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X-ray Crystal Structure of Disazo Dyes. Part 1: C.I. Disperse Orange 29

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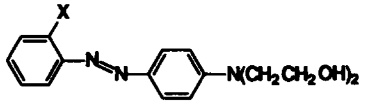
ABSTRACT

Crystals of C.I. Disperse Orange 29, a disazo dye, were grown from a methanol solution and the X-ray structure was solved from 2484 independent reflections to $R = 0.0497$*. Results showed that the crystal examined exists in the triclinic space group P1. Interestingly, the structure generated possessed a* syn *conformation, unlike 4-phenylazoazobenzene which is known to exist in the* anti *conformation.* © *1997 Elsevier Science Ltd*

Keywords: C.I. Disperse Yellow 23, C.I. Disperse Orange 29, *syn* conformation, monoclinic, disazo dyes.

INTRODUCTION

In earlier papers from these laboratories, we reported findings from X-ray studies [1,2] designed to enhance our understanding of experimental results obtained when a group of *ortho*-substituted monoazo disperse dyes **1** ($X = H$, Me, OMe, CN, Br, NO_2) was irradiated with UV light [3]. X-ray data proved particularly useful in explaining the differences in the photostability of the cyano- and nitro-substituted dyes. Subsequently, we have extended our work in this area to a pair of disazo disperse dyes, namely C.I. Disperse Yellow 23 (**2**) and C.I. Disperse Orange 29 (**3**). In a recent paper [4], we reported the photolytic behavior of these two disazo disperse dyes and are now reporting results from studies directed towards determining their crystal structures. Interestingly, it appears that only two disazo dye structures have heretofore been reported—that of 4-phenylazoazobenzene (**4**) [5] and the calcium salt of the hydrophilic dye Congo Red (**5**) [6].



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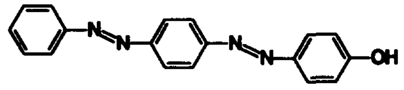

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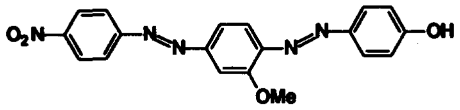

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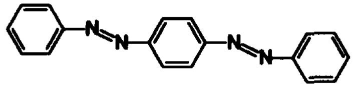

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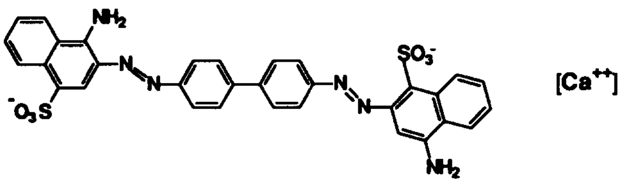

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EXPERIMENTAL

General

Except for dyes, all of the chemicals used in this study were obtained from Fisher Scientific Company. Atlantic Dyes and Chemicals provided a sample of Atlantic Polycron Orange L (C.I. Disperse Orange 29).

A Mel-Temp capillary melting point apparatus was used to determine melting points. ^{1}H NMR spectra of C.I. Disperse Orange 29 in d_6-DMSO was recorded on a Bruker 250 MHz spectrometer, and chemical shifts (parts per million) were measured relative to tetramethylsilane. Fisher chromatographic silica gel (catalog No. S743-1) was used for flash chromatography.

X-ray crystallographic analyses were performed with a Nicolet P3/F diffractometer using 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.

Purification of C.I. Disperse Orange 29 (3)

A 5 g sample of Atlantic Polycron Orange L was extracted with CH_2Cl_2 to separate the colorant from diluents. Evaporation of the solvent gave 1.2 g crude dye. This solid was dissolved in PhMe:EtOAc/10:1 and the solution was filtered through a glass wool plug to produce a solution containing 0.043 g **3** per ml. The dye was purified by flash column chromatography [8,9] using the above mentioned solvent to give 0.45 g of pure dye as a red powder, mp 232°C; ^{1}H NMR ($CDCl_3$): δ8.40 (d, 2H), δ8.10 (d, 2H), δ7.85 (d, 2H), δ7.80 (m, 2H), δ6.95 (d, 2H), δ4.10 (d, 3H). The C.I. mass spectrum showed the $[M+H]^+$ ion ($m/z=378$) to be the base peak.

Growth of dye crystals

Two general procedures were used in growing crystals of dye **3**, namely slow evaporation and slow cooling. In the case of slow evaporation, 50 mg of **3** was stirred with 10 ml MeOH and the resultant solution was filtered through a 0.45 μm Gelman Acrodisc filtered into a 100 ml beaker. The beaker was covered with a paper towel and allowed to stand at room temperature until the solvent evaporated. In growing crystals of **3** by slow cooling, 100 mg of dye and 5 ml of MeOH were placed in a large test tube. The tube was then suspended in a hot water bath and 1 ml portions of MeOH were added at 15-min intervals until the dye dissolved. The heat was turned off and the bath was allowed to reach ambient temperature. The precipitated dye was collected by vacuum filtration and air-dried.

RESULTS AND DISCUSSION

Attempts to grow crystals of C.I. Disperse Yellow 23 (**2**) from alcohols such as methanol, ethanol, 1-propanol, and 2-propanol always gave plates having a thickness less than 0.05 mm, none of which diffracted well enough for solving the crystal structure. Varying the rate of cooling or evaporation provided a greater number of crystals rather than thicker ones. Other solvents proving to be unsatisfactory include nitrobenzene, toluene, cyclohexane, petroleum ether, acetone, CH_3CN, DMSO, $CHCl_3$, Et_2O, CH_2Cl_2, methyl ethyl ketone, and various binary combinations of the aforementioned solvents that are miscible with H_2O. We also pursued methods involving the use of agents such as triphenylphosphine oxide [7] to facilitate crystal growth. All proved unfruitful in generating crystals of acceptable thickness.

We then turned our attention to generating crystals of C.I. Disperse Orange 29 (**3**). Crystallization of this dye from CH_2Cl_2, toluene, EtOAc, cyclohexane, acetone, 2-propanol, and methyl ethyl ketone afforded an amorphous powder. However, acceptable crystals were produced by the slow cooling of a solution of dye **3** in methanol. One of the dark red needles was cut to the proper dimensions (longest dimension was less than 0.6 mm) and mounted on the goniometer. The structure was solved from 2484 independent reflections to $R = 0.0497$, and the crystal was found to exist in the triclinic space group P1. The cell dimensions were determined by a least-squares fit and the data obtained are listed in Table 1. Fourier electron

TABLE 1
Cell Data for C.I. Disperse Orange 29

Composition	$C_{19}H_{15}N_5O_4{\cdot}CH_3OH$
Mr	409.41
Crystal system	Triclinic
Space group	P1
a, Å	8.078(3)[a]
b, Å	10.411(4)[a]
c, Å	12.446(6)[a]
α^0	97.51(3)[a]
β^0	106.34(3)[a]
γ^0	95.55(3)[a]
V, Å^3	986.7[a]
Z	2
Calculated density (g/ml)	1.38
Measured density (g/ml)	1.37
Number of reflections used for cell constant determination	25
2θ min.	3
2θ max.	60

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

density maps indicated that the crystal was comprised of a 1:1 molar mixture of dye and solvent (methanol), with the phenolic proton hydrogen bonded to the oxygen atom of methanol.

Final atomic and thermal parameters are given in Tables 2–6. These data include values of dihedral angles between selected planes (cf. Table 7), and indicate that the phenylazoazobenzene skeleton of dye **3** is essentially planar. This point is evident from an inspection of the view of the molecule provided in Fig. 1. In addition, the angle between the nitro group and the ring to which it is attached is only 3.1°, whereas the methoxy group and ring C(13)–C(18) are not coplanar. A view of the unit cell packing diagram is provided in Fig. 2.

TABLE 2

Fractional Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å^2) 10^3) for C.I. Disperse Orange 29

	x	*y*	*z*	U[a]
C(4)	3218 (3)	5517 (2)	2805 (2)	58 (1)
C(3)	2476 (4)	5344 (2)	1647 (2)	71 (1)
C(2)	1330 (4)	4209 (2)	1132 (2)	68 (1)
C(1)	955 (3)	3296 (2)	1765 (2)	51 (1)
C(6)	1728 (4)	3500 (3)	2931 (2)	66 (1)
C(5)	2888 (4)	4613 (3)	3454 (3)	72 (1)
C(7)	−1904 (3)	680 (2)	−214 (2)	52 (1)
C(8)	−2414 (3)	413 (2)	−1391 (2)	51 (1)
C(9)	−3541 (3)	−717 (2)	−1951 (2)	45 (1)
C(10)	−4182 (3)	−1571 (2)	−1324 (2)	47 (1)
C(11)	−3667 (3)	−1267 (2)	−157 (2)	56 (1)
C(12)	−2512 (3)	−156 (2)	407 (2)	58 (1)
C(13)	−6907 (3)	−4626 (2)	−2038 (2)	48 (1)
C(15)	−8996 (3)	−5887 (2)	−3687 (2)	60 (1)
C(14)	−7764 (3)	−4807 (2)	−3181 (2)	58 (1)
C(16)	−9385 (3)	−6792 (2)	−3060 (2)	56 (1)
C(17)	−8488 (4)	−6643 (3)	−1907 (2)	70 (1)
C(18)	−7262 (4)	−5575 (3)	−1409 (2)	66 (1)
C(19)	−3259 (4)	−353 (2)	−3746 (2)	67 (1)
N(1)	−210 (3)	2084 (2)	1305 (2)	57 (1)
N(2)	−739 (3)	1890 (2)	264 (2)	57 (1)
N(3)	−5403 (2)	−2671 (2)	−1972 (2)	48 (1)
N(4)	−5666 (2)	−3529 (2)	−1408 (2)	53 (1)
N(5)	4442 (3)	6710 (2)	3361 (3)	81 (1)
O(1)	−10 633 (2)	−7835 (2)	−3493 (2)	80 (1)
O(2)	−4062 (2)	−1092 (1)	−3095 (1)	57 (1)
O(3)	4804 (3)	7480 (2)	2785 (2)	107 (1)
O(4)	5039 (3)	6879 (2)	4397 (2)	120 (1)
O(5)	−12 268 (3)	−8218 (2)	−5690 (2)	94 (1)
C(20)	−11 791 (5)	−9241 (4)	−6287 (3)	126 (2)

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

A key feature of the crystal structure of dye **3** is its conformation. Whereas **4** and **5** were found to exist in an *anti* conformation, the aryldisazo skeleton of **3** possesses the *syn* conformation. Figure 3 shows structures corresponding to the *syn* and *anti* conformations of **3**, the difference between them being a 180° rotation about the N(2)–C(7) bond. Interestingly, while the crystal structure of Congo Red reflects an *anti* conformation for the aryldisazo skeleton, it also reveals that the sodium sulfonate groups lie on opposite sides of the axis formed by the conjugated azo linkages.

We also observed differences in the carbon–nitrogen bond lengths adjacent to the two azo linkages. The C(10)–N(3) and C(13)–N(4) bonds are significantly shorter than the C(1)–N(1) and C(7)–N(2) bonds. These differences

TABLE 3
Anisotropic Thermal Parameters (Å^2×10^3) for C.I. Disperse Orange 29

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(4)	48 (1)	39 (1)	66 (2)	−13 (1)	−4 (1)	0 (1)
C(3)	69 (2)	44 (1)	78 (2)	−1 (1)	−1 (1)	−11 (1)
C(2)	65 (2)	55 (1)	58 (2)	−7 (1)	−8 (1)	−8 (1)
C(1)	45 (1)	39 (1)	54 (1)	−7 (1)	2 (1)	−2 (1)
C(6)	70 (2)	54 (2)	60 (2)	−5 (1)	8 (1)	−5 (1)
C(5)	70 (2)	63 (2)	58 (2)	−17 (1)	−4 (1)	0 (1)
C(7)	42 (1)	40 (1)	61 (1)	−2 (1)	3 (1)	−8 (1)
C(8)	46 (1)	42 (1)	53 (1)	5 (1)	1 (1)	−11 (1)
C(9)	40 (1)	38 (1)	47 (1)	5 (1)	2 (1)	−5 (1)
C(10)	37 (1)	40 (1)	52 (1)	−1 (1)	3 (1)	−6 (1)
C(11)	54 (1)	52 (1)	54 (1)	5 (1)	12 (1)	−9 (1)
C(12)	58 (2)	56 (1)	46 (1)	−4 (1)	5 (1)	−5 (1)
C(13)	39 (1)	46 (1)	50 (1)	7 (1)	5 (1)	−9 (1)
C(15)	58 (2)	51 (1)	53 (1)	7 (1)	−2 (1)	−16 (1)
C(14)	56 (2)	45 (1)	63 (2)	13 (1)	5 (1)	−14 (1)
C(16)	46 (1)	44 (1)	67 (2)	11 (1)	7 (1)	−12 (1)
C(17)	69 (2)	64 (2)	64 (2)	24 (1)	6 (1)	−26 (1)
C(18)	64 (2)	69 (2)	51 (1)	14 (1)	1 (1)	−23 (1)
C(19)	79 (2)	55 (2)	58 (2)	6 (1)	18 (1)	−22 (1)
N(1)	57 (1)	53 (1)	51 (1)	−4 (1)	5 (1)	−2 (1)
N(2)	52 (1)	47 (1)	57 (1)	−5 (1)	−0 (1)	−3 (1)
N(3)	41 (1)	40 (1)	55 (1)	1 (1)	7 (1)	−11 (1)
N(4)	47 (1)	49 (1)	52 (1)	6 (1)	7 (1)	−13 (1)
N(5)	65 (2)	47 (1)	97 (2)	−23 (1)	−9 (1)	−2 (1)
O(1)	75 (1)	57 (1)	79 (1)	13 (1)	−6 (1)	−36 (1)
O(2)	59 (1)	49 (1)	47 (1)	2 (1)	3 (1)	−22 (1)
O(3)	89 (2)	52 (1)	149 (2)	−13 (1)	9 (2)	−20 (1)
O(4)	115 (2)	87 (2)	102 (2)	−44 (1)	−21 (1)	−19 (1)
O(5)	78 (1)	91 (1)	80 (1)	11 (1)	−20 (1)	−6 (1)
C(20)	91 (3)	231 (5)	64 (2)	27 (3)	26 (2)	48 (3)

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

TABLE 4

Bond Lengths (Å) of Nonhydrogen Atoms for C.I. Disperse Orange 29, with e.s.d. Values given in Parentheses

C(4)–C(3)	1.377(4)	C(4)–C(5)	1.371(4)
C(4)–N(5)	1.467(3)	C(3)–C(2)	1.386(3)
C(2)–C(1)	1.375(4)	C(1)–C(6)	1.388(3)
C(1)–N(1)	1.443(3)	C(6)–C(5)	1.377(4)
C(7)–C(8)	1.388(3)	C(7)–C(12)	1.379(4)
C(7)–N(2)	1.445(3)	C(8)–C(9)	1.386(3)
C(9)–C(10)	1.410(3)	C(9)–O(2)	1.358(3)
C(10)–C(11)	1.376(3)	C(10)–N(3)	1.424(2)
C(11)–C(12)	1.382(3)	C(13)–C(14)	1.375(3)
C(13)–C(18)	1.394(4)	C(13)–N(4)	1.423(2)
C(15)–C(14)	1.378(3)	C(15)–C(16)	1.368(4)
C(16)–C(17)	1.394(3)	C(16)–O(1)	1.348(3)
C(17)–C(18)	1.365(3)	C(19)–O(2)	1.425(4)
N(1)–N(2)	1.227(3)	N(3)–N(4)	1.244(3)
N(5)–O(3)	1.210(4)	N(5)–O(4)	1.226(4)
O(5)–C(20)	1.367(5)		

TABLE 5

Bond Angles (degrees) for C.I. Disperse Orange 29

C(3)–C(4)–C(5)	122.9(2)	C(3)–C(4)–N(5)	118.3(2)
C(5)–C(4)–N(5)	118.8(2)	C(4)–C(3)–C(2)	117.6(3)
C(3)–C(2)–C(1)	120.7(2)	C(2)–C(1)–C(6)	120.2(2)
C(2)–C(1)–N(1)	124.7(2)	C(1)–C(1)–N(1)	115.1(2)
C(1)–C(1)–C(1)	119.9(3)	C(4)–C(5)–C(6)	118.7(3)
C(8)–C(7)–C(12)	121.0(2)	C(8)–C(7)–N(2)	114.0(2)
C(12)–C(7)–N(2)	125.0(2)	C(7)–C(8)–C(9)	119.5(2)
C(8)–C(9)–C(10)	119.9(2)	C(8)–C(9)–O(2)	124.0(2)
C(10)–C(9)–O(2)	116.1(2)	C(9)–C(10)–C(11)	119.1(2)
C(9)–C(10)–N(3)	116.0(2)	C(11)–C(10)–N(3)	124.9(2)
C(10)–C(11)–C(12)	121.2(2)	C(7)–C(12)–C(11)	119.3(2)
C(14)–C(13)–C(18)	118.9(2)	C(14)–C(13)–N(4)	125.8(2)
C(18)–C(13)–N(4)	115.3(2)	C(14)–C(15)–C(16)	120.5(2)
C(13)–C(14)–C(15)	120.4(2)	C(15)–C(16)–C(17)	119.7(2)
C(15)–C(16)–O(1)	123.3(2)	C(17)–C(16)–O(1)	117.0(2)
C(16)–C(17)–C(18)	119.6(3)	C(13)–C(18)–C(17)	120.8(2)
C(1)–N(1)–N(2)	112.8(2)	C(7)–N(2)–N(1)	113.7(2)
C(10)–N(3)–N(4)	113.8(2)	C(13)–N(4)–N(3)	114.6(2)
C(4)–N(5)–O(3)	119.1(3)	C(4)–N(5)–O(4)	117.7(2)
O(3)–N(5)–O(4)	123.2(2)	C(9)–O(2)–C(19)	117.8(2)

TABLE 6

Hydrogen Atom Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{Å} \times 10^3$) for C.I. Disperse Orange 29

	x	*y*	*z*	U
H(20A)	−10 802	−9579	−5845	113
H(20B)	−11 501	−8887	−6896	113
G(20C)	−12752	−9934	−6594	113
H(5)	3363(35)	4801(24)	4259(22)	80(8)
H(6)	1413(34)	2841(25)	3282(21)	73(8)
H(3)	2760(30)	5963(21)	1289(18)	70(7)
H(2)	831(29)	4103(20)	374(18)	62(6)
H(12)	−2162(30)	−75(22)	1244(18)	71(7)
H(11)	−4142(29)	−1848(20)	284(18)	62(6)
H(8)	−1950(27)	978(18)	−1788(16)	54(6)
H(18)	−6708(29)	−5405(21)	−676(18)	66(7)
H(17)	−8878(33)	−7268(23)	−1516(20)	86(8)
H(14)	−7565(27)	−4207(19)	−3642(16)	55(6)
H(15)	−9530(30)	−5991(21)	−4513(18)	64(6)
H(21)	−11 138(33)	−7902(23)	−4123(20)	78(7)
H(19A)	−3633(37)	581(26)	−3706(23)	110(9)
H(19B)	−1978(32)	−282(22)	−3432(19)	71(7)
H(19C)	−3752(43)	−791(30)	−4557(29)	125(11)
H(22)	−13 226(51)	−8117(36)	−6041(31)	169(13)

TABLE 7

Dihedral Angles (degrees) between Planes for C.I. Disperse Orange 29

Planes	Angle
Plane(1)[a]–plane(2)[b]	10.9
Plane(1)–plane(3)[c]	4.6
Plane(1)–plane(4)[d]	3.1
Plane(1)–plane(5)[e]	17.4
Plane(2)–plane(3)	14.1
Plane(2)–plane(4)	7.9
Plane(2)–plane(5)	7.9
Plane(3)–plane(3)	7.0
Plane(3)–plane(5)	19.2
Plane(4)–plane(5)	14.6

[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(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).

are consistent with resonance interactions between the electron pairs on the OH group and the C(10)–N(3) and C(13)–N(4) bonds, and contribute to the observed higher photolytic stability of these bonds. Figure 4 provides a comparison of key bond lengths of dyes 3 and 4. This includes the intermolecular bonding distance (1.878 Å) between dye 3 and the associated MeOH molecule which is well within the distance required for hydrogen bonding.

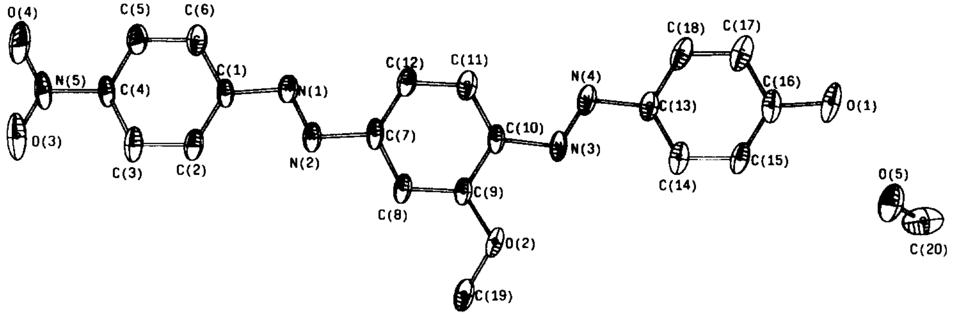

Fig. 1. Thermal ellipsoid plot of C.I. Disperse Orange 29. View is normal to molecular mean plane.

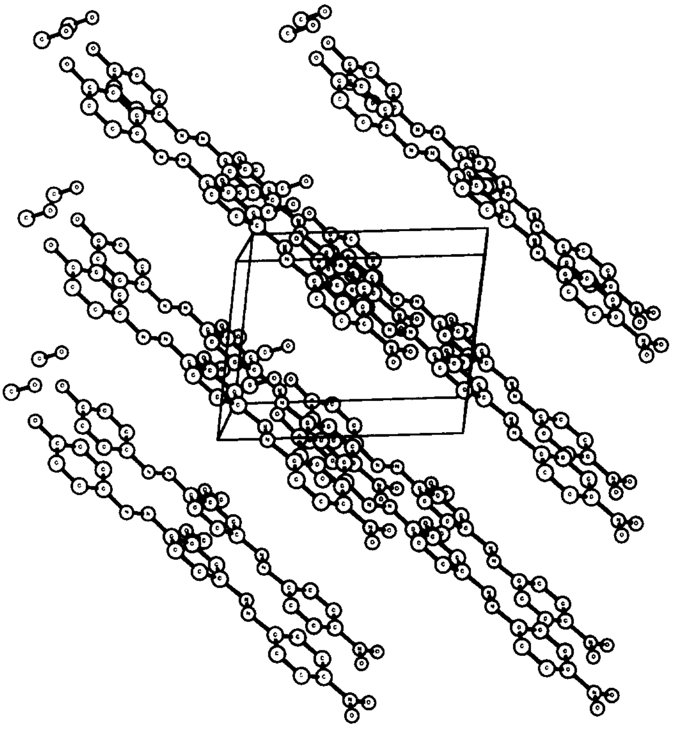

Fig. 2. Unit cell packing diagram of C.I. Disperse Orange 29.

It can also be pointed out that similar results were obtained using crystals of **3** grown from 1-propanol/water, in that the resulting crystals contain a water H-bonded to each dye molecule in the unit cell.

CONCLUSIONS

The X-ray crystal structure of C.I. Disperse Orange 29 (**3**) was determined using crystals grown from MeOH and from 1-propanol/H_2O. This appears to be only the third disazo compound, and first commercial disazo disperse dye, for which a crystal structure has been published. The results show a strong tendency of this disazo dye to form intermolecular H-bonds. We believe that this same property accounts for our inability to produce suitable crystals of C.I. Disperse Yellow 23.

We also found that the bond order of dye **3** was consistent with its photolytic properties.

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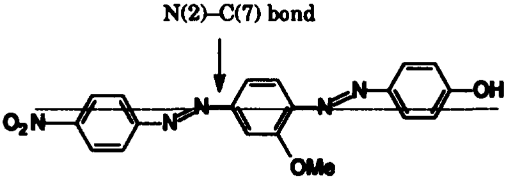
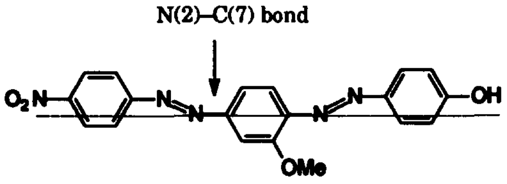
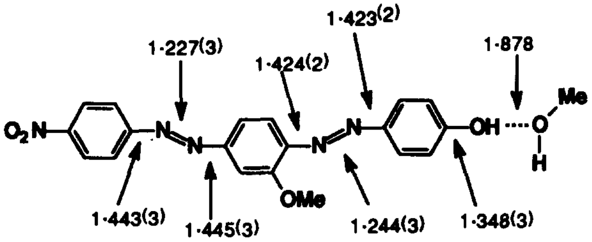


anti

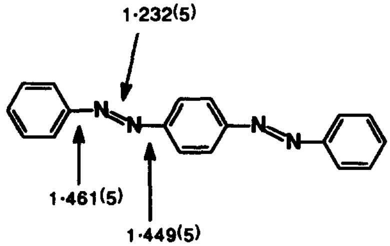


syn

Fig. 3. *Syn* and *anti* conformations of C.I. Disperse Orange 29.



3



4

Fig. 4. Key bond lengths (Å) for dyes 3 and 4.

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