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Structural characterization of C.I. Disperse Yellow 114

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Abstract

The X-ray single-crystal structure of the azo dye molecule, C.I. Disperse Yellow 114, with a 1-methyl-5-cyano-2-hydroxy-4-methyl-6-pyridone component, was studied. The dye crystallizes in the hydrazone form and hydrogen bonding and π−π stacking interactions play essential roles in the formation of a layer framework with a mean interlayer separation of 3.433(4) Å. Theoretical calculations compared the energy differences between single-crystal and energy-minimized structures as well as those between the pyridine-2,6-dione and the 2-hydroxy-6-pyridone isomer.

Keywords: Azo dye; C.I. Disperse Yellow; Hydrogen bonding; π−π Stacking; Supramolecular network

1. Introduction

It is well-known that subtle change of the substituted groups of a given backbone and the coupling components will influence the structures of resulting azo dye molecules, thereby changing their solubility, stability, fastness, optical properties and so on [1–6]. The azo dyes having 1-alkyl-5-cyano-2-hydroxy-4-alkyl-6-pyridone component show good coloration properties and give bright greenish-yellow hues. More importantly, they have excellent color fastness to washing. Generally, C.I. Disperse Yellow 114, like some other C.I. Disperse Yellow dyes such as C.I. Disperse Yellow 103, 119, 123, 126, 134, 211, 221, 231 and 241, can be synthesized by a coupling reaction using 1-alkyl-5-cyano-2-hydroxy-4-methyl-6-pyridone as the coupling component. However, C.I. Disperse Yellow 114 has two enantiotropic isomers from the viewpoint of chemistry (Scheme 1), i.e. the 2-hydroxy-6-pyridone form, 5-(3-phenyl-benzenesulfonate)-azo-6-hydroxy-1-methyl-3-cyano-4-methyl-2-pyridone, and the pyridine-2,6-dione form, benzenesulfonate-3-[(1-methyl-5-cyano-4-methyl-2,6-dioxo-1,2,3,6-tetrahydropyridin-3-ylidene)-hydrazino]benzoate.

Single-crystal X-ray diffraction analysis has been proved to be a powerful tool to give structural information in the solid state, including the conformation, stereochemistry and interactions between the molecules, and to provide templates for the design of new molecules and for the computational studies [7–12]. Nevertheless, good single-crystal samples suitable for X-ray diffraction analysis are difficult to obtain in many cases. To date, there are only three structural reports on this family of compounds where 2-hydroxy-6-pyridone based coupling component is included. They all crystallize in the hydrazone form with pyridine-2,6-dione backbone but with different alkyl groups in 1-position (*N*-substituted) and different phenyl-based coupling components, namely, 1-*n*-butyl-5-((4-chlorophenyl)azo)-1,2,5,6-tetrahydro-4-methyl-2,6-dioxo-3-pyridinecarbonitrile [13], 5-(4-chloro-2-nitrophenyl)-azo-6-hydroxy-1-ethyl-3-cyano-4-methyl-2-pyridone naphthalene [14] and our contribution of C.I. Disperse Yellow 126: 2-(2-methoxyethoxy)ethyl 4-[(1-ethyl-5-cyano-4-methyl-2,6-dioxo-1,2,3,6-tetrahydropyridin-3-ylidene)-hydrazino]benzoate [15]. In this paper, we report the

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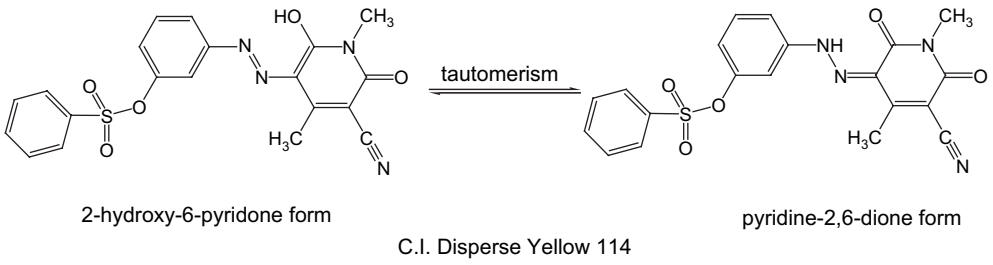

Scheme 1. Two enantiotropic isomers of C.I. Disperse Yellow 114.

molecular and crystal structures of C.I. Disperse Yellow 114 bearing an *N*-methyl group and a 3-benzenesulfonate component, and molecular-modelling studies originating from the provided template (CIF of C.I. Disperse Yellow 114).

2. Experimental section

Commercially available C.I. Disperse Yellow 114 was used as received. All other solvents and reagents were of analytical grade and used without further purification. Single-crystal sample of C.I. Disperse Yellow 114 suitable for X-ray diffraction measurement was grown from the mixed solution of acetone/ethanol in a ratio of 1:2 (v/v) by slow evaporation in air at room temperature.

A yellow single-crystal sample of C.I. Disperse Yellow 114 was glue-covered and mounted on a glass fiber and used for data collection on a Bruker SMART 1K CCD area detector at 291(2) K using graphite mono-chromated Mo *Ka* radiation ($\lambda = 0.71073$ Å). The collected data were reduced by using the program SAINT [16] and empirical absorption correction was done by using the SADABS [17] program. The crystal system was determined by Laue symmetry and the space group was assigned on the basis of systematic absences using XPREP, and then the structure was solved by direct method and refined by least-squares method by using the SHELXTL-PC software package [18]. All non-hydrogen atoms were refined on F^2 by full-matrix least-squares procedure using anisotropic displacement parameters. Hydrogen atoms were inserted in the calculated positions assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they are attached (1.5 times for the methyl groups) and allowed to ride on their respective parent atoms. The summary of the crystal data, experimental details and refinement results for C.I. Disperse Yellow 114 is listed in Table 1, while selected bond distances and bond angles are given in Table 2.

Table 1
Crystal data and structural refinements for C.I. Disperse Yellow 114

Empirical formula	$C_{20}H_{16}N_4SO_5$
Formula weight	424.44
T (K)	291(2)
Crystal system	Triclinic
Space group	P-1 (no. 2)
a/Å	8.348(2)
b/Å	10.173(2)
c/Å	13.022(2)
α/°	67.651(3)
β/°	72.960(4)
γ/°	82.412(3)
V/Å^3	977.7(3)
Crystal size/mm	$0.10 \times 0.12 \times 0.14$
Z	2
D_c/Mg m^{-3}	1.442
μ (Mo Kα)/mm^{-1}	0.207
F(000)	440
Absorption correction	Multi-scan
Data collected/unique	4900/3388
Limiting indices	$-9 \le h \le 9$
	$-11 \le k \le 12$
	$-15 \le l \le 15$
Parameter	273
Max/min transmission	0.978/0.971
$R1$, $wR2$ ($I > 2\sigma(I)$)	$R1 = 0.0462$, $wR2 = 0.0775$
$R1$, $wR2$ (all data)	$R1 = 0.0962$, $wR2 = 0.0974$
Goodness of fit on F^2	0.754
Δ/e Å^{-3} (max, min)	0.189/−0.207

$R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$, $wR2 = [\Sigma[w(Fo^2 - Fc^2)^2]/\Sigma w(Fo^2)^2]^{1/2}$.

3. Results and discussion

3.1. Structural elucidation

The molecular structure of C.I. Disperse Yellow 114 with atom-numbering scheme is shown in Fig. 1. An X-ray crystal

Table 2
Selected bond distances (Å) and angles (°) for C.I. Disperse Yellow 114

Bond distances		Bond angles	
O1–C2	1.227(4)	N4–N3–C1	120.6(3)
O2–C3	1.216(4)	N3–N4–C9	119.6(2)
O3–C11	1.408(4)	N2–C7–C4	179.1(4)
N1–C2	1.385(3)	O4–S1–O5	121.4(2)
N1–C3	1.382(4)	O4–S1–O3	103.9(1)
N2–C7	1.135(5)	O5–S1–O3	108.1(1)
N3–N4	1.303(3)	O4–S1–C15	109.3(1)
N3–C1	1.330(3)	O5–S1–C15	109.2(2)
N4–C9	1.413(3)	O3–S1–C15	103.3(1)
C1–C2	1.458(4)		
C1–C5	1.427(4)		
C3–C4	1.460(5)		
C4–C5	1.352(4)		
C4–C7	1.427(5)		
S1–O3	1.600(2)		
S1–O4	1.418(3)		
S1–O5	1.419(2)		
S1–C15	1.758(3)		

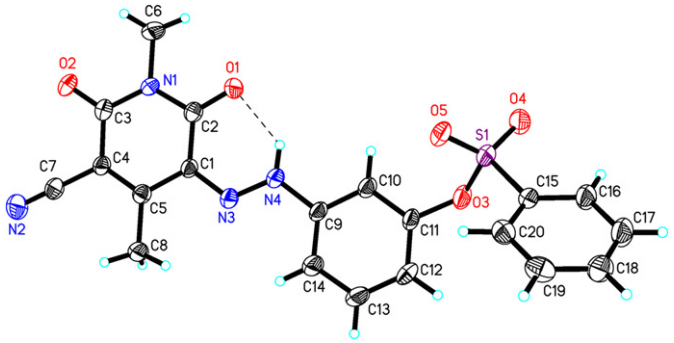

Fig. 1. An ORTEP drawing of C.I. Disperse Yellow 114 with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and the H atoms are shown as small spheres of arbitrary radii.

Table 3
Hydrogen bonding interactions (Å, °) in C.I. Disperse Yellow 114

D–H···A	D–H	H···A	D···A	∠DHA	Symmetry code
N4–H4···O1	0.86	1.92	2.583(3)	133.0	
C6–H6C···O2	0.96	2.53	3.423(4)	154.0	$3-x, -y, 1-z$
C10–H10···O4	0.93	2.39	3.287(4)	162.0	$2-x, 1-y, 2-z$
C12–H12···O2	0.93	2.53	3.338(4)	145.0	$-1+x, y, 1+z$
C16–H16···O1	0.93	2.48	3.355(4)	157.0	$2-x, 1-y, 2-z$
C20–H20···O5	0.93	2.43	3.230(8)	144.0	$1-x, 1-y, 2-z$

structural study indicates that C.I. Disperse Yellow 114 crystallizes in the triclinic *P*-1 space group without the presence of any solvent molecule. The bond distances and angles of two phenyl rings and pyridine-2,6-dione ring are comparable with previously reported structures [13–15]. The dihedral angle between the pyridine-2,6-dione ring and the middle phenyl ring is only 0.4°, forming an extended π-system linked by the hydrazone unit. However, the phenyl ring of benzenesulfonate is not coplanar with the middle phenyl ring due to the distorted tetrahedral geometry of the sulfur atom (Table 2). The dihedral angle between them is 43.4°.

C.I. Disperse Yellow 114 exists in the hydrazone form, which can be deduced by the bond lengths of related atoms. The bond lengths of O1–C2 and N3–C1 are 1.227(4) and 1.330(3) Å, exhibiting partial double bond character. In contrast, the bond lengths of C1–C2, N1–C2 and N3–N4 are 1.458(4), 1.385(3) and 1.303(3) Å, displaying predominantly single bond character. These bond lengths are comparable with afore-mentioned three reported hydrazone form structures.

Hydrogen bonding and π–π stacking interactions are the most interesting feature of this structure. Fig. 1 shows a strong intramolecular N4–H4···O1 hydrogen bonding forming a six-membered hydrogen-bond ring. As illustrated in Table 3, weak intermolecular C–H···O hydrogen bonding interactions are observed where every molecule of C.I. Disperse Yellow 114 links four adjacent ones constructing a hydrogen-bond network (Fig. 2). In addition, the coplanar part of C.I. Disperse Yellow 114 (hydrazone bridged two coplanar aromatic rings) is parallel with its adjacent counterpart showing typical π–π stacking interactions. The mean interlayer separation between them is 3.433(4) Å, which can be seen in Fig. 3.

Structural comparison between C.I. Disperse Yellow 114 and three previously reported structures [13–15] having the same pyridine-1-alkyl-3-cyano-4-methyl-2,6-dione component reveals that the formation of strong intramolecular N–H···O hydrogen bonding interactions, i.e. a six-membered hydrogen-bond ring, is vital to stabilize the hydrazone form. In addition, layer packing structures are common due to the essentially planar conformation of azo molecules. However, different packing modes with different interlayer separations are observed because of the use of different substituted groups. For example, four-molecule aggregates can be observed for C.I. Disperse Yellow 126 when a long methoxyethoxyethyl ester group is present. The shortest interlayer separation (3.3 Å) is found in the case of 1-*n*-butyl-5-((4-chlorophenyl)azo)-1,2,5,6-tetrahydro-4-methyl-2,6-dioxo-3-pyridinecarbonitrile when a low steric hindrance group (chlorine atom) is selected.

3.2. Quantum chemical calculations

All the Density Function Theory (DFT) computations were carried out with the Gaussian 03, Revision C.02 programs [19]

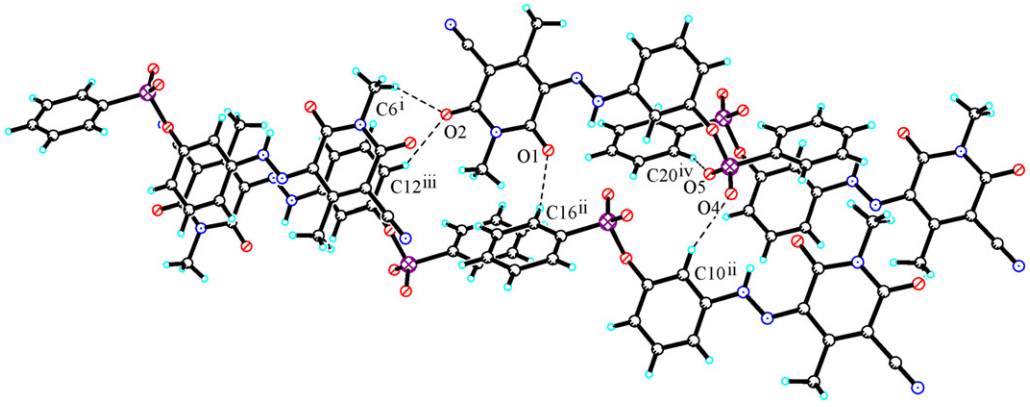

Fig. 2. A perspective view of the hydrogen-bond contacts in C.I. Disperse Yellow 114. Hydrogen bonds are indicated as dashed lines. For clarity, labels are given only once. [Symmetry codes: (i) $3-x, -y, 1-z$; (ii) $2-x, 1-y, 2-z$; (iii) $-1+x, y, 1+z$; (iv) $1-x, 1-y, 2-z$.]

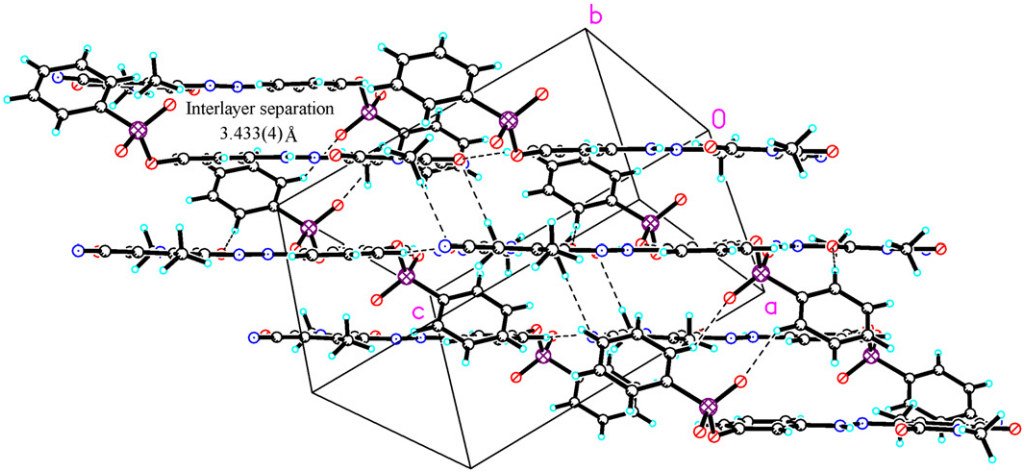

Fig. 3. A perspective view of the interlayer π−π stacking in C.I. Disperse Yellow 114 together with the unit cell.

using the MPW1PW91 method and the LanL2DZ basis set. The fixed atom coordinates of C.I. Disperse Yellow 114, originating from the structural parameters determined by the X-ray diffraction method, were used as the input file for the total energy calculation.

DFT calculations are carried out to compare the energy differences between the single-crystal structure and the energy-minimized structures for both isomers of C.I. Disperse Yellow 114. The total energy and the dipole moment for the single-crystal structure are −3 608 767.2 kJ/mol and 3.8×10^{-29} C m, while the ground state optimization for the pyridine-2,6-dione isomer which is the same as the solid structure of C.I. Disperse Yellow 114 gives the energy and the dipole moment of −3 609 880.7 kJ/mol and 3.8×10^{-29} C m. In contrast, the ground state optimization for the 2-hydroxy-6-pyridone isomer gives a higher energy of −3 609 727.2 kJ/mol and a lower dipole moment of 2.6×10^{-29} C m.

The results demonstrate a large energy gap (1113.5 kJ/mol) between the single-crystal structure and the energy-minimized structures in the same hydrazone form, which may be the reflection of the energy compensation of the formation of hydrogen bonding and π−π stacking between molecules. They also indicate that the pyridine-2,6-dione isomer is somewhat more thermally stable than the 2-hydroxy-6-pyridone isomer with the energy gap of 153.5 kJ/mol, which is suggested to be a theoretical support for the crystallization in the hydrazone form in the case of C.I. Disperse Yellow 114.

4. Conclusion

X-ray single-crystal structure of C.I. Disperse Yellow 114 is discussed in this paper, which gives us some useful structural information and may help us have a better understanding on the properties of this type of azo dyes. It crystallizes in the hydrazone form and hydrogen bonding and π−π stacking supramolecular interactions are believed to be responsible for the arrangement of molecules in parallel way with the mean interlayer separation of 3.433(4) Å. DFT calculations hint that the pyridine-2,6-dione isomer is somewhat more thermally stable than the 2-hydroxy-6-pyridone isomer with the energy gap of 153.5 kJ/mol, which is suggested to be a theoretical support for the crystallization in the hydrazone form in the case of C.I. Disperse Yellow 114.

Supplementary material. CCDC reference number 648471 for C.I. Disperse Yellow 114 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44 1223/336 033; e-mail: deposit@ccdc.cam.ac.uk].

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.dyepig.2007.07.012.

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