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X-Ray Crystal Structure of Disazo Dyes. Part 2: Derivatives of C.I. Disperse Yellow 23 and C.I. Disperse Orange 29

Harold S. Freeman[a], Stanley A. McIntosh[a] and Phirtu Singh[1,b]

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

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ABSTRACT

Crystals of the 2,6-dichlorobenzoyl ester of C.I. Disperse Yellow 23 and C.I. Disperse Orange 29 were grown from chloroform, and cell dimensions were determined by a least-squares fit. Crystals of both esters were found to exist in the monoclinic space group $P2_1/C$. The structures of these dyes possessed the anti *conformation, unlike that of underivatized C.I. Disperse Orange 29, but the same as that reported for 4-phenylazoazobenzene.* © *1997 Elsevier Science Ltd*

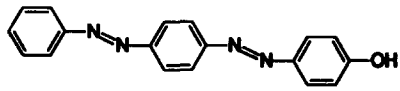
Keywords: crystal structure, diazo dyes, anti-conformation, monoclinic.

INTRODUCTION

In the previous paper in this series, we reported results of studies aimed at solving the crystal structures of C.I. Disperse Yellow 23 (**1**) and C.I. Disperse Orange 29 (**2**) [1]. In those studies, it was determined that suitable crystals of the former dye could not be generated, despite the variety of conditions and solvents employed. It was possible, however, to solve the crystal structure of the latter dye using crystals grown from methanol or 1-propanol/water. The results showed that dye **2** existed in a *syn* conformation and that the key to generating useful crystals of these dyes is the elimination of intermolecular H-bonding between dye molecules. This was accomplished, in the case of dye **2**, when a solvent capable of undergoing strong interactions with the phenolic-OH group was used. In view of these observations, a number of

[1]Present address: North Carolina Central University, Durham, NC 27707.

acylated derivatives of dye **1** were synthesized and examined for their ability to give crystals suitable for X-ray analysis.



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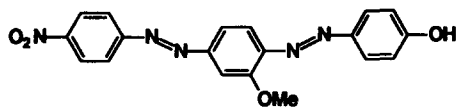

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EXPERIMENTAL

General

Except for dyes, all chemicals used in this study were obtained from Fisher Scientific Company. Atlantic Dyes and Chemicals provided samples of Atlantic Transfer Yellow 5R (C.I. Disperse Yellow 23) and Atlantic Polycron Orange L (C.I. Disperse Orange 29).

A Mel-Temp capillary melting point apparatus was used to determine melting points. The ^{1}H NMR spectrum of dye **2** was recorded in d_6-DMSO

TABLE 1
Cell Data for Dye **3**

Composition:	$C_{25}H_{16}N_4O_2Cl_2$
M_r	475.34
Crystal system	Monoclinic
Space group	$P2_1/C$
a (Å)	5.671(2)[a]
b (Å)	11.225(3)[a]
c (Å)	35.078(13)[a]
β°	94.02(3)[a]
V (Å^3)	2227.2
Z	4
Calculated density (g/ml)	1.42
Measured density (g/ml)	1.42
Number of reflections used for cell constant determination	25
2-θ min.	3
2-θ max.	55

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

using a Bruker 250 MHz spectrometer and the spectrum of dye **3** was recorded in $CDCl_3$ using a General Electric GN300 300 MHz spectrometer. Chemical shifts (parts per million) were measured relative to tetramethylsilane (TMS). Elemental microanalyses were performed by Atlantic Microlab Incorporated. Fisher chromatographic silica gel (catalog No. S743-1) was used for flash chromatography [4, 5].

X-ray crystallographic analyses were performed using a Nicolet P3/F diffractometer and MoKα radiation (graphite monochromator, 0.71073 Å wavelength). Structures were solved by direct methods using the Nicolet SHELXTL crystallographic software package, which was running on a Data General Micro-Eclipse model 30 computer.

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

	x	*y*	*z*	U[a]
C(1)	1879(9)	−1835(4)	−1129(2)	47(2)
C(2)	3542(10)	−1968(5)	−1388(2)	68(3)
C(3)	3288(11)	−2833(5)	−1669(2)	74(3)
C(4)	1369(11)	−3585(5)	−1681(2)	71(3)
C(5)	−274(11)	−3458(5)	−1423(2)	78(3)
C(6)	−47(9)	−2592(5)	−1141(2)	64(2)
N(1)	1986(7)	−973(3)	−826(1)	49(2)
N(2)	3769(7)	−312(3)	−829(1)	50(2)
C(7)	3903(8)	561(4)	−531(1)	42(2)
C(8)	5927(8)	1270(4)	−521(2)	53(2)
C(9)	6219(8)	2150(4)	−246(1)	53(2)
C(10)	4557(8)	2340(4)	13(1)	40(2)
C(11)	2539(8)	1625(4)	3(2)	54(2)
C(12)	2224(8)	745(4)	−272(1)	51(2)
N(3)	4704(7)	3235(3)	302(1)	49(2)
N(4)	6478(7)	3895(4)	285(1)	49(2)
C(13)	6629(10)	4796(4)	575(2)	43(2)
C(14)	8605(8)	5533(4)	569(1)	51(2)
C(15)	8902(9)	6431(5)	839(2)	51(2)
C(16)	7277(9)	6593(4)	1097(2)	44(2)
C(17)	5284(8)	5882(4)	1108(1)	51(2)
C(18)	4998(9)	4978(4)	839(2)	52(2)
O(1)	7469(5)	7560(3)	1357(1)	49(1)
C(19)	8978(8)	7439(5)	1667(1)	44(2)
O(2)	10 178(6)	6575(3)	1734(1)	67(2)
C(20)	8954(9)	8527(4)	1913(2)	40(2)
C(21)	10 540(9)	9436(5)	1852(2)	47(2)
C(22)	10 621(11)	10 447(5)	2078(2)	69(3)
C(23)	9115(12)	10 532(6)	2363(2)	77(3)
C(24)	7505(11)	9647(6)	2433(2)	65(3)
C(25)	7476(10)	8650(5)	2203(2)	53(2)
Cl(1)	12 438(3)	9334(1)	1493(1)	72(1)
Cl(2)	5477(3)	7516(2)	2275(1)	85(1)

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

Purification of C.I. Disperse Yellow 23 (1)

A 2 g sample of Atlantic Transfer Yellow 5R was dissolved in toluene:ethyl acetate 10:1 and the solution was filtered through a glass wool plug. The solution contained 0.037 g of dye **1** per ml. A flash column was packed using a slurry of 120 g of silica gel in toluene:ethyl acetate 10:1 eluent, and a 1-inch layer of coarse sand was poured on top of the silica gel. A 25-ml portion of the dye solution was loaded onto the column directly. After developing the column, 0.79 g of pure **1** was obtained, mp 186°C; ^{1}H NMR spectrum

TABLE 3
Anisotropic Thermal Parameters ($Å^2 \times 10^3$) for Dye **3**

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	55(3)	35(3)	49(4)	−5(3)	−0(4)	−6(3)
C(2)	75(4)	57(4)	73(5)	−27(4)	13(5)	−18(4)
C(3)	95(5)	68(4)	62(5)	−18(4)	35(5)	−14(4)
C(4)	99(5)	45(3)	67(5)	−17(4)	−8(5)	−6(4)
C(5)	76(4)	73(4)	83(6)	−27(5)	3(5)	−33(4)
C(6)	67(4)	75(4)	52(4)	−23(4)	22(4)	−29(4)
N(1)	57(3)	45(3)	46(3)	−9(3)	5(3)	−12(2)
N(2)	55(3)	44(3)	52(3)	−3(3)	5(3)	−17(2)
C(7)	47(3)	40(3)	37(3)	−1(3)	1(3)	−11(3)
C(8)	51(3)	60(3)	50(4)	−17(3)	20(4)	−14(3)
C(9)	50(3)	56(3)	53(4)	−15(3)	1(4)	−20(3)
C(10)	47(3)	38(3)	34(3)	1(3)	6(3)	−6(3)
C(11)	53(3)	57(3)	56(4)	−17(4)	20(4)	−14(3)
C(12)	49(3)	54(3)	52(4)	−12(3)	10(4)	−16(3)
N(3)	52(3)	44(2)	49(3)	−10(3)	−10)	−5(2)
N(4)	49(2)	48(3)	48(3)	−9(3)	4(3)	−14(2)
C(13)	51(3)	40(3)	38(4)	−6(3)	−1(4)	−5(3)
C(14)	55(3)	60(3)	40(4)	−16(3)	17(4)	−13(3)
C(15)	45(3)	55(4)	54(4)	−13(4)	7(4)	−14(3)
C(16)	53(3)	38(3)	41(4)	−2(3)	−5(4)	3(3)
C(17)	52(3)	57(3)	46(4)	−11(3)	18(4)	−2(3)
C(18)	52(3)	51(3)	54(4)	−18(4)	12(4)	−14(3)
O(1)	58(2)	43(2)	45(2)	−12(2)	−10(2)	3(2)
C(19)	50(3)	42(3)	40(4)	3(3)	2(4)	−7(3)
O(2)	99(3)	42(2)	58(3)	−5(2)	−20(3)	12(2)
C(20)	50(3)	33(3)	37(4)	−60)	−5(4)	−2(3)
C(21)	53(3)	51(3)	38(4)	−8(4)	5(4)	2(3)
C(22)	86(5)	53(4)	69(5)	−13(5)	5(5)	−9(4)
C(23)	101(5)	62(4)	64(5)	−24(5)	−12(5)	2(5)
C(24)	77(4)	84(5)	37(4)	−11(4)	24(5)	25(4)
C(25)	59(4)	59(4)	43(4)	−1(4)	7(4)	4(4)
Cl(1)	76(1)	69(1)	76(1)	−3(1)	30(1)	−19(1)
Cl(2)	75(1)	95(1)	87(1)	21(1)	30(1)	−15(1)

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

($CDCl_3$): δ10.5 (s,1H), δ8.10 (d, 2H), δ8.00 (m, 3H), δ7.90 (d, 2H), δ7.76 (m, 2H), δ7.70 (d, 2H). The CI/MS spectrum showed the $[M+1]^+$ ion (m/z 303) to be the base peak.

TABLE 4

Bond Lengths (Å) of Nonhydrogen Atoms for Dye **3**, with e.s.d. Values Given in Parentheses

C(1)–C(2)	1.363(8)	C(1)–C(6)	1.382(7)
C(1)–N(1)	1.436(7)	C(2)–C(3)	1.383(8)
C(3)–C(4)	1.375(9)	C(4)–C(5)	1.351(9)
C(5)–C(6)	1.386(8)	N(1)–N(2)	1.255(6)
N(2)–C(7)	1.431(6)	C(7)–C(8)	1.395(6)
C(7)–C(12)	1.379(7)	C(8)–C(9)	1.383(7)
C(9)–C(10)	1.370(7)	C(10)–C(11)	1.397(6)
C(10)–N(3)	1.425(6)	C(11)–C(12)	1.384(7)
N(3)–N(4)	1.255(6)	N(4)–C(13)	1.430(7)
C(13)–C(14)	1.394(7)	C(13)–C(18)	1.371(8)
C(14)–C(15)	1.385(7)	C(15)–C(16)	1.348(8)
C(16)–C(17)	1.387(7)	C(16)–O(1)	1.428(6)
C(17)–C(18)	1.387(7)	O(1)–C(19)	1.344(6)
C(19)–O(2)	1.198(6)	C(19)–C(20)	1.495(7)
C(20)–C(21)	1.386(7)	C(20)–C(25)	1.371(8)
C(21)–C(22)	1.383(8)	C(21)–Cl(1)	1.719(6)
C(22)–C(23)	1.363(10)	C(23)–C(24)	1.383(9)
C(24)–C(25)	1.379(9)	C(25)–Cl(2)	1.735(6)

TABLE 5

Bond Angles (degrees) for Dye **3**

C(2)–C(1)–C(6)	119.7(5)	C(2)–C(1)–N(1)	124.9(5)
C(6)–C(1)–N(1)	115.4(5)	C(1)–C(2)–C(3)	120.6(5)
C(2)–C(3)–C(4)	119.8(6)	C(3)–C(4)–C(5)	119.7(6)
C(4)–C(5)–C(6)	121.2(6)	C(1)–C(6)–C(5)	119.1(5)
C(1)–N(1)–N(2)	112.6(4)	N(1)–N(2)–C(7)	113.6(4)
N(2)–C(7)–C(8)	114.3(4)	N(2)–C(7)–C(12)	125.6(4)
C(8)–C(7)–C(12)	120.1(4)	C(7)–C(8)–C(9)	119.0(5)
C(8)–C(9)–C(10)	121.3(4)	C(9)–C(10)–C(11)	119.6(4)
C(9)–C(10)–N(3)	124.9(4)	C(11)–C(10)–N(3)	115.4(4)
C(10)–C(11)–C(12)	119.6(5)	C(7)–C(12)–C((11)	120.4(4)
C(10)–N(3)–N(4)	113.0(4)	N(3)–N(4)–C(13)	113.1(4)
N(4)–C(13)–C(14)	114.7(5)	N(4)–C(13)–C(18)	125.2(5)
C(14)–C(13)–C(18)	120.1(5)	C(13)–C(14)–C(15)	118.8(5)
C(14)–C(15)–C(16)	120.1(5)	C(15)–C(16)–C(17)	122.6(5)
C(15)–C(16)–O(1)	120.7(4)	C(17)–C(16)–O(1)	116.6(4)
C(16)–C(17)–C(18)	117.3(5)	C(13)–C(18)–C(17)	121.2(5)
C(16)–O(1)–C(19)	117.4(4)	O(1)–C(19)–O(2)	124.0(5)
O(1)–C(19)–C(20)	110.6(4)	O(2)–C(19)–C(20)	125.3(4)
C(19)–C(20)–C(21)	118.8(5)	C(19)–C(20)–C(25)	122.7(5)
C(21)–C(20)–C(25)	118.5(5)	C(20)–C(21)–C(22)	120.8(5)
C(20)–C(21)–Cl(1)	120.6(4)	C(22)–C(21)–Cl(1)	118.6(4)
C(21)–C(22)–C(23)	118.7(6)	C(22)–C(23)–C(24)	122.3(6)
C(23)–C(24)–C(25)	117.5(6)	C(20)–C(25)–C(24)	122.2(5)
C(20)–C(25)–Cl(2)	118.3(4)	C(24)–C(25)–Cl(2)	119.4(5)

Preparation of dye 3

The thallium salt of C.I. Disperse Yellow 23 was prepared by mixing 238 mg of pure C.I. Disperse Yellow 23 with 196 mg of thallous ethoxide in 10 ml methanol in a 50-ml round-bottom flask. The solvent was removed, and 2 ml of pyridine was added. An orange crystalline precipitate formed immediately from the ruby-colored solution, when 126 mg of 2,6-dichlorobenzoyl chloride was added. The solid was collected by vacuum filtration, rinsed with water, 1% $NaHCO_3$, and with water again. The solid was vacuum dried to

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

	x	*y*	*z*	U
H(2)	4903	−1457	−1376	78
H(3)	4446	−2908	−1854	87
H(4)	1198	−4197	−1872	81
H(5)	−1622	−3978	−1435	81
H(6)	−1212	−2519	−957	80
H(8)	7099	1149	−702	61
H(9)	7614	2637	−236	56
H(11)	1378	1743	186	63
H(12)	828	259	−282	58
H(14)	9740	5419	382	61
H(15)	10 266	6938	842	60
H(17)	4148	6010	1294	59
H(18)	3634	4472	838	62
H(22)	11 717	11 076	2035	80
H(23)	9175	11 231	2521	87
H(24)	6448	9723	2634	83

TABLE 7
Dihedral Angles (degrees) Between Planes for Dye 3

Planes	*Angle*
Plane(1)[a]–plane(2)[b]	2.3
Plane(1)–plane(3)[c]	1.3
Plane(1)–plane(6)[d]	102.1
Plane(1)–plane(7)[e]	15.3
Plane(2)–plane(3)	2.3
Plane(2)–plane(6)	104.4
Plane(2)–plane(7)	17.1
Plane(3)–plane(6)	102.4
Plane(3)–plane(7)	14.7
Plane(6)–plane(7)	90.6

[a]Plane(1) is defined by atoms C(1)–C(6). [b]Plane(2) is defined by atoms C(7)–C(12). [c]Plane(3) is defined by atoms C(13)–C(18). [d]Plane(6) is defined by atoms C(20), C(19), and O(2). [e]Plane(7) is defined by atoms C(20)–C(25).

provide 358 mg (96%) of dye **3**. TLC analysis using chloroform as the eluent showed the R_f of the product to be 0.90. The solid had a melting point of 203°C, and CI mass spectrometric and elemental analysis confirmed the molecular formula. Calculated for $C_{25}H_{16}N_4O_2Cl_2$: C, 63.16; H, 3.37; N, 11.79; found: C, 63.12; H, 3.41; N, 11.73.

Preparation of dye 5

The ester was prepared in 91% yield using the procedure outlined above for the synthesis of **3**. The amounts of reactants used were 43 μl of 2,6-dichlorobenzoyl chloride, 48 mg of pure C.I. Disperse Orange 29, and 32 mg of thallous ethoxide. After the rinsing and drying steps, 70 mg of a red, crystalline compound was obtained which had a melting point of 217°C. EI mass spectrometry showed the M^+ (m/z 549) and $M+2$ (m/z 551) ions in the expected 1:0.66 ratio for an organic compound having two chlorine atoms.

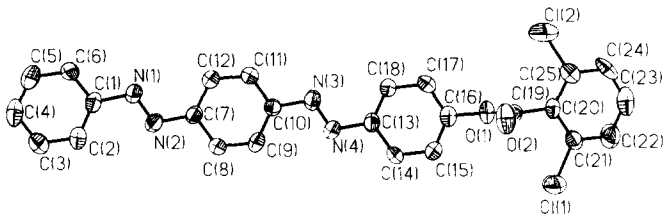


Fig. 1. Thermal ellipsoid plot of dye **3**. View is normal to the molecular mean plane.

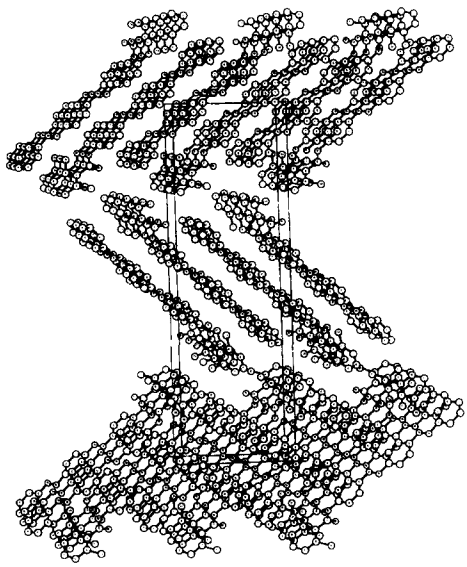
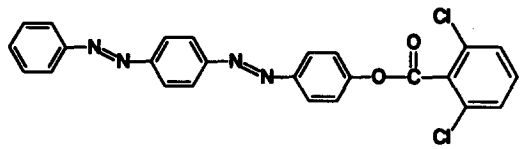


Fig. 2. Unit cell packing diagram of dye **3**.

RESULTS AND DISCUSSION

The 2,6-dichlorobenzoyl ester of dye **1** was prepared in two steps [2] (1) formation of the thallium salt of the phenolic group and (2) acylation using 2,6-dichlorobenzoyl chloride in pyridine. The product (**3**) did not require further purification. Instead, it was crystallized directly by slow evaporation of a $CHCl_3$ solution to give orange needles.



3

TABLE 8
Cell Data for Dye **5**

Composition:	$C_{26}H_{17}N_5O_5Cl_2$
M_r	550.36
Crystal system	Monoclinic
Space group	$P2_1/C$
a (Å)	11.913(7)[a]
b (Å)	14.843(8)[a]
c (Å)	14.003(6)[a]
β^o	91.79(3)[a]
V (Å^3)	803.7
Z	4
Calculated density (g/ml)	1.47
Measured density (g/ml)	1.47
Number of reflections used for cell constant determination	25
2-θ min.	3
2-θ max.	55, 30

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

TABLE 9
Reflections that were Omitted in the Refinement of the Crystal Structure of Dye **5**

h	k	l
−1	2	2
0	2	3
5	2	3
−1	1	3
−1	0	4
−1	1	4
0	2	4
1	2	4

The structure of **3** was solved from 1602 independent reflections to $R = 0.0546$. The crystal used exists in the monoclinic space group $P2_1/C$. The unit cell data, atomic and thermal parameters, bond lengths and angles, and associated dihedral angles are reported in Table 1–7. Views of the dye structure inside and outside the unit cell are provided in Figs 1 and 2. It can be seen from these figures that the phenylazoazobenzene skeleton of dye **3** is planar and that the carbonyl group of the dichlorobenzoyl moiety is essen-

TABLE 10

Fractional Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for Dye **5**

	x	*y*	*z*	U[a]
N(5)	9564(2)	6445(2)	6064(2)	66(1)
O(4)	10254(2)	7006(2)	6312(2)	100(1)
O(3)	9756(2)	5642(2)	6100(2)	97(1)
C(1)	6357(2)	7291(2)	5145(2)	44(1)
C(6)	7229(2)	7909(2)	5185(2)	53(1)
C(5)	8285(2)	7635(2)	5471(2)	54(1)
C(4)	7601(2)	6742(2)	5716(2)	49(1)
C(3)	6548(2)	6118(2)	5659(2)	52(1)
C(2)	5218(2)	6394(2)	5368(2)	50(1)
N(1)	5019(2)	7502(2)	4883(1)	50(1)
N(2)	3871(2)	8308(2)	4726(1)	50(1)
C(7)	3575(2)	8479(2)	4472(2)	46(1)
C(12)	2472(2)	9370(2)	4331(2)	53(1)
C(11)	1662(2)	9576(2)	4107(2)	51(1)
C(10)	1970(2)	8916(2)	4014(2)	47(1)
C(9)	3073(2)	8014(2)	4148(2)	50(1)
C(8)	1426(3)	7801(2)	4369(2)	50(1)
C(19)	1132(2)	6472(2)	4203(2)	70(1)
O(2)	509(2)	7393(1)	4037(1)	67(1)
N(3)	236(2)	9082(2)	3802(1)	51(1)
N(4)	−926(2)	9892(2)	3743(2)	52(1)
C(13)	−1306	10023(2)	3528(2)	43(1)
C(18)	−2427	10897	3472	59
C(17)	−3149	11086	3281	58
C(16)	−2795	10385	3130	45
C(15)	−1681	9515	3181	61
C(14)	−4308	9332	3377	58
O(1)	−4705	10558	2985	51
C(20)	−4144	10599	2070	43
O(5)	−5934	10498	1392	61
C(21)	−6307	11655	2050	43
C(22)	−7431	11863	2278	54
C(23)	−8196	11219	2249	76
C(24)	−7864	10364	1992	84
C(25)	−6728	10167	1759	79
C(26)	−5337	12481	1779	58
Cl(1)	−6296	9095	2585	69
Cl(2)			1463	96

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

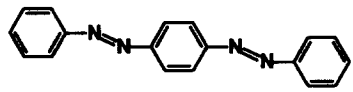
tially perpendicular to this skeleton. The dihedral angles between selected planes are provided in Table 7. These data include dihedral angles for the three planes represented by C(1)–C(6), C(7)–(12), and C(13)–C(18), all of which are less than 3°. The dihedral angles between the 2,6-dichlorophenyl group and the phenyl rings of the chromophoric system are relatively small (15–17°).

TABLE 11
Anisotropic Thermal Parameters ($Å^2 \times 10^3$) for Dye **5**

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(5)	41(2)	67(2)	90(2)	1(2)	−7(1)	10(1)
O(4)	56(2)	84(2)	157(2)	−2(2)	−44(1)	−2(1)
O(3)	56(2)	66(2)	169(2)	7(2)	−13(1)	20(1)
C(1)	38(2)	51(2)	44(2)	1(1)	−2(1)	3(1)
C(6)	48(2)	45(2)	64(2)	6(1)	−11(1)	−1(1)
C(5)	39(2)	53(2)	70(2)	6(1)	−7(1)	−1(1)
C(4)	34(2)	58(2)	53(2)	−1(1)	−2(1)	9(1)
C(3)	46(2)	42(2)	67(2)	4(1)	2(1)	8(1)
C(2)	36(2)	49(2)	65(2)	2(1)	−1(1)	−4(1)
N(1)	38(1)	54(1)	56(1)	5(1)	−7(1)	1(1)
N(2)	40(1)	51(2)	60(1)	4(1)	−3(1)	4(1)
C(7)	32(1)	53(2)	52(2)	1(1)	−3(1)	5(1)
C(12)	37(2)	56(2)	67(2)	6(1)	−10(1)	−4(1)
C(11)	43(2)	45(2)	65(2)	8(1)	−9(1)	3(1)
C(10)	33(2)	52(2)	55(2)	5(1)	−6(1)	7(1)
C(9)	39(2)	52(2)	60(2)	−1(1)	−4(1)	−1(1)
C(8)	39(2)	45(2)	67(2)	4(1)	−5(1)	9(1)
C(19)	57(2)	48(2)	106(2)	7(2)	−6(2)	−5(2)
O(2)	41(1)	51(1)	108(1)	6(1)	−11(1)	−1(1)
N(3)	37(1)	49(2)	68(1)	3(1)	−9(1)	5(1)
N(4)	33(1)	52(2)	69(1)	1(1)	−10(1)	1(1)
C(13)	33(2)	43(2)	53(2)	4(1)	−6(1)	−0(1)
C(18)	37	45	94	2	−14	−6
C(17)	44	43	86	4	−11	8
C(16)	28	56	49	1	−4	5
C(15)	40	45	97	1	−18	−7
C(14)	42	39	92	−2	−15	0
O(1)	31	71	51	5	−5	7
C(20)	39	37	52	−1	−8	1
O(5)	46	81	55	−7	0	14
C(21)	32	54	43	6	−3	5
C(22)	48	75	39	9	5	14
C(23)	63	96	69	19	7	35
C(24)	34	147	72	21	2	25
C(25)	40	123	72	14	−16	−17
C(26)	42	71	61	4	−7	−1
Cl(1)	84	53	70	−3	5	9
Cl(2)	78	72	137	−19	−19	−18

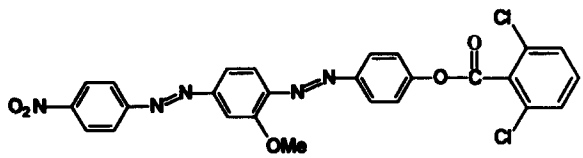
The aniosotropic temperature factor exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$.

Disazo dye **3** was found to exist in the *anti* conformation, as reported for dye **4** [3]. The bond lengths were essentially the same for C(1)–N(1), C(7)–(N2), C(10)–N(3), and C(13)–N(4) bonds that are adjacent to the azo linkages. In addition, the C(16)–O(1) bond length corresponds to that of a single bond.



4

In view of the differences between the conformation of **3** and that found earlier [1] for **2**, we elected to synthesize dye **5** and examine its crystal structure.



5

TABLE 12
Bond Lengths (Å) of Nonhydrogen Atoms for Dye **5**, with e.s.d. Values Given in Parentheses

N(5)–O(4)	1.215(3)	N(5)–O(3)	1.217(4)
N(5)–C(4)	1.466(4)	C(1)–C(6)	1.387(4)
C(1)–C(2)	1.386(4)	C(1)–N(1)	1.431(3)
C(7)–C(12)	1.371(4)	C(5)–C(4)	1.384(4)
C(4)–C(3)	1.376(4)	C(3)–C(2)	1.370(4)
N(1)–N(2)	1.240(3)	N(2)–C(7)	1.426(3)
C(7)–C(12)	1.383(4)	C(7)–C(8)	1.390(4)
C(12)–C(11)	1.377(4)	C(11)–C(10)	1.380(4)
C(10)–C(9)	1.402(4)	C(10)–N(3)	1.418(3)
C(9)–C(8)	1.379(4)	C(9)–O(2)	1.365(3)
C(19)–O(2)	1.431(3)	N(3)–N(4)	1.250(3)
N(4)–C(13)	1.422(3)	C(13)–C(18)	1.377(2)
C(13)–C(14)	1.378(2)	C(18)–C(17)	1.384(1)
C(17)–C(16)	1.364(1)	C(16)–C(15)	1.361(1)
C(16)–O(1)	1.413(1)	C(15)–C(14)	1.375(1)
O(1)–C(20)	1.354(1)	C(20)–O(5)	1.188(1)
C(20)–C(21)	1.493(1)	C(21)–C(22)	1.391(1)
C(21)–C(26)	1.376(1)	C(22)–C(23)	1.373(1)
C(22)–Cl(1)	1.732(1)	C(23)–C(24)	1.364(1)
C(24)–C(25)	1.374(1)	C(25)–C(26)	1.385(1)
C(26)–Cl(2)	1.735(1)		

Following the two-step synthesis of this dye using methods developed for **3**, crystals were grown via slow evaporation of a chloroform solution of **5** and by slow cooling of a toluene solution. The crystal selected from the latter solution was satisfactory for determining cell constants, but was apparently twinned slightly, and proved unsuitable for data collection. The cell dimensions were determined by a least-squares fit and are shown in Table 8. The data shown arose from a crystal produced from chloroform; however, practically no differences existed between these values and those obtained using the crystal produced from toluene. The crystal exists in the monoclinic space group $P2_1/c$. The structure was solved from 3211 independent reflections to $R = 0.0596$. However, in the refinement of the crystal structure, some reflections had to be omitted (cf. Table 9). These reflections were so strong that the quanta could not be counted fast enough by the detector. Tables 10–14 contain final atomic and thermal parameters, and Table 15 contains a listing of dihedral angles for key planes.

TABLE 13
Bond Angles (degrees) for Dye **5**

O(4)–N(5)–O(3)	122.5(3)	O(4)–N(5)–C(4)	119.0(3)
O(3)–N(5)–C(4)	118.4(2)	C(6)–C(1)–C(2)	120.7(2)
C(6)–C(1)–N(1)	124.7(2)	C(2)–C(1)–N(1)	114.6(2)
C(1)–C(6)–C(5)	119.7(2)	C(6)–C(5)–C(4)	118.8(2)
N(5)–C(4)–C(5)	119.6(2)	N(5)–C(4)–C(3)	118.3(2)
C(5)–C(4)–C(3)	122.1(2)	C(4)–C(3)–C(2)	118.8(2)
C(1)–C(2)–C(3)	119.8(2)	C(1)–N(1)–N(2)	115.6(2)
N(1)–N(2)–C(8)	113.1(2)	N(2)–C(7)–C(12)	116.4(2)
N(2)–C(7)–C(8)	123.0(2)	C(12)–C(7)–C(8)	120.6(2)
C(7)–C(12)–C(11)	118.9(2)	C(12)–C(11)–C(10)	121.6(3)
C(11)–C(10)–C(9)	119.2(2)	C(11)–C(10)–N(3)	124.6(2)
C(9)–C(10)–N(3)	116.2(2)	C(10)–C(9)–C(8)	119.6(2)
C(10)–C(9)–O(2)	116.3(2)	C(8)–C(9)–O(2)	124.1(2)
C(7)–C(8)–C(9)	120.2(2)	C(9)–O(2)–C(19)	117.0(2)
C(10)–N(3)–N(4)	115.4(2)	N(3)–N(4)–C(13)	113.3(2)
N(4)–C(13)–C(18)	117.2(2)	N(4)–C(13)–C(14)	123.9(2)
C(18)–C(13)–C(14)	118.9(2)	C(13)–C(18)–C(17)	121.1(1)
C(18)–C(17)–C(16)	118.4(1)	C(17)–C(16)–C(15)	121.6(1)
C(17)–C(16)–O(1)	119.5(1)	C(15)–C(16)–O(1)	118.7(1)
C(16)–C(15)–C(14)	119.7(1)	C(13)–C(14)–C(15)	120.3(1)
C(16)–O(1)–C(20)	117.2(1)	O(1)–C(20)–O(5)	124.1(1)
O(1)–C(20)–C(21)	109.9(1)	O(5)–C20)–C(21)	125.9(1)
C(20)–C(21)–C(22)	119.8(1)	C(20)–C(21)–C(26)	122.5(1)
C(22)–C(21)–C(26)	117.7(1)	C(21)–C(22)–C(23)	121.2(1)
C(21)–C(22)–Cl(1)	119.4(1)	C(23)–C(22)–Cl(1)	119.4(1)
C(22)–C(23)–C(24)	119.6(1)	C(23)–C(24)–C(25)	121.1(1)
C(24)–C(25)–C(26)	118.7(1)	C(21)–C(26)–C(25)	121.7(1)
C(21)–C(26)–Cl(2)	119.2(1)	C(25)–C(26)–Cl(2)	119.1(1)

TABLE 14
Hydrogen Atom Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å$\times 10^3$) for Dye **5**

	x	*y*	*z*	U
H(6)	7094	8526	5012	52
H(5)	8899	7985	5500	67
H(4)	7741	5500	5821	52
H(2)	5944	5968	5319	49
H(2)	4129	9837	4388	53
H(11)	2261	10 194	4014	51
H(8)	3290	7304	4429	29
H(19B)	1686	6393	4843	89
H(19C)	1919	6286	3713	109
H(19A)	741	6134	4126	110
H(18)	−784	11 383	3568	56
H(17)	−2690	11 696	3254	61
H(15)	−3321	9033	3080	59
H(14)	−1429	8719	3409	56
H(23)	−7675	12 458	2409	79
H(24)	−8981	11 365	1974	92
H(25)	−8408	9912	1586	80

TABLE 15
Dihedral Angles (degrees) Between Key Planes for Dye **5**

Planes	*Angle*
Plane(1)[a]–plane(2)[b]	7.1
Plane(1)–plane(3)[c]	12.7
Plane(1)–plane(4)[d]	15.0
Plane(1)–plane(5)[e]	5.6
Plane(1)–plane(6)[f]	82.1
Plane(1)–plane(7)[g]	28.9
Plane(2)–plane(3)	5.6
Plane(2)–plane(4)	10.9
Plane(2)–plane(5)	2.1
Plane(2)–plane(6)	88.6
Plane(2)–plane(7)	21.9
Plane(3)–plane(4)	9.5
Plane(3)–plane(5)	7.2
Plane(3)–plane(6)	93.9
Plane(3)–plane(7)	16.4
Plane(4)–plane(5)	10.5
Plane(4)–plane(6)	83.6
Plane(4)–plane(7)	21.4
Plane(5)–plane(6)	87.6
Plane(5)–plane(7)	23.7
Plane(6)–plane(7)	107.5

[a]Plane(1) is defined by atoms C(1)–C(6). [b]Plane(2) is defined by atoms C(7)–C(12). [c]Plane(3) is defined by atoms C(13)–C(18). [d]Plane(4) is defined by atoms N(5), O(3), and O(4). [e]Plane(5) is defined by atoms C(9), C(19), and O(2). [f]Plane(6) is defined by atoms C(21), C(20), and O(5). [g]Plane(7) is defined by atoms C(21)–C(26).

It is clear from an examination of the data in Tables 12 and 13, and Table 15 and from an inspection of Figs 3 and 4 that dye **5** possesses an *anti* conformation and, like **3**, the chromophoric system lies essentially perpendicular to the carbonyl group of the 2,6-dichlorobenzoyl moiety. The dihedral angles between the C(1)–C(6), C(7)–C(12), and C(13)–C(18) planes are slightly greater than those observed in dye **3**. It is worthwhile to point out that an examination of molecular models and data from molecular mechanics calculations revealed that the *syn* and *anti* forms of the chromophoric system of dyes **1–3** and **5** are of comparable energy (e.g. heat of formation).

Figure 5 provides a comparison of key bond lengths of dyes **3** and **5**. The C(16)–O(1) bond lengths are the same but all of the other corresponding bond lengths differ slightly, with the N(1)–N(2) bonds having the most significant difference.

It is also interesting to note the large difference in cell volume between **3** and **5**. Although **5** has more molecules in its unit cell ($Z=4$) the cell volume is about one-third (803 $Å^3$ vs 2227 $Å^3$) that of dye **3** (where $Z=2$).

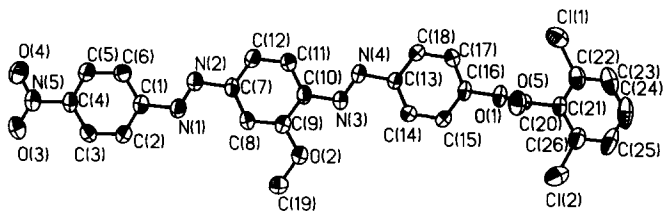


Fig. 3. Thermal ellipsoid plot of dye **5**. View is normal to the molecular mean plane.

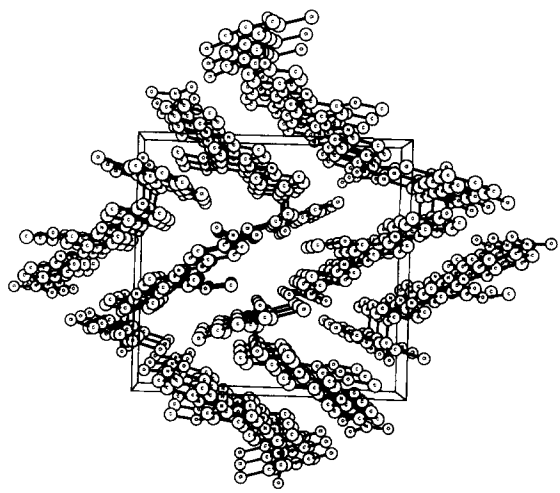
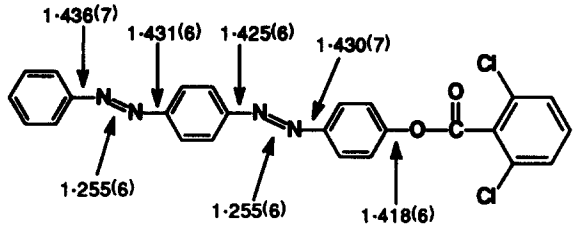
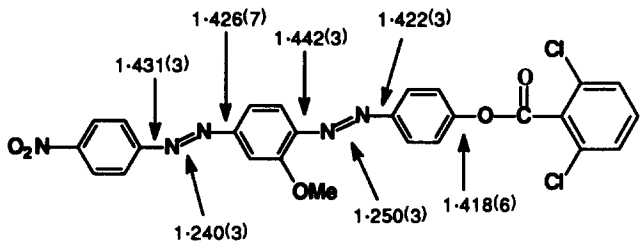


Fig. 4. Unit cell packing diagram of dye **5**.



3



5

Fig. 5. Key bond lengths (Å) for dyes **3** and **5**.

CONCLUSIONS

The removal of intermolecular H-bonding between molecules of C.I. Disperse Yellow 23 by acylation of the OH group with 2,6-dichlorobenzoyl chloride has permitted the characterization of the crystal structure of another disazo dye. It is clear from a comparison of the crystal structures of C.I. Disperse Orange 29 and its 2,6-dichlorobenzoyl ester that the free hydroxy group of the former has a noticeable impact on the lengths of the azo bonds and the adjacent C–N bonds. This, in turn, plays a role in the site at which photolytic cleavage reactions occur, with the longer bonds being more susceptible to attack.

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