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X-ray crystal structure of C.I. Disperse Yellow 86

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Abstract

In conjunction with studies pertaining to the design of lightfast dyes for PET, the X-ray crystal structure of C.I. Disperse Yellow 86 has been solved to $R = 0.067$ using 1999 independent reflections of MoK$_\alpha$ radiation, collected by the ω-scan method at a variable speed. Results showed that C.I. Disperse Yellow 86 is non-planar, with a dihedral angle of 35.3° between the phenyl rings. In addition, the *ortho*-nitroanilino moiety of this dye is planar, due to a hydrogen bond between the nitro group and the adjacent amino hydrogen atom. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: C.I. Disperse Yellow 86; X-ray structure; H-bonding; Semi-empirical methods

1. Introduction

As part of ongoing studies aimed at designing lightfast dyes for automotive applications, our group solved the X-ray crystal structure of some monoazo and disazo dyes [1–6]. Such data proved useful in accounting for differences in the photostability of *ortho*-nitro and *ortho*-cyano substituted azobenzenes. Similarly, X-ray crystallography revealed the presence of a bifurcated hydrogen bond involving the acetamido hydrogen, the α-azo nitrogen atom, and the chlorine atom of C.I. Disperse Red 167 (**1**). It is believed that the presence of this interaction imparts photostability to this dye [4]. ^{13}C solid state and solution NMR have also been used to show acetamido-azo hydrogen bonding interactions in similar compounds [7].

C.I. Disperse Yellow 42 (**2**) and C.I. Disperse Yellow 86 (**3**) are two examples of nitrodiphenylamine dyes that continue to find use as colorants for automotive fabrics. In our studies, dyes **1**, **2**, and **3** have served as prototypes for molecular modeling studies directed towards the design of disperse yellow dyes with improved lightfastness. A key element in our work has been the use of data from X-ray crystal structures to test the reliability of data arising from our calculations [8–11]. Despite the commercial significance of this dye class, a search of the literature suggested that the X-ray structures of nitrodiphenylamine dyes had not been published.

With these points in mind, we elected to determine the X-ray crystal structure of C.I. Disperse Yellow 86 (**3**). Of particular interest to us was whether the distance between the N–H hydrogen

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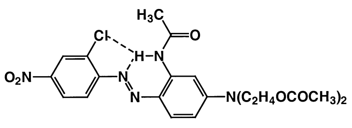
and the oxygen atom on the adjacent nitro group would be consistent with intramolecular hydrogen bonding. The presence of intramolecular hydrogen bonding in **2** and **3** has been generally accepted [12]. Indeed, it has been proposed that this interaction may facilitate excited state intramolecular proton transfer, providing an efficient mechanism for rapid deactivation of the photoexcited dye [13,14]. In recent modeling studies [11], we showed that the AM1 and PM3 semiempirical methods predicted hydrogen bonding interactions in **1** and **3**. While the details of the modeling work have been published [11], the X-ray crystal structure of **3** was not included.



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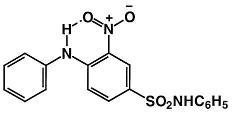

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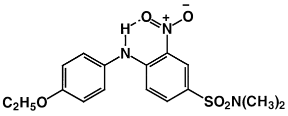

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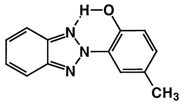

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2. Experimental

Crystals suitable for X-ray structure determination of C.I. Disperse Yellow 86 were grown by slow evaporation of a methanol solution of the purified dye. This afforded bright red prisms [mp 128–129°C (literature: 127°C) [15], λ_{max} 414 nm (acetone), ε_{max} 5800 L mol^{-1} cm^{-1}, $R_f = 0.69$ (silica gel using 4 toluene/1 ethyl acetate) [16]. Cell parameters were determined from 20 reflections with 2θ between 15 and 25° measured on a Nicolet P3/F diffractometer using MoK$_\alpha$ radiation (graphite moderator, $\lambda = 0.71073$ Å). Intensity data were collected by the ω-scan method at variable speed between 2 and 29.3 degrees per min, depending on intensity. The structure was solved by direct methods and refined to $R = 0.067$ for 1999 independent reflections, with intensities, I, $\geqslant 2.5\sigma$. Hydrogen atoms were placed in calculated positions, except for the NH H-atom, the position of which was obtained from a difference fourier synthesis and refined with isotropic displacement parameters [$U_{Iso} = 0.052(16)$]. All calculations were performed using a Data General micro-eclipse desktop computer equipped with a crystallographic program package SHELXTL from Nicolet Instrument Corporation, Madison, Wisconsin.

3. Results and discussion

The X-ray structure and packing diagram that were determined for dye **3** are shown in Figs. 1 and 2. Bond angles and bond lengths are presented in Tables 3 and 4. Table 1 contains the cell dimensions obtained by a least-squares fit and the final atomic and thermal parameters are given in Tables 2, 5 and 6.

We found that C.I. Disperse Yellow 86 crystals are orthorhombic, and belong to the $P2_12_12_1$ space group. As expected, the molecule has an intramolecular hydrogen bond (2.0 Å) between the nitro group and the nearby NH hydrogen. Although

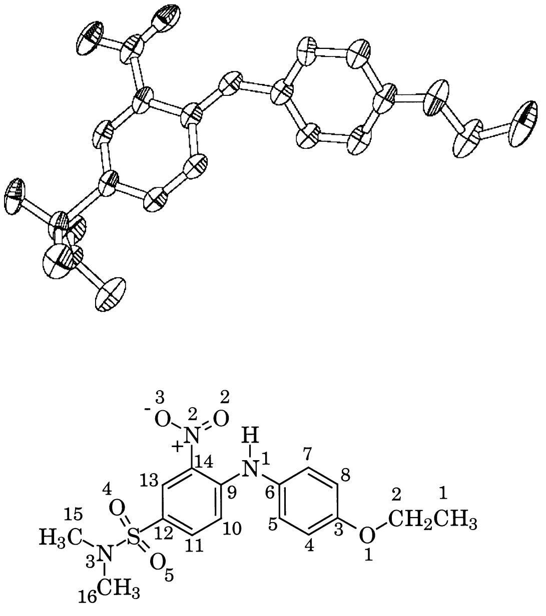


Fig. 1. X-ray structure (telp plot) and numbering scheme for C.I. Disperse Yellow 86 (**3**).

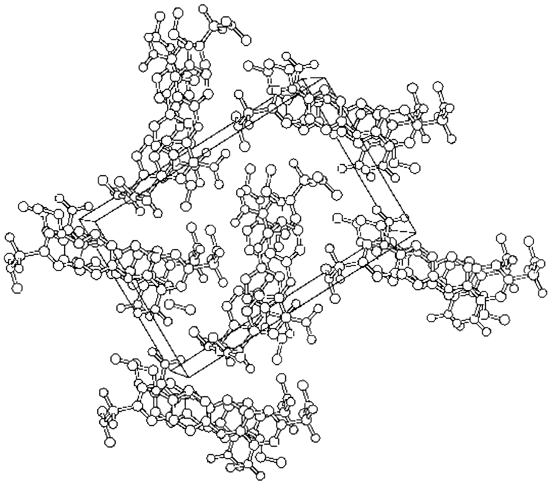


Fig. 2. Crystal packing diagram for C.I. Disperse Yellow 86

Table 1
Crystal data for C.I. Disperse Yellow 86 (**3**)

Molecular formula	$C_{16}H_{19}N_3O_5S$
Molecular weight	365.41 Daltons
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	7.419 (2)
b (Å)	12.470 (8)
c (Å)	18.711 (7)
α	90°
β	90°
γ	90°
V (Å^3)	1731
Z	4
Density (calc.) (g cm^{-3})	1.40
Number of reflections	1999
$2\theta_{max}$	57°

Table 2
Atomic coordinates (Ã$\times 10^4$) and anisotropic thermal parameters (Å$^2\times 10^3$) for dye **3**

	x	y	z	U*
C1	4694 (12)	−7266 (5)	11556 (4)	83 (3)
C2	4927 (8)	−6403 (4)	10998 (3)	58 (2)
O1	4275 (7)	−5431 (3)	11306 (2)	59 (1)
C3	4448 (7)	−4488 (3)	10945 (2)	42 (1)
C4	5044 (7)	−4400 (3)	10240 (2)	43 (1)
C5	5216 (7)	−3392 (3)	9926 (2)	42 (1)
C6	4742 (6)	−2472 (3)	10307 (2)	39 (1)
C7	4143 (6)	−2578 (3)	11004 (2)	42 (1)
C8	3987 (8)	−3570 (4)	11326 (2)	46 (1)
N1	4962 (7)	−1403 (3)	10043 (2)	44 (1)
C9	4602 (6)	−998 (3)	9392 (2)	36 (1)
C10	3886 (7)	−1630 (3)	8836 (2)	40 (1)
C11	3544 (7)	−1228 (3)	8169 (2)	42 (1)
C12	3949 (6)	−146 (3)	8011 (2)	38 (1)
C13	4613 (6)	507 (3)	8536 (2)	39 (1)
C14	4900 (6)	103 (3)	9224 (2)	37 (1)
N2	5506 (7)	887 (3)	9750 (2)	50 (1)
O2	5881 (9)	566 (3)	10355 (2)	81 (2)
O3	5620 (9)	1816 (3)	9585 (2)	75 (2)
S	3731 (2)	361 (1)	7139 (1)	49 (1)
O4	3872 (8)	1511 (3)	7186 (2)	70 (2)
O5	2167 (7)	−112 (4)	6819 (2)	71 (2)
N3	5467 (8)	−53 (3)	6683 (2)	50 (1)
C15	7207 (11)	371 (6)	6902 (3)	72 (2)
C16	5506 (12)	−1194 (4)	6497 (3)	73 (2)

Table 3
X-ray bond lengths for dye **3**

Bond	Length (Å)	Bond	Length (Å)
C2–C1	1.510 (9)	C2–O1	1.426 (6)
O1–C3	1.364 (5)	C3–C4	1.396 (6)
C3–C8	1.391 (6)	C4–C5	1.392 (6)
C5–C6	1.396 (6)	C6–C7	1.385 (5)
C6–N1	1.430 (5)	C7–C8	1.381 (6)
N1–C9	1.345 (5)	C9–C10	1.409 (5)
C9–C14	1.425 (5)	C10–C11	1.370 (5)
C11–C12	1.413 (5)	C12–C13	1.367 (5)
C12–S	1.759 (4)	C13–C14	1.400 (5)
C14–N2	1.449 (5)	N2–O2	1.229 (6)
N2–O3	1.214 (5)	S–O4	1.441 (4)
S–O5	1.433 (5)	S–N3	1.628 (5)
N3–C15	H1–O2	1.454 (9)	1.997
N3–C16	1.466 (7)		

well within the normal range of hydrogen bond length of ca. 1.5–2.5 Å, we found the N–H...O hydrogen bond in **3** (2.0 Å) to be significantly longer than the reported NH...N hydrogen bond in **1** (1.7 Å) [4] and the hydrogen bond distance reported for photostabilizer **4** (1.8Å) [17].

C.I. Disperse Yellow 86 was found to be non-planar overall, with a dihedral angle of 35.33° between the two phenyl rings. The lack of planarity is probably due to mutual steric crowding by the two phenyl rings. Indeed, the structure of pararosaniline, **5** (C.I. Basic Red 9), is distorted into a propeller shape by dint of steric interactions. Each phenyl ring is twisted out of plane by approximately 30° [18]. Gust and Mislow [19] have

Table 4
X-ray bond angles (°) for dye **3**

Bond	Angle	Bond	Angle
C1–C2–O1	106.7 (5)	C2–O1–C3	120.0 (4)
O1–C3–C4	124.5 (4)	O1–C3–C8	115.6 (4)
C4–C3–C8	119.9 (4)	C3–C4–C5	119.8 (4)
C4–C5–C6	120.3 (4)	C5–C6–C7	118.9 (4)
C5–C6–N1	124.2 (3)	C7–C6–N1	116.8 (3)
C6–C7–C8	21.5 (4)	C3–C8–C7	119.5 (4)
C6–N1–C9	29.8 (4)	N1–C9–C10	122.2 (4)
N1–C9–C14	122.0 (4)	C10–C9–C14	115.8 (3)
C9–C10–C11	122.6 (4)	C10–C11–C12	120.0 (4)
C11–C12–C13	119.7 (3)	C11–C12–S	121.2 (3)
C13–C12–S	119.0 (3)	C12–C13–C14	120.0 (3)
C9–C14–C13	121.7 (3)	C9–C14–N2	122.7 (3)
C13–C14–N2	115.6 (3)	C14–N2–O2	119.0 (4)
C14–N2–O3	119.4 (4)	O2–N2–O3	121.5 (4)
C12–S–O4	107.1 (2)	C12–S–O5	108.3 (2)
O4–S–O5	119.6 (3)	C12–S–N3	107.4 (2)
O4–S–N3	106.9 (3)	O5–S–N3	107.0 (3)
S–N3–C15	116.1 (4)	S–N3–C16	116.6 (4)
C15–N3–C16	113.7 (6)		

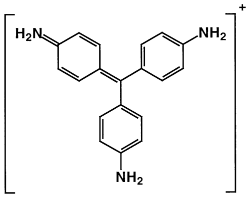
Table 5
Anisotropic thermal parameters (Å^2×10^3) for dye **3**

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	108 (7)	44 (2)	96 (5)	12 (3)	10 (5)	6 (4)
C2	54 (3)	44 (2)	75 (3)	−2 (2)	4 (3)	−5 (2)
O1	79 (3)	39 (1)	59 (2)	4 (1)	19 (2)	2 (2)
C3	47 (2)	38 (2)	42 (2)	1 (1)	6 (2)	−1 (2)
C4	48 (2)	39 (2)	43 (2)	−7 (1)	4 (2)	−2 (2)
C5	49 (2)	46 (2)	30 (1)	−3 (1)	2 (1)	−4 (2)
C6	45 (2)	40 (2)	32 (1)	0 (1)	2 (1)	−2 (2)
C7	52 (2)	42 (2)	32 (1)	−2 (1)	4 (1)	9 (2)
C8	57 (3)	44 (2)	37 (2)	0 (1)	9 (2)	1 (2)
N1	62 (3)	39 (2)	32 (1)	1 (1)	−4 (1)	−8 (2)
C9	40 (2)	39 (2)	30 (1)	1 (1)	−1 (1)	−1 (1)
C10	46 (2)	39 (2)	33 (1)	1 (1)	−0 (1)	−8 (2)
C11	53 (3)	42 (2)	33 (2)	3 (1)	−8 (2)	−7 (2)
C12	45 (2)	35 (2)	32 (1)	5 (1)	−2 (1)	1 (1)
C13	46 (2)	31 (1)	39 (1)	1 (1)	0 (1)	1 (1)
C14	43 (2)	32 (1)	35 (1)	−4 (1)	−0 (1)	0 (1)
N2	68 (3)	37 (2)	46 (2)	−8 (1)	−2 (2)	−4 (2)
O2	143 (5)	51 (2)	49 (2)	−7 (2)	−31 (3)	−17 (3)
O3	125 (5)	38 (2)	63 (2)	−7 (2)	−6 (3)	−8 (2)
S	66 (1)	42 (1)	38 (1)	7 (1)	−12 (1)	6 (1)
O4	111 (4)	43 (2)	57 (2)	10 (2)	−13 (3)	13 (2)
O5	72 (3)	83 (3)	59 (2)	7 (2)	−29 (2)	−1 (2)
N3	71 (3)	47 (2)	33 (1)	2 (1)	−3 (2)	−6 (2)
C15	86 (5)	79 (4)	51 (2)	11 (3)	10 (3)	−9 (4)
C16	106 (6)	51 (3)	63 (3)	−10 (2)	27 (4)	−12 (3)

Table 6
H-atom coordinates (Å×10^4) and isotropic thermal parameters (Å×10^3) for dye **3**

	x	y	Z	U
H (1A)	5003	−7932	11329	98
H (1B)	3443	−7276	11687	98
H (1C)	5419	−7274	11977	98
H (2A)	4244	−6577	10578	64
H (2B)	6177	−6330	10874	64
H (4)	5333	−5033	9971	41
H (5)	5662	−3331	9447	54
H (7)	3827	−1947	11271	45
H (8)	3563	−3627	11809	58
H (1N)	5303 (83)	−998 (42)	10340 (31)	52 (16)
H (10)	3629	−2371	8929	47
H (11)	3028	−1681	7808	47
H (13)	4883	1244	8432	48
H (15A)	7154	1138	6942	80
H (15B)	8080	177	6546	80
H (15C)	7550	68	7354	80
H (16A)	4351	−1405	6313	85
H (16B)	5825	−1649	6891	85
H (16C)	6397	−1259	6127	85

surveyed Ar–X–Ar systems in which *X* is a sulfur, oxygen, selenium, tellurium, or arsenic atom, or a carbonyl group, or a methylene group. These authors found that almost all the systems examined contained benzene rings that were mutually twisted, however, not perpendicular to each other. Consequently, it appears reasonable to find the two phenyl rings of **3** to be mutually twisted by about 30°.



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The amino group was found to be planar as opposed to pyramidal, with an improper torsion angle of 3.08°. The planarity of the amino group is almost certainly due to the stabilization brought about by overlap of the non-bonding p-orbital on the sp^2 nitrogen with the π-orbitals of the phenyl rings. If the nitrogen were pyramidal (sp^3 hybridized), overlap between the lone pair orbital and the phenyl π-system would be less efficient. The

X-ray crystal structure of C.I. Disperse Red 167 contains an amino group attached to a phenyl ring, and it is also planar, having an improper torsion angle of 4.75° [4].

The nitro group was found to be coplanar with the ring to which it is attached, due to intramolecular hydrogen bonding. Thus, the bright yellow color of this dye may be attributed to the planarity of the *ortho*-nitroaniline chromogen. In a recent paper [11], we reported that AM1 and PM3 semi-empirical methods predicted a planar *ortho*-nitroaniline chromogen for **3**, and mutual twisting between the two phenyl rings. While intramolecular H-bonding exists in **3**, we found no indication of intermolecular H-bonding.

4. Conclusions

The X-ray crystal structure of C.I. Disperse Yellow 86 indicates the presence of hydrogen bonding interaction between the nitro group and the phenylamine hydrogen atom. This interaction is believed to augment the photostability of this dye by maintaining a geometry conducive to excited state intramolecular hydrogen bonding. The information obtained from this study has also enabled us to confirm the validity of data generated from molecular modeling studies.

Acknowledgements

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