cdot}0442$ *for 1115 independent reflections. This monoazo dye possesses a planar azobenzene skeleton, as the dihedral angle between the planes made by the two aromatic rings is 1·5°. The non-bonding distance between the hydrogen atom of the acetamido group and azo nitrogen N(1) is well within the expected distance for intramolecular hydrogen bonding. Interestingly, the chloro and acetamido groups lie on the same side of the azo bond, and each unit cell of this dye contains 8 molecules.*

INTRODUCTION

While engaged in the synthesis of lightfast azo disperse dyes, we elected to prepare[1] and evaluate a number of analogues of CI Disperse Red 167. Among the dyes made was one in which an *o*-hydroxybenzoyl group was substituted for the acetamido group (cf. **1**). It was anticipated that the presence of the built-in benzophenone moiety would enhance the photostability of the commercially important parent dye. Evaluation of dye **1** under the conditions[2] required by General Motors Corporation for

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‡ To whom correspondence should be addressed.

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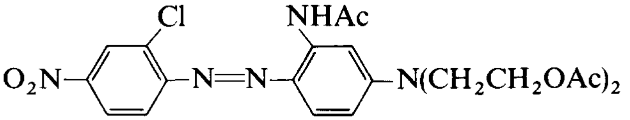
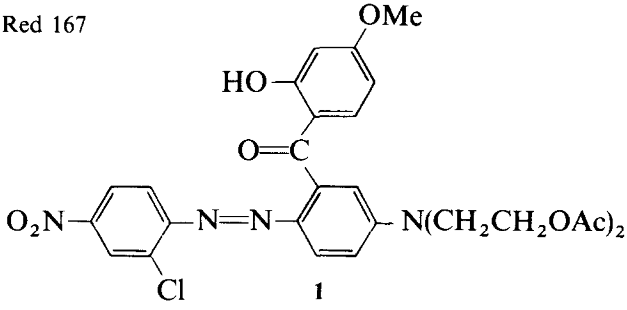


Disperse Red 167



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automotive dyes for polyesters revealed that this experimental dye was not as lightfast as the parent structure. To facilitate future design work in this area, the structure of Disperse Red 167 was determined from X-ray diffractometer data.

EXPERIMENTAL

Disperse Red 167 (commercial presscake) was purified by recrystallization from PhMe. Crystals suitable for diffraction studies were prepared by slow evaporation from a 1 : 1/$CHCl_3$: 1-BuOH solution. This process afforded brittle, dark red needles having a melting point of 145°C, λ_{max} = 507 nm, and ε_{max} (acetone) = 45 500.

Cell parameters were determined from 25 reflections measured on a Nicolet P3/F diffractometer using M_0K_α radiation (graphite monochrometer, λ = 0·710 73 Å). Intensity data were collected by the ω-scan method at variable speeds between 4 and 29·3 deg min^{-1}. The structure was solved by direct methods and refined to R = 0·0442 for 1115 independent reflections. Atoms C(20) through C(22), Table 2, are disordered and have occupancies of 0·55. Their disordered counterparts, atoms C(23) through C(25), have occupancies of 0·45. All calculations were performed using a Data General micro-eclipse desktop computer using the crystallographic program package SHELXTL supplied by the Nicolet Instrument Corporation, Madison, Wisconsin.

RESULTS AND DISCUSSION

Table 1 contains the cell dimensions obtained by a least-squares fit, and the final atomic and thermal parameters are given in Tables 2 and 3. Disperse

TABLE 1
Cell Data for Disperse Red 167

Composition	$C_{22}H_{24}N_5O_7Cl$
Molecular weight	505·92
Crystal system	Monoclinic
Space group	C2/c
a (Å)	15·774 (6)
b (Å)	36·415 (4)
c (Å)	8·559 (0)
α (deg)	90
β (deg)	104·33 (1)
γ (deg)	90
V (Å^3)	4763·41
Z	8
Density (calc)(g/cm^3)	1·41
Number of reflections	1115
$2\theta_{max}$ (deg)	55

Red 167 crystals are monoclinic and belong to the C2/c space group. These results and the number of molecules per unit cell are the same as those found when the crystal structure of **2**[3] was solved, but differ from the data obtained when **1**, **3–5**[4,5] were analysed (cf. Fig. 1). Similarly, the unit cell volume per molecule of the present dye is quite similar to that of **2** (4191 Å^3), but more than twice as large as that of dyes **3–5** (2016, 2027 and 2105 Å^3, respectively) and more than three times the size of **1** (1452 Å^3).

A complete listing of the bond lengths and bond angles for Disperse Red 167 is given in Tables 4 and 5. The length of the azo bond is significantly longer than that of azobenzene (1·247(2) Å), and the C–N bonds on each side of the azo linkage (N=N group) are appreciably shorter than those of azobenzene (1·428(2) Å), as would be anticipated from an azobenzene skeleton containing conjugated strong electron-withdrawing and electron-donating groups. Some key bond angles of **1** and Disperse Red 167 are compared in Table 6. It is clear that no significant differences exist between the values for the corresponding angles. A 3-D view of the structure of Disperse Red 167 is provided in Fig. 2, and Figs 3 and 4 contain a picture of the unit cell with and without the pendant side chains. The view of the packing diagram becomes much clearer when the pendant side chains are deleted (cf. Fig. 4).

The N(4) hydrogen atom of this dye is separated from N(1) by the distance 1·701 Å. This arrangement and the planar azobenzene skeleton facilitate hydrogen bonding between these two atoms. Steric repulsion between the *cis* chloro and acetamido groups is minimized by a rotation of the carbonyl oxygen away from the chloro group, as seen in the related structures **4–5**.

TABLE 2
Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) of Disperse Red 167

	x	y	z	U
N (1)	1 286 (4)	2 763 (2)	3 659 (8)	47 (3)[a]
N (2)	916 (4)	2 470 (2)	4 025 (7)	46 (3)[a]
C (1)	916 (5)	3 085 (2)	4 121 (10)	42 (4)[a]
C (2)	1 245 (5)	3 422 (2)	3 756 (9)	42 (4)[a]
C (3)	934 (5)	3 755 (2)	4 195 (9)	54 (4)[a]
C (4)	263 (5)	3 741 (2)	4 970 (9)	47 (4)[a]
C (5)	−89 (5)	3 419 (2)	5 327 (9)	51 (4)[a]
C (6)	235 (5)	3 091 (2)	4 910 (9)	46 (4)[a]
N (3)	−108 (4)	4 097 (2)	5 340 (8)	70 (4)[a]
O (1)	256 (4)	4 374 (2)	5 104 (9)	108 (4)[a]
O (2)	−734 (4)	4 082 (2)	5 934 (9)	102 (4)[a]
Cl (1)	2 066 (2)	3 431 (1)	2 724 (3)	61 (1)[a]
C (7)	1 230 (5)	2 135 (2)	3 695 (9)	45 (4)[a]
C (8)	1 930 (5)	2 049 (2)	2 942 (9)	40 (4)[a]
C (9)	2 121 (5)	1 687 (2)	2 695 (10)	45 (4)[a]
C (10)	1 682 (5)	1 401 (2)	3 212 (9)	42 (4)[a]
C (11)	981 (5)	1 478 (2)	3 959 (10)	48 (4)[a]
C (12)	789 (5)	1 833 (2)	4 134 (9)	47 (4)[a]
N (4)	2 397 (4)	2 344 (2)	2 525 (8)	43 (3)[a]
C (13)	3 111 (6)	2 330 (2)	1 865 (11)	60 (5)[a]
O (3)	3 388 (4)	2 047 (2)	1 392 (8)	66 (3)[a]
C (14)	3 532 (6)	2 693 (2)	1 738 (10)	59 (4)[a]
N (5)	1 900 (4)	1 039 (2)	3 029 (8)	50 (3)[a]
C (15)	1 454 (6)	731 (2)	3 597 (10)	58 (5)[a]
C (16)	1 748 (6)	670 (2)	5 407 (11)	71 (5)[a]
O (4)	2 620 (4)	523 (2)	5 818 (8)	79 (3)[a]
C (17)	2 773 (7)	217 (2)	6 680 (11)	71 (5)[a]
O (5)	2 215 (4)	55 (2)	7 074 (10)	133 (5)[a]
C (18)	3 699 (6)	89 (3)	6 977 (15)	99 (7)[a]
C (19)	2 552 (5)	932 (2)	2 107 (10)	69 (5)[a]
C (20)	2 078 (8)	983 (3)	78 (15)	41 (4)[a]
O (6)	1 680 (7)	658 (3)	−425 (13)	76 (4)
C (21)	806 (13)	633 (5)	−644 (24)	106 (8)
O (7)	436 (11)	838 (5)	−17 (19)	76 (7)
O (22)	435 (13)	278 (5)	−1356 (21)	121 (8)
C (23)	2 162 (12)	775 (5)	422 (22)	46 (6)
O (8)	1 651 (7)	1 098 (3)	−544 (13)	52 (4)
C (24)	815 (12)	1 104 (5)	−847 (22)	48 (6)
O (9)	377 (14)	905 (6)	−538 (24)	70 (8)
C (25)	453 (12)	1 418 (5)	−1 777 (21)	68 (7)

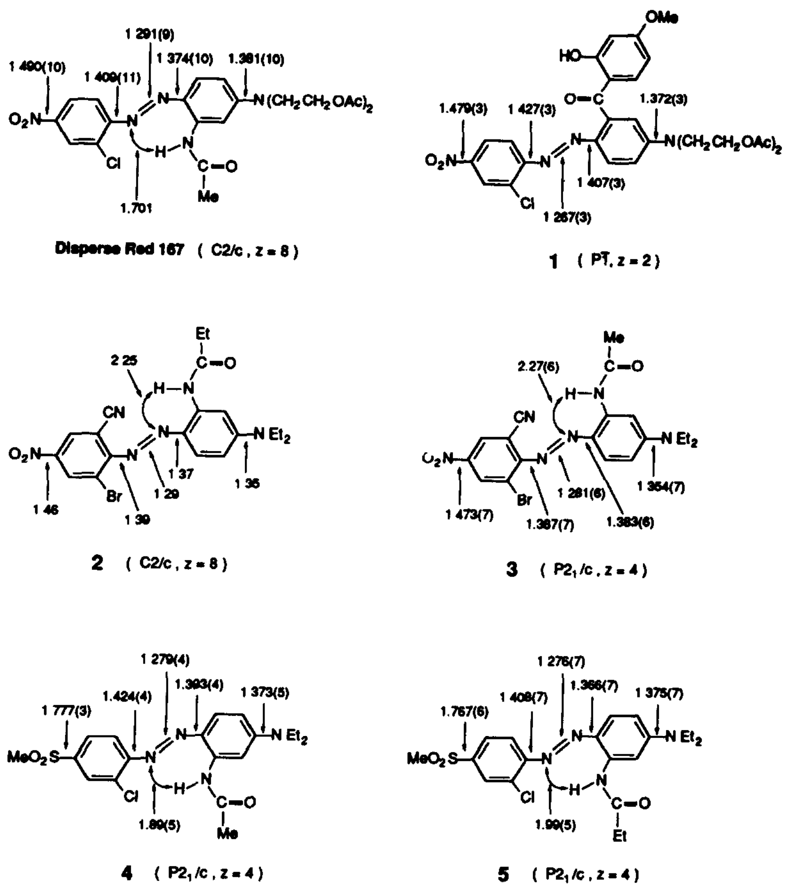
[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3

Anisotropic Thermal Parameters (Å × 10^3) of Disperse Red 167

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N (1)	47 (5)	50 (5)	50 (5)	−9 (4)	22 (4)	−7 (4)
N (2)	37 (4)	57 (5)	42 (5)	−6 (4)	5 (4)	4 (4)
C (1)	48 (7)	45 (6)	40 (7)	−12 (6)	23 (6)	−9 (6)
C (2)	28 (6)	69 (6)	26 (6)	1 (5)	1 (5)	−9 (5)
C (3)	51 (7)	47 (6)	72 (7)	1 (6)	27 (6)	−2 (5)
C (4)	26 (5)	55 (6)	53 (6)	0	0	0
C (5)	52 (6)	49 (6)	59 (7)	−12 (6)	32 (6)	−11 (5)
C (6)	59 (6)	36 (6)	35 (6)	0	0	0
N (3)	66 (6)	62 (6)	85 (7)	−6 (5)	26 (5)	1 (5)
O (1)	122 (7)	54 (5)	182 (8)	10 (5)	104 (6)	11 (4)
O (2)	89 (6)	76 (5)	168 (7)	−18 (5)	81 (5)	5 (4)
Cl (1)	57 (2)	64 (2)	72 (2)	0 (2)	38 (1)	−4 (2)
C (7)	51 (7)	48 (6)	45 (6)	12 (5)	28 (6)	11 (5)
C (8)	47 (7)	45 (6)	32 (6)	−2 (5)	17 (5)	−9 (5)
C (9)	44 (6)	53 (6)	49 (6)	−7 (6)	28 (5)	−11 (5)
C (10)	56 (6)	27 (5)	43 (6)	1 (5)	12 (5)	12 (5)
C (11)	40 (6)	51 (7)	53 (7)	−5 (6)	13 (5)	−8 (6)
C (12)	39 (6)	49 (6)	51 (7)	−13 (5)	8 (5)	−2 (5)
N (4)	46 (5)	48 (5)	42 (5)	5 (4)	25 (4)	−0 (4)
C (13)	68 (8)	47 (7)	71 (8)	6 (6)	29 (7)	−2 (6)
O (3)	51 (4)	58 (5)	81 (5)	0	0	0
C (14)	58 (7)	70 (7)	55 (7)	−8 (6)	27 (6)	−12 (6)
N (5)	41 (5)	56 (5)	57 (6)	2 (5)	18 (4)	−8 (4)
C (15)	61 (7)	48 (7)	69 (8)	−16 (6)	29 (7)	−8 (5)
C (16)	70 (9)	63 (7)	85 (10)	20 (7)	29 (8)	4 (6)
O (4)	61 (5)	62 (5)	116 (6)	36 (4)	29 (5)	3 (4)
C (17)	87 (9)	50 (7)	82 (9)	24 (6)	31 (8)	8 (6)
O (5)	119 (7)	78 (5)	236 (9)	77 (6)	108 (7)	14 (5)
C (18)	91 (11)	73 (9)	137 (11)	39 (8)	36 (10)	16 (8)
C (19)	57 (7)	47 (6)	112 (9)	13 (6)	41 (7)	10 (5)

The anisotropic temperature factor exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12})$.



Disperse Red 167 (C2/c, z = 8)

1 ($P\bar{1}$, z = 2)

2 (C2/c, z = 8)

3 ($P2_1/c$, z = 4)

4 ($P2_1/c$, z = 4)

5 ($P2_1/c$, z = 4)

Fig. 1. Key bond distances (Å) and cell data for Disperse Red 167 and dyes **1–5**.

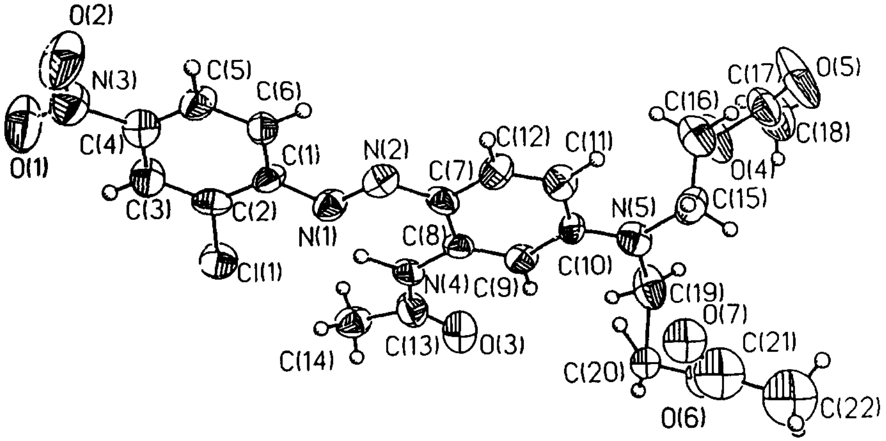


Fig. 2. Structure of Disperse Red 167 viewed perpendicular to the mean plane.

TABLE 4
Bond Lengths (Å) of Disperse Red 167

N (1)–N (2)	1·291 (9)	N (1)–C (1)	1·409 (11)
N (2)–C (7)	1·374 (10)	C (1)–C (2)	1·396 (12)
C (1)–C (6)	1·403 (13)	C (2)–C (3)	1·396 (12)
C (2)–Cl (1)	1·738 (9)	C (3)–C (4)	1·383 (12)
C (4)–C (5)	1·363 (11)	C (4)–N (3)	1·490 (10)
C (5)–C (6)	1·381 (11)	N (3)–O (1)	1·204 (9)
N (3)–O (2)	1·218 (11)	C (7)–C (8)	1·444 (12)
C (7)–C (12)	1·401 (11)	C (8)–C (9)	1·378 (11)
C (8)–N (4)	1·399 (10)	C (9)–C (10)	1·384 (12)
C (10)–C (11)	1·434 (13)	C (10)–N (5)	1·381 (10)
C (11)–C (12)	1·343 (11)	N (4)–C (13)	1·379 (13)
C (13)–O (3)	1·225 (11)	C (13)–C (14)	1·495 (12)
N (5)–C (15)	1·469 (11)	N (5)–C (19)	1·494 (12)
C (15)–C (16)	1·519 (13)	C (16)–O (4)	1·436 (11)
O (4)–C (17)	1·323 (10)	C (17)–O (5)	1·179 (13)
C (17)–C (18)	1·495 (14)	C (19)–C (20)	1·723 (15)
C (19)–C (23)	1·531 (19)	C (20)–O (6)	1·360 (15)
C (20)–C (23)	0·813 (21)	C (20)–O (8)	0·856 (15)
O (6)–C (21)	1·348 (23)	O (6)–C (23)	1·007 (19)
O (6)–O (8)	1·605 (15)	C (21)–O (7)	1·159 (28)
C (21)–C (22)	1·486 (26)	C (21)–C (24)	1·726 (26)
C (21)–O (9)	1·217 (29)	O (7)–C (24)	1·417 (27)
O (7)–O (9)	0·496 (26)	C (23)–O (8)	1·545 (20)
O (8)–C (24)	1·279 (22)	C (24)–O (9)	1·078 (30)
C (24)–C (25)	1·428 (25)		

TABLE 5
Bond Angles (°) of Disperse Red 167

N (2)–N (1)–C (1)	112·1 (7)	N (1)–N (2)–C (7)	118·6 (7)
N (1)–C (1)–C (2)	117·7 (8)	N (1)–C (1)–C (6)	124·5 (7)
C (2)–C (1)–C (6)	117·9 (8)	C (1)–C (2)–C (3)	121·9 (8)
C (1)–C (2)–Cl (1)	119·7 (7)	C (3)–C (2)–Cl (1)	118·4 (7)
C (2)–C (3)–C (4)	117·3 (7)	C (3)–C (4)–C (5)	122·9 (7)
C (3)–C (4)–N (3)	117·2 (7)	C (5)–C (4)–N (3)	119·9 (7)
C (4)–C (5)–C (6)	119·3 (8)	C (1)–C (6)–C (5)	120·8 (7)
C (4)–N (3)–O (1)	117·8 (7)	C (4)–N (3)–O (2)	116·8 (6)
O (1)–N (3)–O (2)	125·3 (7)	N (2)–C (7)–C (8)	129·7 (7)
N (2)–C (7)–C (12)	114·5 (8)	C (8)–C (7)–C (12)	115·7 (7)
C (7)–C (8)–C (9)	119·8 (7)	C (7)–C (8)–N (4)	117·2 (7)
C (9)–C (8)–N (4)	123·0 (8)	C (8)–C (9)–C (10)	121·6 (8)
C (9)–C (10)–C (11)	119·8 (7)	C (9)–C (10)–N (5)	121·6 (8)
C (11)–C (10)–N (5)	118·6 (7)	C (10)–C (11)–C (12)	117·3 (8)
C (7)–C (12)–C (11)	125·7 (8)	C (8)–N (4)–C (13)	127·7 (7)
N (4)–C (13)–O (3)	124·1 (8)	N (4)–C (13)–C (14)	114·8 (7)
O (3)–C (13)–C (14)	121·1 (9)	C (10)–N (5)–C (15)	122·5 (7)
C (10)–N (5)–C (19)	122·2 (7)	C (15)–N (5)–C (19)	115·1 (6)
N (5)–C (15)–C (16)	113·5 (6)	C (15)–C (16)–O (4)	109·7 (8)
C (16)–O (4)–C (17)	118·9 (8)	O (4)–C (17)–O (5)	122·4 (9)
O (4)–C (17)–C (18)	113·3 (9)	O (5)–C (17)–C (18)	124·2 (8)
N (5)–C (19)–C (20)	108·7 (7)	N (5)–C (19)–C (23)	115·3 (9)
C (20)–C (19)–C (23)	28·1 (8)	C (19)–C (20)–O (6)	106·0 (9)
C (19)–C (20)–C (23)	62·7 (15)	O (6)–C (20)–C (23)	47·4 (14)
C (19)–C (20)–O (8)	139·3 (16)	O (6)–C (20)–O (8)	89·9 (12)
C (23)–C (20)–O (8)	135·5 (21)	C (20)–O (6)–C (21)	118·6 (12)
C (20)–O (6)–C (23)	36·5 (11)	C (21)–O (6)–C (23)	133·9 (18)
C (20)–O (6)–O (8)	32·2 (6)	C (21)–O (6)–O (8)	92·6 (11)
C (23)–O (6)–O (8)	68·1 (12)	O (6)–C (21)–O (7)	120·4 (17)
O (6)–C (21)–C (22)	113·6 (16)	O (7)–C (21)–C (22)	124·1 (20)
O (6)–C (21)–C (24)	85·0 (13)	O (7)–C (21)–C (24)	54·7 (14)
C (22)–C (21)–C (24)	146·7 (15)	O (6)–C (21)–O (9)	120·2 (18)
O (7)–C (21)–O (9)	24·0 (13)	C (22)–C (21)–O (9)	124 8 (19)
C (24)–C (21)–O (9)	38·3 (14)	C (21)–O (7)–C (24)	83·5 (17)
C (21)–O (7)–O (9)	84·7 (35)	C (24)–O (7)–O (9)	39·1 (29)
C (19)–C (23)–C (20)	89·2 (17)	C (19)–C (23)–O (6)	153·1 (21)
C (20)–C (23)–O (6)	96 2 (18)	C (19)–C (23)–O (8)	104·8 (12)
C (20)–C (23)–O (8)	22·9 (11)	O (6)–C (23)–O (8)	74·7 (12)
C (20)–O (8)–O (6)	57·9 (10)	C (20)–O (8)–C (23)	21·6 (11)
O (6)–O (8)–C (23)	37·2 (8)	C (20)–O (8)–C (24)	138·4 (18)
O (6)–O (8)–C (24)	92·5 (11)	C (23)–O (8)–C (24)	119·9 (14)
C (21)–C (24)–O (7)	41·8 (12)	C (21)–C (24)–O (8)	89·7 (13)
O (7)–C (24)–O (8)	115·3 (15)	C (21)–C (24)–O (9)	44·4 (15)
O (7)–C (24)–O (9)	16·9 (12)	O (8)–C (24)–O (9)	129·0 (20)
C (21)–C (24)–C (25)	147·1 (15)	O (7)–C (24)–C (25)	131·8 (18)
C (8)–C (24)–C (25)	112·1 (17)	O (9)–C (24)–C (25)	118·8 (20)
C (21)–O (9)–O (7)	71·4 (33)	C (21)–O (9)–C (24)	97·3 (22)
O (7)–O (9)–C (24)	124·0 (36)	C (24)–C (25)–C (25A)	124·9 (11)

TABLE 6
Comparison of Some Key Bond Angles (°) of Disperse Red 167 and Dye **1**

Bond	*Disperse Red 167*	*Dye 1*
C (2)–C (1)–C (6)	117·7 (8)	119·1 (2)
C (8)–C (7)–C (12)	115·7 (7)	118·6 (2)
C (2)–C (1)–N (1)	117·7 (8)	117·3 (2)
C (6)–C (1)–N (1)	124·5 (7)	123·6 (2)
C (8)–C (7)–N (2)	129·7 (7)	125·7 (2)
C (12)–C (7)–N (2)	114·5 (8)	115·6 (2)
N (2)–N (1)–C (1)	112·1 (7)	112·6 (2)

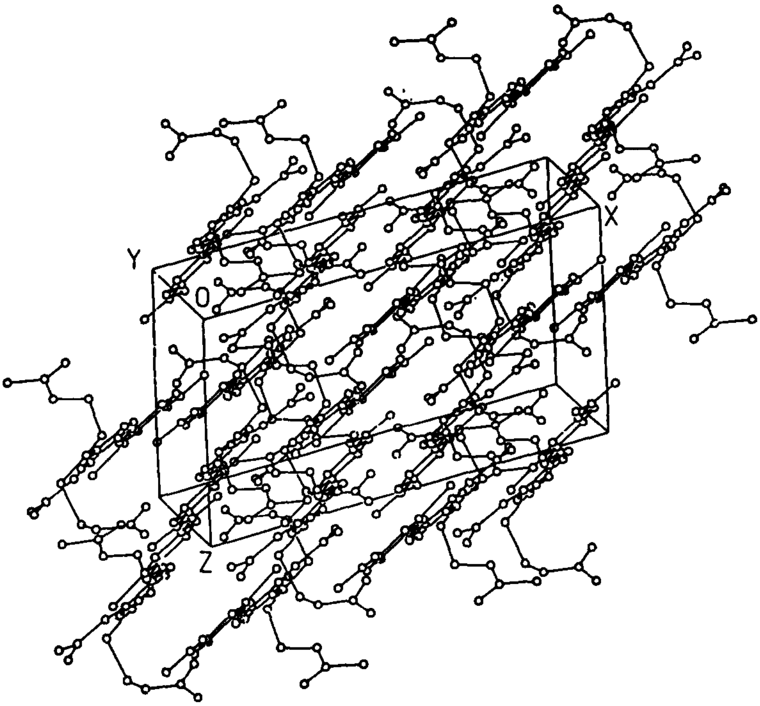


Fig. 3. Packing arrangement of Disperse Red 167 viewed down the *Y* axis.

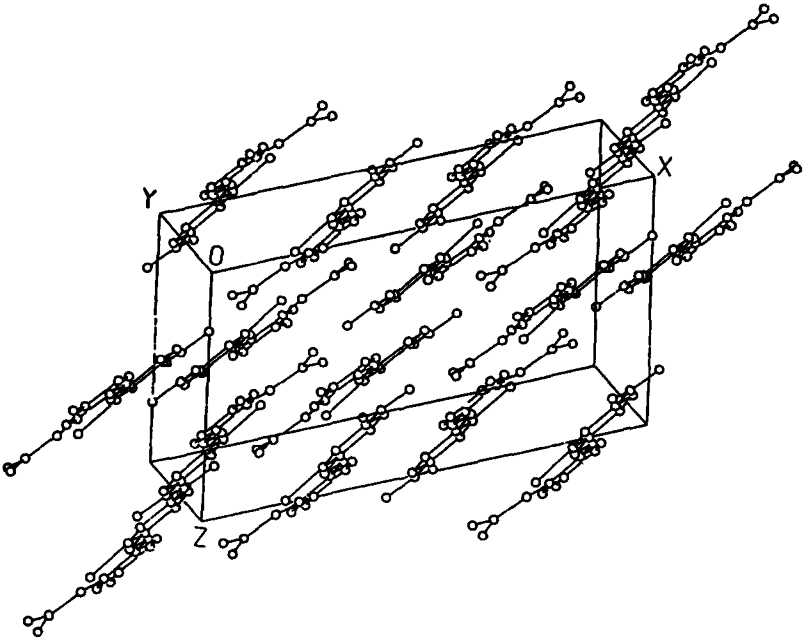


Fig. 4. Packing arrangement of Disperse Red 167, with pendant side chains omitted, viewed down the *Y* axis.

CONCLUSIONS

Determination of the crystal structure of Disperse Red 167 to help explain differences in the photostability of this dye and experimental dye **1** indicates that both dyes possess *trans* geometry about the azo linkage and a planar azobenzene skeleton. In addition, the two have comparable bond order and key bond angles. The major difference between the two is the presence of (a) the '*cis*-like' arrangement of the *o*,*o*'-groups and (b) intramolecular hydrogen bonding between the N(4) proton and the azo linkage in Disperse Red 167. These two features afford protection to the azo bond that cannot be achieved in the '*trans*-like' arrangement of the groups *ortho* to the azo linkage of dye **1**.

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