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Synthesis, optical characterization and crystal and molecular X-ray structure of a phenylazojulolidine derivative

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Abstract

The synthesis, spectroscopic characterization, and X-ray crystal structure of [4-(2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-9-ylazo)-phenyl]-methanol azodye are reported. A 37e47 nm bathochromic shift has been observed by comparison with analogous azodyes where diethylamino or dimethylamino groups act as donor moiety in agreement with the larger electronic donating properties of julolidine. The azobenzene skeleton adopts a planar *trans*-configuration and intra- and inter-molecular hydrogen bonds have been detected. A correlation between the spectroscopic and the molecular features has been attempted.

Keywords: Azodyes Dipolar dyes X-ray analysis, Crystal structure H bond Nonlinear optics (NLO)

1. Introduction

In recent decades, organic colour chemistry is undergoing very exciting developments as a result of the opportunities presented by dye applications in high technology fields [1]: electronic devices [2,3], linear and non-linear optics (NLO) [4], sensors [5,6], fluorescent probes [7,8], biomedical uses [9e12] and solar cells [13,14]. Owing to the importance of functions performed by dyes, beyond the simple provision of colour, they are in general referred as "functional dyes" [15,16].

Azo compounds in particular are used in the fields of non-linear optics and optical data storage [17e21]. Their optical and spectroscopic properties depend not only on the atomic arrangement in the molecular structure [22] but also on the crystal packing.

Spectroscopic data (UVeVis) [23,24], proton magnetic resonance spectra [25], and dipole moments measurements [26] of dipolar azodyes suggest that julolidine is a particularly powerful electron donor moiety, thanks to the nearly planar sp² conformation at the

nitrogen atom, that allows a more efficient delocalization of the electron lone pair. Second harmonic generation efficiency confirmed the larger push-pull nature of dipolar NLO-phores containing julolidine moiety compared with no-cyclic arylamines derivatives [27]. It is also known that the derivatives of 9-phenylazojulolidine have a pronounced bathochromic shift of the first band in comparison with the corresponding derivatives of 4-dimethylaminoazobenzene [24]. This large bathochromic shift is associated with the improved conjugation of the amino-nitrogen atom with the aromatic ring brought by the methylene bridges in the julolidine system. A red shift has also been reported for stilbene dyes [28] where replacing 4-(dimethylamino)phenyl with julolidine lead to an increase of second order hiperpolarizability (b₀) due to the greater p-electron donating ability of julolidine.

Despite the interesting results related to azodyes containing julolidine moiety, no crystallographic data have been published at the moment even if X-ray analysis can give information about the planarity of the molecule. Actually, Hallas et al. [26] suggested that the terminal nitrogen atom in the 9-phenylazojulolidines is more nearly sp²-hybridized than that in the 4-phenylazo-N,N-diethylanilines.

In the present paper, we report the synthesis, spectroscopic characterization and single crystal X-ray analysis of the

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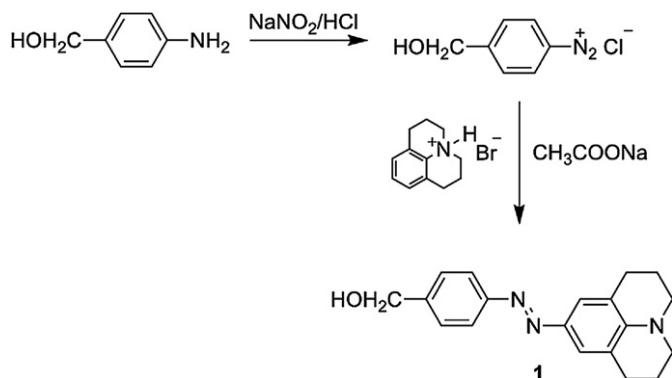


Fig. 1. Synthesis of azodye 1.

[4-(2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-9-ylazo)-phenyl]-methanol (1) (Fig. 1), an interesting intermediate for NLO-dye based on julolidine moiety.

2. Experimental

2.1. Materials

Starting materials as well as synthetic grade solvents were purchased from Aldrich and used without further purification. Chromatographic separation was carried out on direct silica gel (200e300 mesh).

2.2. Synthesis of [4-(2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-9-ylazo)-phenyl]-methanol (1)

A solution of NaNO_2 (6.80 g, 20 ml of water) was added dropwise into a mixture of 4-aminophenylmethanol (12.14 g), HCl (36%, 40 ml) and water (100 ml) with vigorous stirring at 273 K. After 30 min of stirring, the diazonium salt solution was filtered and dropwise added to coupling agent solution, cooled at 273e5 K and prepared by adding 25 g of julolidine hydrobromide in 750 ml of water and equimolar quantity of sodium acetate. During the addition of diazonium salt solution, pH was monitored continuously by pHmeter owing to maintain the pH 4 by addition of solid sodium acetate. After 1 h of reaction, solid NaHCO_3 was added until neutralization and the mixture extracted with ethyl acetate. The organic phases were anhydried with anhydrous Na_2SO_4 , filtered and evaporated. The crude solid was purified by flash chromatography on silical gel, using petroleum ether/ethyl acetate (70/30 v/v) mixture as eluent. Dye 1 was obtained as red-violet powder in 55% yield.

The red crystals suitable for X-ray analysis were obtained by dissolving the powder in acetonitrile at 60 °C, and slowly cooling the solution at room temperature with partial slow evaporation of solvent; m.p. 135e137 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3): 1.99 ppm (m, 4H, H₅), 2.81 ppm (t, 4H, H₆), 3.27 ppm (t, 4H, H₄), 4.73 ppm (s, 2H, CH₂OH), 7.43 ppm (m, 4H, H₇, H₈), 7.78 ppm (d, 2H, H₂); $^{13}\text{C-NMR}$ (50 MHz, CDCl_3): 21.4, 27.8, 49.9, 64.8, 120.7, 121.2, 122.6, 127.3, 141.6, 142.5, 145.5, 152.6 ppm. MS-EI (m/z): 307 (M⁺), 172 (100%), 142, 107, 91, 77; FT-IR (cm^{-1}): 3340 (OH), 2927 and 2837 cm^{-1} (aliphatic CH), 1600 and 1529 (benzene CeC). Elemental analysis: $\text{C}_{19}\text{H}_{21}\text{N}_3\text{O}$ Calc: C, 74.24; H, 6.89; N, 13.67; found: C, 74.20; H, 6.90; N, 13.66.

Table 1
Crystal data, experimental details and refinement parameters for azodye 1.

Empirical formula	$\text{C}_{19}\text{H}_{21}\text{N}_3\text{O}$ (1)
Formula weight (amu)	307.39
Colour/shape	Red/prismatic
Crystal dimension (mm)	0.14 × 0.22 × 0.42
Lattice type, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a ¼ 8.398(1) Å b ¼ 24.591(4) Å c ¼ 7.785(1) Å β ¼ 99.704(3)°
Volume (Å ³)	1584.7(4)
Z (number of molecules in unit cell)	4
Measurement temperature (K)	293(2)
Density (calculated) (g/cm ³)	1.288
$F(000)$	656
Absorption coefficient (mm^{-1})	0.082
Reflection collected	5124
Unique P reflection	2477
R_{int} ¼ $\sum_j F_{\text{oj}} ^2 - \sum_j F_{\text{oj}} ^2 / \sum_j F_{\text{oj}} ^2$	0.0293
h, k, l limits	−10 $\leq h \leq 6$ −32 $\leq k \leq 22$ −9 $\leq l \leq 9$
Q min./max. deg.	1.66/28.30
N_p (Number of parameters)	208
R_{wp} ¼ $\sum_j F_{\text{oj}} - F_{\text{oj}} / \sum_j F_{\text{oj}} $	0.0839
R_{p} ¼ $\sum_j F_{\text{oj}} - F_{\text{oj}} / \sum_j F_{\text{oj}} $	0.1941
Goodness-of-fit ¼ $\sum_j F_{\text{oj}} - F_{\text{oj}} ^2 / \sum_j F_{\text{oj}} ^2$	1.214
Δ no: of unique reflections − no: of parameters ^b	1=2
Largest peak and hole in final difference map ($\text{e}^{-\text{Å}^3}$)	0.20 and −0.23

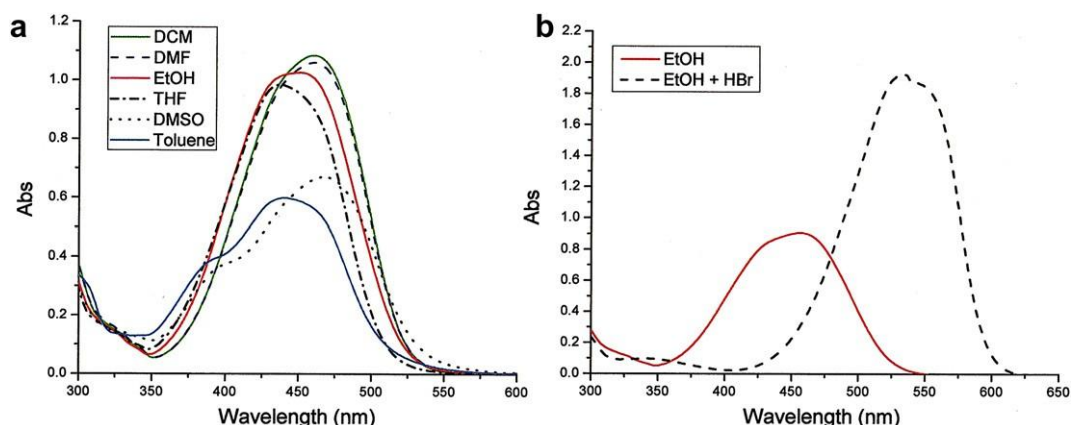


Fig. 2. a. Solvatochromism of azodye 1. b. Halochromism of azodye 1.

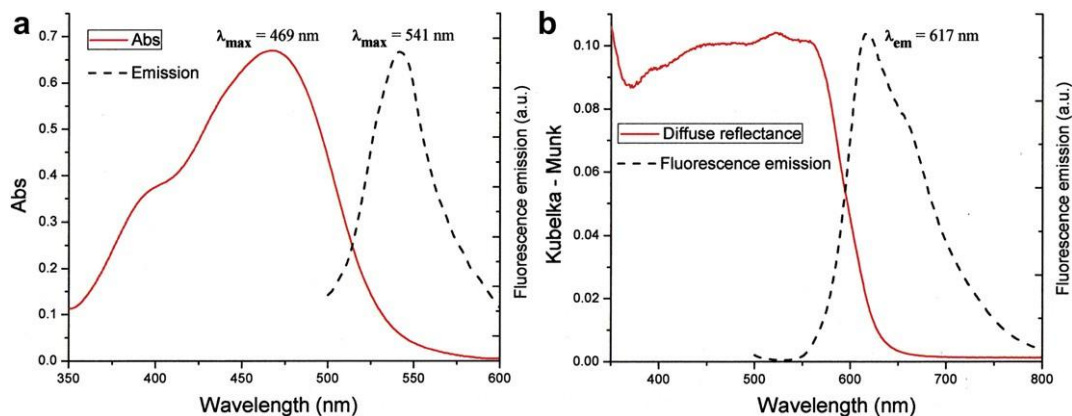


Fig. 3. Comparison between a) absorption and fluorescence emission spectrum of azodye 1 in DMSO and b) diffuse reflectance and fluorescence emission spectrum on the solid sample.

2.3. Characterization

The $^1\text{H-NMR}$ spectrum was recorded on a Jeol EX400 NMR spectrometer, while $^{13}\text{C-NMR}$ was recorded on a Bruker AC200 in CDCl_3 using CHCl_3 (d_{H} 7.25 ppm, d_{C} 77.36 ppm) as reference. Mass spectrum was recorded on a Thermo Finnigan, EI direct injection, 70 eV. IR spectrum was recorded in the region of $4000\text{e}400\text{ cm}^{-1}$ using a Shimadzu FT-IR 8400 spectrophotometer (KBr pellets). UVeVis spectra were recorded on a Shimadzu UV-1700 spectrometer using different solvents in order to investigate the solvatochromic behaviour of dye 1. A stock solution (3.5×10^{-3} M) in dimethylsulphoxide (DMSO) was prepared and dilutions (3.5×10^{-5} M) in tetrahydrofuran (THF), toluene, dichloromethane, dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and ethanol were analysed. An halochromic study has been performed in ethanol solution ($w10^{-5}$ M) by adding different quantities of acidic (HCl, H_2SO_4 , HBr) water solutions. Diffuse reflectance spectrum was performed on a Cary 5000 UVeViseNIR Spectrophotometer after dilution with Poly(tetrafluoroethylene).

Fluorescence measurements were recorded using a LS55 Perkin Elmer spectrofluorimeter equipped with a xenon lamp source and a 5 mm path length quartz cell. Fluorescence spectrum of dye 1 in DMSO was recorded in the range of 500e600 nm upon excitation at 470 nm.

X-ray crystal data have been collected on a Siemens P4 diffractometer equipped with a Bruker APEX CCD detector using graphite-monochromatized $\text{MoK}\alpha$ radiation (λ 0.71073 Å). The intensities have been semi-empirically corrected for absorption, using symmetry equivalent reflections and the refinement was made using full-matrix least-squares on F^2 . All non-hydrogen

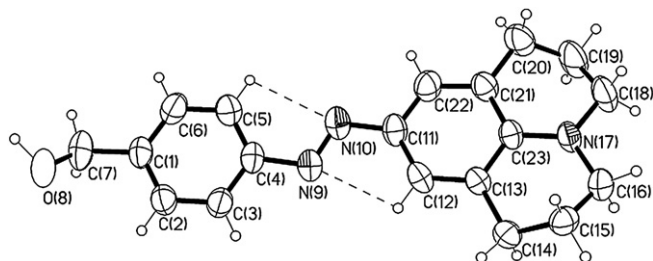


Fig. 4. ORTEP plot (50% probability) of azodye 1.

atoms were anisotropically refined. All hydrogen atoms have been located on the last difference Fourier maps and in order to better refine the structure all but H(8) of the eOH group have been calculated and refined riding on the connected C atom ($U_{\text{iso}}(\text{H})$ 1.2 times $U_{\text{eq}}(\text{C})$). Only the coordinates of H(8) were fixed at the value found in the last difference Fourier maps, and its U_{iso} has been set at 1.5 times U_{eq} of C(8). Programs used were SHELXTL [29] for structure solution, refinement and molecular graphics, Bruker AXS SMART (diffractometer control), SAINT (integration), SADABS (absorption correction) [30]. Crystallographic data, experimental details, and refinement parameters are listed in Table 1.

CCDC 830926 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: þ44 1223 336033.

Table 2
Selected bond lengths (Å) and angles ($^\circ$) of azodye 1.

C(1)eC(2)	1.371(5)	C(1)eC(7)eO(8)	112.6(3)
C(1)eC(6)	1.376(5)	C(4)eN(9)eN(10)	113.9(3)
C(1)eC(7)	1.520(5)	N(9)eN(10)eC(11)	113.9(3)
C(2)eC(3)	1.382(5)	C(22)eC(11)eC(12)	118.5(3)
C(3)eC(4)	1.371(5)	C(13)eC(12)eC(11)	121.6(3)
C(4)eC(5)	1.379(5)	C(12)eC(13)eC(23)	119.4(3)
C(4)eN(9)	1.434(4)	C(12)eC(13)eC(14)	121.5(3)
C(5)eC(6)	1.378(5)	C(23)eC(13)eC(14)	119.1(3)
C(7)eO(8)	1.408(5)	C(13)eC(14)eC(15)	109.3(3)
N(9)eN(10)	1.255(4)	C(16)eC(15)eC(14)	109.1(3)
N(10)eC(11)	1.410(4)	N(17)eC(16)eC(15)	112.6(3)
C(11)eC(22)	1.388(5)	C(23)eN(17)eC(18)	122.7(3)
C(11)eC(12)	1.392(5)	C(23)eN(17)eC(16)	122.2(3)
C(12)eC(13)	1.368(4)	C(18)eN(17)eC(16)	115.1(3)
C(13)eC(23)	1.409(5)	N(17)eC(18)eC(19)	113.1(3)
C(13)eC(14)	1.501(4)	C(18)eC(19)eC(20)	111.9(4)
C(14)eC(15)	1.520(5)	C(19)eC(20)eC(21)	110.8(4)
C(15)eC(16)	1.499(5)	C(22)eC(21)eC(23)	118.3(3)
C(16)eN(17)	1.457(4)	C(22)eC(21)eC(20)	122.5(3)
N(17)eC(23)	1.367(4)	C(23)eC(21)eC(20)	119.2(3)
N(17)eC(18)	1.445(4)	C(21)eC(22)eC(11)	122.2(3)
C(18)eC(19)	1.481(5)	N(17)eC(23)eC(13)	120.2(3)
C(19)eC(20)	1.486(5)	N(17)eC(23)eC(21)	119.8(3)
C(20)eC(21)	1.496(5)	C(13)eC(23)eC(21)	120.0(3)
C(21)eC(22)	1.377(5)		
C(21)eC(23)	1.414(5)		

Table 3
Crystallographic comparison of the azo-skeleton between some azo-compounds with different structure type.

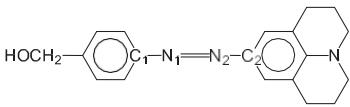
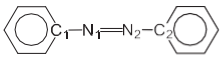
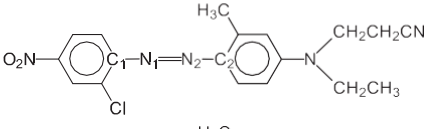
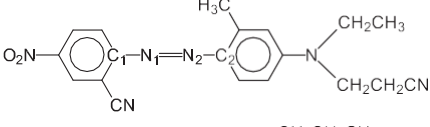
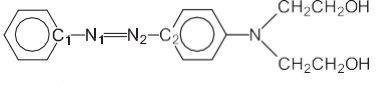
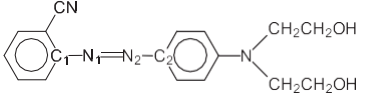
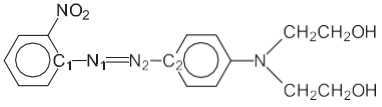
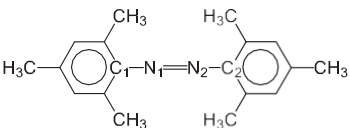
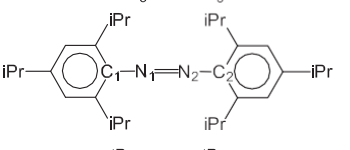
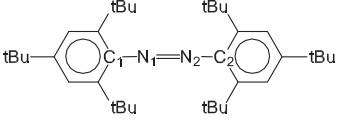
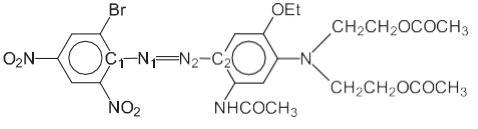
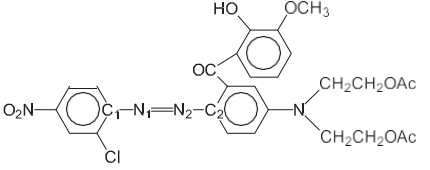
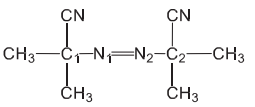
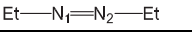
Compound	$N_1]N_2$	C_1eN_1	C_2eN_2	Angle between phenyl groups	Ref.
1 	1.255(4)	1.434(4)	1.410(4)	5.8°	This work
2 	1.247(2)	1.428(2)	1.428(2)	planar	[36]
3 	1.276(4)	1.415(5)	1.394(5)	3.45°	[41]
4 	1.272(4)	1.414(4)	1.387(4)	2.44°	[41]
5 	1.260(4)	1.439(4)	1.420(4)	10.3°	[39]
6 	1.255(3)	1.431(3)	1.414(3)	5.5°	[39]
7 	1.263(2)	1.427(3)	1.405(3)	42.2°	[39]
8 	1.217(3)	1.442(3)	1.442(3)	0°	[40]
9 	1.253(6)	1.454(6)	1.454(6)	76.2°	[42]
10 	1.257(7)	1.460(7)	1.464(7)	68.7°	[47]
11 	1.295(4)	1.407(5)	1.371(5)	9.4°	[38]
12 	1.267(3)	1.427(3)	1.407(3)	planar	[37]
13 	1.221(3)	1.490(3)	1.490(3)		[45]
14 	1.209(7)	1.674(7)	1.674(7)		[46]

Table 4
Intra- and inter-molecular H-bonds geometry for azodye 1.

DeH\$\$\$A	DeH (Å)	H\$\$\$A (Å)	D\$\$\$A (Å)	D-H\$\$\$A (°)	H\$\$\$AeX (°)
<i>Intramolecular bonds</i>					
C(5)eH(5)\$\$\$N(10)	2.50	0.930 ^a	2.740	95	85
C(12)eH(12A)\$\$\$N(9)	2.48	0.930 ^a	2.728	96	85
<i>Intermolecular bonds</i>					
O(8)eH(8A)\$\$\$N(9)	2.07	1.01	2.971	149	130
C(16)eH(16A)\$\$\$O(8)	2.56	0.970 ^a	3.474	157	109
C(3)eH(3A)\$\$\$O(8)	2.86	0.930 ^a	3.477	125	128
C(2)eH(2A)\$\$\$O(8)	2.93	0.930 ^a	3.514	122	158
C(20)eH(20A)\$\$\$N(10)	3.14	0.970 ^a	3.674	131	115
C(19)eH(19A)\$\$\$N(10)	3.20	0.970 ^a	3.852	112	119

^a H position calculated and refined riding on the corresponding C atom (see experimental).

3. Results and discussion

3.1. Synthesis

The synthetic approach of azodye 1 is reported in Fig. 1. Conventional diazotation with sodium nitrite and hydrochloric acid of 4-aminophenylmethanol gave the required diazonium salt that was reacted with a water solution of julolidine hydrobromide. The reaction was performed in acidic aqueous solution between 0 and 5 °C and solid sodium acetate was added to obtain the optimal pH conditions (pH ¼ 4) for the coupling reaction on the tertiary aryl amine, before and during the addition of diazonium salt solution. After pH adjustment with sodium bicarbonate, a red solid was obtained.

3.2. Spectroscopic properties

The UVeVis characterization (reported in Fig. 2) confirmed what previewed: the presence of the julolidine ring instead of a dimethyl or diethyl benzene moiety caused a red shift of the maximum of absorption. The I_{\max} of the julolidine compound is 450 nm in ethanol versus 410 nm for the dimethyl benzene compound [31] and 420 nm for the diethyl benzene compound. [32] Moreover, a positive solvatochromic behaviour is observed (Fig. 2a), ranging from 440 nm in toluene to 469 nm in DMSO. A complete reversible bathochromic (b80 nm) and hyperchromic shift (b100%) of the $\rho \nearrow \rho^*$ band were obtained by acidification (HCl and HBr) of ethanol solution (Fig. 2b) as generally already observed for push-pull azodye owing to reversible protonation at the azo group [1].

Surprisingly, dye 1 also shows a fluorescence signal, even if weak, in DMSO with a Stoke's shift of 72 nm (Fig. 3) and with higher intensity on the crystalline solid sample (Stoke's shift of 150 nm). In fact, it has been proven that pseudo-stilbenes type azobenzenes are not good emitters, even at low temperature and adsorbed to surfaces, their non-radiative decay rate overwhelms their radiative decay [33], unless an hydroxyl group is in *orto* position with respect to N=N bond [34,35].

3.3. Crystal structure

The ORTEP plot of the molecular structure, with the atom labelling, of azodye 1 is showed in Fig. 4 and relevant bond lengths and angles are listed in Table 2.

The azobenzene skeleton adopts a *trans*-configuration with the two phenyl rings forming a dihedral angle of 5.8°, in agreement with most of the structures of the related azodye molecules [36e40]. The planarity around N(17) is confirmed. The rough planarity of this dye may suggest a wide p-electron delocalization, reflected in a shortness of the NePh bonds and an increase of the N=N double bond with respect to a molecule without aromatic groups. This effect on the N=N and NePh bonds should be enhanced by the electron donor ability of the substituents connected to the aromatic rings.

In azodye 1 the N(9)eN(10) bond distance is 1.255(4) Å, in agreement with that of azobenzene (1.247(2) Å) [36], and some of its derivatives [37,38,40,42]. In order to assess the effect of the presence of a strong donating group (such as julolidine with respect to standard linear alkylamino), crystallographic features of several azo-compounds are reported for a comparison in Table 3. The N=N bond distance can vary widely, and it is difficult to find a strict correlation with the electron features of the substituents. In particular, considering the e.s.d.'s of all distance data, biphenyl azodyes 1e7 and 9e12 show a slight elongation of N=N distance with respect to azodyes 13 and 14, where no aromatic rings is connected to this bond.

The NePh bond distances, instead, seem to be influenced by the presence of both donor and acceptor groups. In fact, in compounds 3, 4, 6, 7, 11, 12 a shortness of the NePh bond can be observed when an electron donor substituent is present in para position with respect to the azo bond. Also in the azodye 1 this shortness is detected even if only a donor group is present: the N(10)eC(11) and C(4)eN(9) bond distances are 1.410(4) and 1.434(4) Å, respectively. Harada et al. [43] have carried out a crystallographic study on the particular behaviour of the N=N and NePh bonds at different temperatures. They have observed an increasing of the N=N bond length with the decreasing of the temperature from 296 to 90 K and justified this behaviour as an artifact caused by the torsional vibration of the NePh bonds in crystals. This behaviour can occur also in the azodye of this work, and cannot put in evidence the expected lengthening of the N=N.

Intramolecular H-bond of CeH\$\$\$N type [44] (Table 4 and Fig. 4) have been detected in the azodye 1. The presence of such type of stabilizing interactions, that contribute to the planarity of the molecule, has been reported also for the planar azobenzene derivatives 3, 4 and 11.

In the crystal packing two inter-molecular OeH\$\$\$N and CeH\$\$\$O hydrogen bonds are noticeable. They involve the same OH group and connect 3 molecules (Fig. 5 and Table 4). These two types of interaction are responsible of the formation of layers of parallel molecules, shown in Fig. 6. In particular O(8)eH(8A)\$\$\$N(9) is a very short interaction (2.07 Å), responsible for the elongation of

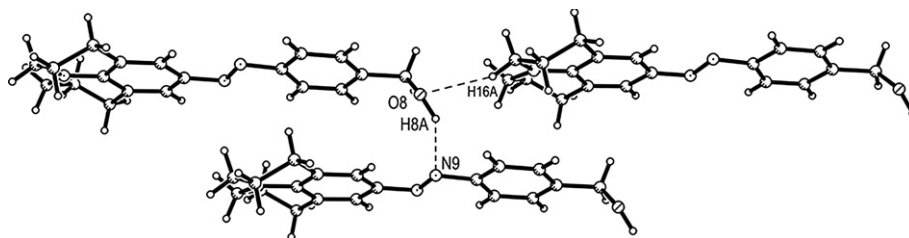


Fig. 5. Representation of OeH\$\$\$N and CeH\$\$\$O inter-molecular hydrogen bonds.

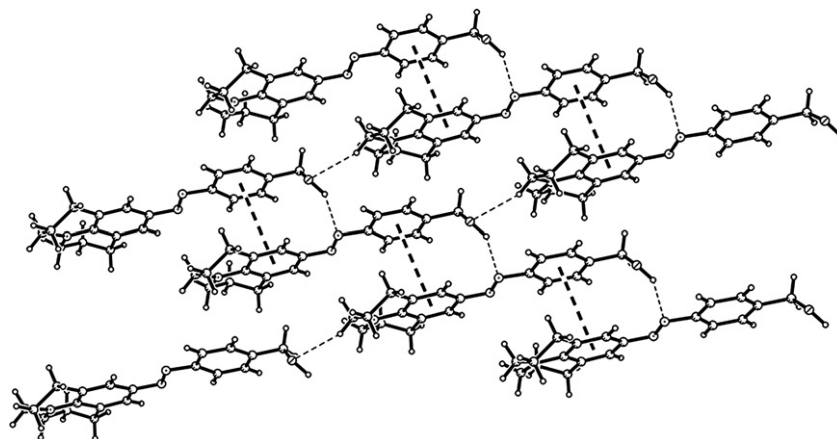


Fig. 6. Representation of the plane of molecules connected towards the OeH\$\$\$N and CeH\$\$\$O inter-molecular hydrogen bonds, with the sandwich pep stacking interaction evidenced.

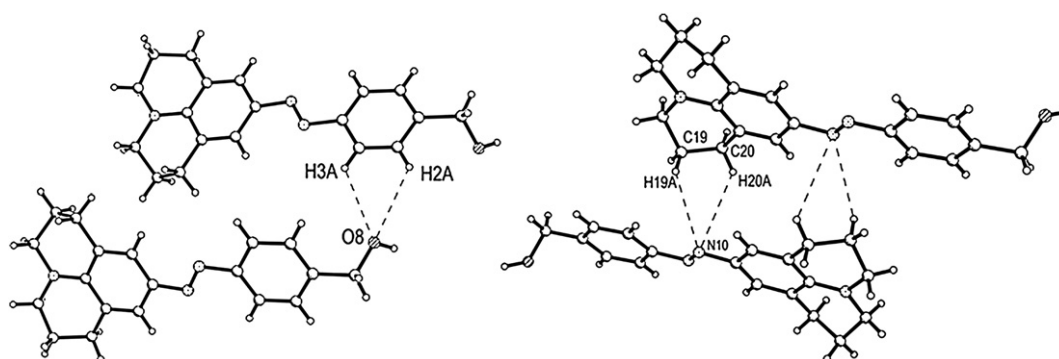


Fig. 7. Representation of the weak CeH\$\$\$O hydrogen bonds that are responsible of the cohesion of the layers of molecules.

the O(8)eH(9) bond (1.01 Å) and for the orientation of H(8) toward the N(9) atom. The C(16)eH(16A)\$\$\$O(8) hydrogen bond is instead longer (2.56 Å) and involves a hydrogen atom of one methylene group of the julolidine. A sandwich pep stacking interaction, involving the C(1)eC(6) ring and the aromatic ring of the julolidine, is also present in this layer, with a distance between aromatic rings of 4.083 Å (see Fig. 6).

Other inter-molecular hydrogen bonds (see Fig. 7) involve the oxygen of the OH group with two hydrogen atoms of benzene (2.93 and 2.86 Å) and the N(10) with the hydrogens of two methylene groups of the julolidine (3.20 and 3.14 Å). These two weaker inter-molecular contacts are responsible of the cohesion between the previous layers of the molecules. The inter-molecular hydrogen bonds observed in azodye 1 are common to benzene azodyes and the lengths found are in agreement with literature data [22,38].

4. Conclusions

The synthesis of a julolidine substituted azodye has been performed, its spectroscopic properties, as well as its X-ray crystal structure have been determined. This is the first X-ray structure of julolidine azo-compound in literature. Julolidine moiety induces a large bathochromic shift with respect to diethylamino or dimethylamino groups present as donor moiety, confirming the larger electronic donating properties. Moreover, this dye presents an unusual detectable fluorescence emission with very large Stoke's shift, both in solid state and in solution, even at room temperature.

The azobenzene skeleton adopts a planar *trans*-configuration; the influence, however, of the electron donating feature of the julolidine substituent can be detected only in the shortening of the NePh bond but not on the lengthening of the N]N bond, probably due to the torsional vibrations of the azo fragment. The data show a strong tendency of this compound to form intra and inter-molecular H-bonds, similar to those found in other azobenzene derivatives.

The obtained results can be useful and important for the design of functional dyes (i.e. NLO-octopolar dyes, DSC sensitizers etc.) containing azobenzenejulolidine moiety.

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