### Dyes and Pigments 92 (2012) 1177-1183

Contents lists available at SciVerse ScienceDirect

### Dyes and Pigments



journal homepage: www.elsevier.com/locate/dyepig

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

Nadia Barbero<sup>a</sup>, Claudia Barolo<sup>a</sup>, Domenica Marabello<sup>b,\*</sup>, Roberto Buscaino<sup>a</sup>, Giuliana Gervasio<sup>b</sup>, Guido Viscardi<sup>a,\*\*</sup>

<sup>a</sup> Department of General Chemistry and Organic Chemistry and NIS, Interdepartmental Centre of Excellence, University of Torino, C.so M. d'Azeglio 48, I-10125 Torino, Italy <sup>b</sup> Dipartimento di Chimica IFM and CrisDi (Centro Interdipartimentale Cristallografia Diffrattometrica), Università di Torino, Via Pietro Giuria 7, I-10125 Torino, Italy

### ARTICLE INFO

Article history: Received 4 July 2011 Received in revised form 2 September 2011 Accepted 5 September 2011 Available online 22 September 2011

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 [9–12] 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 [17–21]. 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 (UV–Vis) [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 sp<sup>2</sup> conformation at the

### 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 37–47 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.

© 2011 Elsevier Ltd. All rights reserved.

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 ( $\beta_0$ ) due to the greater  $\pi$ -electron donating ability of julolidine.

Despite the interesting results related to azodyes containing juloildine 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-phenylazojuloildines is more nearly sp<sup>2</sup>-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



<sup>\*</sup> Corresponding author. Tel.: +39 011 6707504; fax: +39 011 6707855.

<sup>\*\*</sup> Corresponding author. Tel.: +39 011 6707598; fax: +39 011 6707591.

*E-mail addresses:* domenica.marabello@unito.it (D. Marabello), guido.viscardi@unito.it (G. Viscardi).

<sup>0143-7208/\$ –</sup> see front matter @ 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.dyepig.2011.09.001



Fig. 1. Synthesis of azodye 1.

#### Table 1

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

Empirical formula	$C_{19}H_{21}N_{3}O(1)$
Formula weight (amu)	307.39
Colour/shape	Red/prismatic
Crystal dimension (mm)	$0.14 \times 0.22 \times 0.42$
Lattice type, space group	Monoclinic, P2 <sub>1</sub> /c
Unit cell dimensions	a = 8.398(1) Å
	b = 24.591(4) Å
	c = 7.785(1)  Å
	$eta=99.704(3)^\circ$
Volume (Å <sup>3</sup> )	1584.7(4)
Z (number of molecules in unit cell)	4
Measurement temperature (K)	293(2)
Density (calculated) (g/cm <sup>3</sup> )	1.288
F(000)	656
Absorption coefficient (mm <sup>-1</sup> )	0.082
Reflection collected	5124
Unique reflection	2477
$R_{\rm int} = \sum   F_0 ^2 -  F_0 ^2 ({\rm mean})  / \sum  F_0 ^2$	0.0293
h,k,l limits	$-10 \le h \le 6$
	$-32 \le k \le 22$
	$-9 \le l \le 9$
$\theta$ min./max. deg.	1.66/28.30
N <sub>p</sub> (Number of parameters)	208
$R(F) = \sum   F_0  - k F_c   / \sum  F_0 $	0.0839
$Rw = \left[ \sum (wF_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \right]^{1/2}$	0.1941
Goodness-of-fit = $\left[\sum (wF_o^2 - F_c^2)^2\right]$	1.214
(no. of unique reflections – no. of parameters)] $\left[\frac{1}{2}\right]^{1/2}$	
Largest peak and hole in final difference map (e <sup>-</sup> Å <sup>3</sup> )	0.20 and -0.23

[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 NLOdye 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 (200–300 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<sub>2</sub> (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 273-5 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 NaHCO3 was added until neutralization and the mixture extracted with ethyl acetate. The organic phases were anhydrified with anhydrous Na<sub>2</sub>SO<sub>4</sub>, 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% vield.

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. 135–137 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 1.99 ppm (m, 4H, H<sub>5</sub>), 2.81 ppm (t, 4H, H<sub>6</sub>), 3.27 ppm (t, 4H, H<sub>4</sub>), 4.73 ppm (s, 2H, <u>CH</u><sub>2</sub>OH); 7.43 ppm (m, 4H, H<sub>1</sub> + H<sub>3</sub>), 7.78 ppm (d, 2H, H<sub>2</sub>); <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>): 21.4; 27.6; 49.9; 64.6; 120.7; 121.9; 122.6; 127.3; 141.6; 142.5; 145.5; 152.6 ppm. MS-EI (*m/z*): 307 (M<sup>+</sup>), 172 (100%), 142, 107, 91, 77; FT-IR (cm<sup>-1</sup>): 3340 (O–H), 2927 and 2837 cm<sup>-1</sup> (aliphatic CH), 1600 and 1529 (benzene C–C). Elemental analysis: C<sub>19</sub>H<sub>21</sub>N<sub>3</sub>O Calc: C, 74,24; H, 6,89; N, 13,67; found: C, 74,20; H, 6.90; N, 13.66.



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 <sup>1</sup>H-NMR spectrum was recorded on a leol EX400 NMR spectrometer, while <sup>13</sup>C-NMR was recorded on a Brucker AC200 in CDCl<sub>3</sub> using CHCl<sub>3</sub> ( $\delta_{\rm H} = 7.25$  ppm,  $\delta C = 77.36$  ppm) as reference. Mass spectrum was recorded on a Thermo Finnigan, EI direct injection, 70 eV. IR spectrum was recorded in the region of 4000-400 cm<sup>-1</sup> using a Shimadzu FT-IR 8400 spectrophotometer (KBr pellets). UV-Vis 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  $\times$  10<sup>-3</sup> M) in dimethylsulphoxide (DMSO) was prepared and dilutions  $(3.5 \times 10^{-5} \text{ M})$  in tetrahydrofuran (THF), toluene, dichloromethane, dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and ethanol were analysed. An halocromic study has been performed in ethanol solution  $(\sim 10^{-5} \text{ M})$  by adding different quantities of acidic (HCl, H<sub>2</sub>SO<sub>4</sub>, HBr) water solutions. Diffuse reflectance spectrum was performed on a Cary 5000 UV-Vis-NIR Spectrophotometer after dilution with Poly(tetrafluoroethylene).

Fluorescence measurements were recorded using a LS55 Perkin Elmer spectrofluorimeter equipped with a xenon lampsource and a 5 mm path length quarz cell. Fluorescence spectrum of dye **1** in DMSO was recorded in the range of 500–600 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 MoK $\alpha$  radiation ( $\lambda = 0.71073$  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 –OH group have been calculated and refined riding on the connected C atom  $(U_{iso}(H) 1.2 \text{ times } U_{eq}(C))$ . 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: +44 1223 336033.

**Table 2**Selected bond lenghts (Å) and angles (°) of azodye 1.

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

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

Compor	und	N <sub>1</sub> =N <sub>2</sub>	C <sub>1</sub> -N <sub>1</sub>	C <sub>2</sub> -N <sub>2</sub>	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	$O_2N$ $O_2N$ $O_2$ $O_$	1.276(4)	1.415(5)	1.394(5)	3.45°	[41]
4	$H_3C$ $O_2N$ $C_1$ $N_1$ $N_2$ $C_2$ $N_1$ $C_2C_2$ $C_2$ $C_2C_2$ $C_2C$	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	CN $C_1 - N_1 - N_2 - C_2$ $CH_2CH_2OH$ $CH_2CH_2OH$	1.255(3)	1.431(3)	1.414(3)	5.5°	[39]
7	$NO_2$ $C_1-N_1=N_2-C_2$ $CH_2CH_2OH$ $CH_2CH_2OH$	1.263(2)	1.427(3)	1.405(3)	42.2°	[39]
8	$H_{3}C \longrightarrow CH_{3} H_{3}C \longrightarrow CH_{3}$ $H_{3}C \longrightarrow CH_{3} H_{3}C \longrightarrow CH_{3}$	1.217(3)	1.442(3)	1.442(3)	0°	[40]
9	iPr $iPr$ $iPr$ $iPr$ $iPr$ $iPr$ $iPr$ $iPr$ $iPr$ $iPr$	1.253(6)	1.454(6)	1.454(6)	76.2°	[42]
10	tBu $tBu$	1.257(7)	1.460(7)	1.464(7)	68.7°	[47]
11	tBu tBu $O_2N$ $C_1$ $N_1$ $N_2$ $C_2$ $N_1$ $C_2$	1.295(4)	1.407(5)	1.371(5)	9.4°	[38]
12	$O_2N$ $C_1$ $N_1$ $N_2$ $C_2$ $N$ $CH_2CH_2OAc$ $CH_2CH_2OAc$ $CH_2CH_2OAc$	1.267(3)	1.427(3)	1.407(3)	planar	[37]
13	$CN \qquad CN \qquad CN CH_3 - C_1 - N_1 = N_2 - C_2 - CH_3$	1.221(3)	1.490(3)	1.490(3)		[45]
14	ĊH₃ ĊH₃ EtN₁==N₂Et	1.209(7)	1.674(7)	1.674(7)		[46]

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

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

<sup>a</sup> 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 = 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 UV–Vis 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  $\lambda_{max}$  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 bathocromic (+80 nm) and hypercromic shift (+100%) of the  $\pi \rightarrow \pi^*$  band were obtained by acidification (HCl and HBr) of ethanol solution (Fig. 2b) as generally already observed for pushpull 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  $5.8^{\circ}$ , in agreement with most of the structures of the related azodye molecules [36–40]. The planarity around N(17) is confirmed. The rough planarity of this dye may suggest a wide  $\pi$ -electron delocalization, reflected in a shortness of the N–Ph 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 N–Ph bonds should be enhanced by the electron donor ability of the substituents connected to the aromatic rings.

In azodye **1** the N(9)–N(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 **1**–7and **9**–12 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 N–Ph 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 N–Ph 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)–C(11) and C(4)–N(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 N-Ph 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 N-Ph 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  $C-H\cdots N$  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  $O-H\cdots N$  and  $C-H\cdots O$  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  $O(8)-H(8A)\cdots N(9)$  is a very short interaction (2.07 Å), responsible for the elongation of



Fig. 5. Representation of O-H···N and C-H···O inter-molecular hydrogen bonds.



**Fig. 6.** Representation of the plane of molecules connected towards the  $O-H\cdots N$  and  $C-H\cdots O$  inter-molecular hydrogen bonds, with the sandwich  $\pi-\pi$  stacking interaction evidenced.



Fig. 7. Representation of the weak C-H···O hydrogen bonds that are responsible of the cohesion of the layers of molecules.

the O(8)–H(9) bond (1.01 Å) and for the orientation of H(8) toward the N(9) atom. The C(16)–H(16A)···O(8) hydrogen bond is instead longer (2.56 Å) and involves an hydrogen atom of one methylene group of the julolidine. A sandwich  $\pi$ – $\pi$  stacking interaction, involving the C(1)–C(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 N—Ph 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 intermolecular 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 azobenzene—julolidine moiety.

### Acknowledgements

NB, CB, RB and GV acknowledge financial support of this work by the EU project "Innovasol" grant agreement number 227057-2, DyeCells project (grant cod. 121) from Ministero dell'Ambiente e della Tutela del Territorio e del Mare (Italy) and thank Compagnia di San Paolo and Fondazione CRT for continuous equipment supply.

### References

- Zollinger H. Color chemistry. Synthesis, properties and applications of organic dyes and pigments. 2nd ed. Weinheim: VCH; 1991.
- [2] Baranoff E, Suàrez S, Bugnon P, Barolo C, Buscaino R, Scopelliti R, et al. Sublimation not an innocent technique: a case of bis-cyclometalated iridium emitter for OLED. Inorg Chem 2008;47:6575–7.
- [3] Xia ZY, Su JH, Fan HH, Cheah KW, Tian H, Chen CH. Multifunctional diarylamine-substituted benzo[k]fluoranthene derivatives as green

electroluminescent emitters and nonlinear optical materials. J Phys Chem 2010;114:11602-6.

- [4] Nalwa HS, Miyata S, editors. Nonlinear optics of organic molecules and polymers. Boca Raton, FL: CRC Press; 1997.
- [5] Fiorilli S, Onida B, Barolo C, Viscardi G, Brunel D, Garrone E. Tethering of modified Reichardt's dye on SBA-15 mesoporous silica: the effect of the linker flexibility. Langmuir 2007;23:2261–8.
- [6] Zu LL, Li X, Ji FY, Ma X, Wang QC, Tian H. Photolockable ratiometric viscosity sensitivity of cyclodextrin polypseudorotaxane with light-active rotor graft. Langmuir 2009;25:3482–6.
- [7] Quagliotto P, Barbero N, Barolo C, Costabello K, Marchese L, Coluccia S, et al. Characterization of monomeric and gemini cationic amphiphilic molecules by fluorescence intensity and anisotropy. Dyes Pigments 2009;82:124–9.
- [8] Barbero N, Quagliotto P, Barolo C, Artuso E, Buscaino R, Viscardi G. Characterization of monomeric and gemini cationic amphiphilic molecules by fluorescence intensity and anisotropy. Part 2. Dyes Pigments 2009;83:396-402.
- [9] Barbero N, Napione L, Quagliotto P, Pavan S, Barolo C, Barni E, et al. Fluorescence anisotropy analysis of protein-antibody interaction. Dyes Pigments 2009;83:225-9.
- [10] Benzi C, Bertolino CA, Miletto I, Ponzio P, Barolo C, Viscardi G, et al. The design, synthesis and characterization of a novel acceptor for real time polymerase chain reaction using both computational and experimental approaches. Dyes Pigments 2009;83:111–20.
- [11] Barbero N, Barni E, Barolo C, Quagliotto P, Viscardi G, Napione L, et al. A study of the interaction between fluorescein sodium salt and bovine serum albumin by steady-state fluorescence. Dyes Pigments 2009;80:307–13.
- [12] Barbero N, Napione L, Visentin S, Alvaro M, Veglio A, Bussolino F, et al. A transient kinetic study between signaling proteins: the case of the MEK-ERK interaction. Chem Sci 2011;2:1804–9.
- [13] Nazeeruddin MK, De Angelis F, Fantacci S, Selloni A, Viscardi G, Liska P, et al. Combined experimental and DFT-TDDFT computational study of photoelectrochemical cell ruthenium sensitizers. J Am Chem Soc 2005;127:16835–47.
- [14] Buscaino R, Baiocchi C, Barolo C, Medana C, Grätzel M, Nazeeruddin MdK, et al. A mass spectrometric analysis of sensitizer solution used for dye-sensitized solar cell. Inorg Chim Acta 2008;361:798–805.
- [15] Functional or "high technology" dyes and pigments. In: Christie RM, editor. Colour chemistry. Cambridge: RSC; 2001. p. 168–90.
- [16] Yoshida Z, Shirota Y. Chemistry of functional dyes, vol. 2. Mita Press; 1993.
- [17] Piron R, Brasselet S, Josse D, Zyss J, Viscardi G, Barolo C. Matching molecular and optical multipoles in photoisomerizable nonlinear systems. J Opt Soc Am B-Opt Phys 2005;22:1276–82.
- [18] Ledoux I, Zyss J, Barni E, Barolo C, Diulgheroff N, Quagliotto P, et al. Properties of novel azodyes containing powerful acceptor groups and thiophene moiety. Synth Met 2000;115:213–7.
- [19] Li Z, Wu W, Li Q, Yu G, Xiao L, Liu Y, et al. High-generation second-order nonlinear optical (NLO) dendrimers: convenient synthesis by click chemistry and the increasing trend of NLO effects. Angew Chem Int Ed 2010;49: 2763–7.
- [20] Li Z, Wang L, Xiong B, Ye C, Qin J, Li Z. Novel, side-on, PVK-based nonlinear optical polymers: synthesis and NLO properties. Dyes Pigments 2010;84: 134–9.
- [21] Zeng Q, Qiu G, Ye C, Qin J, Li Z. New second-order nonlinear optical polyphosphazenes: convenient postfunctionalization synthetic approach and application of the concept of suitable isolation group. Dyes Pigments 2010;84: 229–36.
- [22] Seferoğlu Z, Ertan N, Kickelbick G, Hökelek T. Single crystal X-ray structure analysis for two thiazolylazo indole dyes. Dyes Pigments 2009;82:20–5.
- [23] Hepworth JD, Mason D, Hallas G, Marsden R. The effects of cyclic terminal groups in 4-aminoazobenzene and related azo dyes. 2. -Pka values of some monoazo dyes derived from N-phenylpyrrolidine and N-phenylpiperidine. Dyes Pigments 1985;6:389–96.

- [24] Castelino RW, Hallas G. Electronic absorption spectra of some julolidine (2,3,6,7-tetrahydro-1H, 5H-benzo[ij]quinolizine) analogues of 4-dimethyl aminoazobenzenes. J Chem Soc B Phys Org 1971;5:793–5.
- [25] Hallas G. Proton magnetic resonance spectra of some para-substituted derivatives of 9-phenylazojulolidine (9-phenylazo-2,3,6,7-tetrahydro-1H,5Hbenzo[ij]quinolizine). J Chem Soc C Org 1971;17:2847-8.
- [26] Hallas G, Saadatjou N, Hepworth JD, Ibbitson DA, Jones AM, Keane TP, et al. Dipole moments of derivatives of 4-phenylazo-NN-diethylaniline and of 9-phenylazojulolidine (9-phenylazo-2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizine). J Chem Soc. Perkin Trans 1981;2(9):1292–4.
- [27] Zyss J, editor. Molecular nonlinear optics: materials, physics and devices. Boston: Academic Press; 1994.
- [28] Coe BJ, Foxon SP, Harper EC, Harris JA, Helliwell M, Raftery J, et al. The syntheses, structures and nonlinear optical and related properties of salts with julolidinyl electron donor groups. Dyes Pigments 2009;82:171–86.
- [29] Sheldrick GM. SHELXTL, Version 5.1. Madison, WI: Bruker AXS Inc.; 1997.
- [30] SMART, SAINT, SADABS, Xprep Software for CCD diffractometers. Madison, WI: Bruker AXSInc.; 2003.
- [31] Mori Y, Niwa T, Toyoshi K. Carcinogenic azo dyes. XVIII. Synthesis of azo dyes related to 3'-Hyroxy-methyl-4-(dimethylamino)azobenzene, a New Potent Hepatocarcinogen. Chem Pharm Bull 1981;29:1439–42.
- [32] Fisichella S. Azo-composti da p-amminobenzilalcool per acetilcellulosa e nylon. Tinctoria 1970;10:329–30.
- [33] Toro C, Thibert A, De Boni L, Masunov AE, Hernández FE. Fluorescence emission of Disperse Red 1 in solution at room temperature. J Phys Chem B 2008;112:929–37. and reference therein.
- [34] Susdorf T, Bansal AK, Penzkofer A, Guo SL, Shi JM. Absorption and emission spectroscopic characterization of some azo dyes and a diamino-maleonitrile dye. Chem Phys 2007;333:49–56.
- [35] Misra A, Shahid M, Srivastava P. An efficient fluoroionophore for selective recognition of Hg<sup>2+</sup> and Cu<sup>2+</sup> ions. Thin Solid Films 2010;519:1235–9.
- [36] Bouwstra JA, Schouten A, Kroon J. Structural studies of the system transazobenzene/trans-stilbene. I. A reinvestigation of the disorder in the crystal structure of trans-azobenzene, C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>. Acta Crystallogr Sect C-Cryst Struct Commun 1983;39:1121–3.
- [37] Freeman HS, Posey JC, Singh J-P. X-ray crystal-structure of Disperse Red-167. Dyes Pigments 1992;20:279–89.
- [38] Park K-M, Yoon I, Lee SS, Choi G, Lee JS. X-ray crystal structure of CI Disperse Blue 79. Dyes Pigments 2002;54:155–61.
- [39] McIntosh SA, Freeman HS, Singh P. X-ray crystal-structure of the dye 4-(N, N-bis-(beta-hydroxyethyl) amino) azobenzene. Dyes Pigments 1991;17:1–10.
- [40] Le Page Y, Gabe EJ, Wang J, Barclay LRC, Holm HL. 2,2',4,4',6,6'-Hexa-tert-butylazobenzene. Acta Crystallogr Sect B-Struct Sci 1980;36:2846-8.
  [41] Lee I-E, Kim HI, Han MR, Lee SY, Io WI, Lee SS, et al. Crystal structures of CI.
- [41] Lee J-E, Kim HJ, Han MR, Lee SY, Jo WJ, Lee SS, et al. Crystal structures of C.I. Disperse Red 65 and C.I. Disperse Red 73. Dyes Pigments 2009;80:181–6.
- [42] Le Page Y, Gabe EJ, Barclay LRC, Dust JM. 2,2',4,4',6,6'-Hexaisopropylazobenzene. Acta Crystallogr Sect B-Struct Sci 1981;37:976–8.
- [43] Harada J, Ogawa K, Tomoda S. Molecular motion and conformational interconversion of azobenzenes in crystals as studied by X-ray diffraction. Acta Crystallogr Sect B-Struct Sci 1997;53:662–72.
- [44] Desiraju GR, Steiner T. The weak hydrogen bond in structural chemistry and biology. Oxford University Press; 1999.
- [45] Argay G, Sasvári K. The crystal and molecular structure of azobisisobutyronitrile, C<sub>8</sub>H<sub>12</sub>N<sub>4</sub>. Acta Crystallogr Sect B-Struct Sci 1971;27:1851–8.
- [46] Bindu P, Varghese B, Rao MNS. Six coordinate tris(catecholato)silicates of primary amine residues-synthesis, characterization, and thermolysis studies. X-ray structures of [n-C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub>](2)[Si(C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>)<sub>3</sub>]center dot 1/2(C<sub>6</sub>H<sub>1</sub>A<sub>V</sub>) and of a bulky secondary ammonium ion, [(i-C<sub>4</sub>H<sub>9</sub>)(2)NH<sub>2</sub>](2)[Si(C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>)(3)] center dot H<sub>2</sub>O. Phosphorus Sulfur Silicon Relat Elem 2003;178:2373-6.
- [47] Gabe EJ, Wang Y, Barclay LRC, Holm HL. 2, 2', 4, 4', 6, 6'-Hexamethylazobenzene. Acta Crystallogr Sect B-Struct Sci 1981;37:978-9.