

## Note

# X-Ray crystallographic study of 1-methyl-4-(4-*N,N*-dimethylamino) styryl pyridinium iodide

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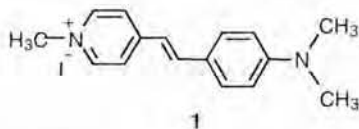
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Styryl pyridinium iodide dye (C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>I), is monoclinic *P*2<sub>1</sub>/*c*, *a* = 6.3313(8) Å, *b* = 7699(2) Å, *c* = 32.119(7) Å, β = 90.39(1)°, *V* = 1565.6(9) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.544 g cm<sup>-3</sup>, λ(MoKα) = 0.71073 Å, μ = 20.12 cm<sup>-1</sup>, *F*<sub>000</sub> = 728, *T* = 298 °K, 4707 unique reflections measured; final *R* = 0.032 for 3959 reflections with *I* > 1.0 σ(*I*). The three dimensional structure of the dye is presented. The structure analysis shows that the dye exist in trans form and is approximately planar.

In continuation to our work on the synthesis of styrylpyridinium dyes with varying alkyl chain length to study their spectral and aggregation behaviour in various solvents and surfactant systems<sup>1-5</sup>. We have embarked upon the investigation of linear optical properties of the dyes. During the course of our study an attempt has been made to make single crystal of the dyes **1**. In the present communication, the crystal structure determination of a representative dye (**1**, R=CH<sub>3</sub>, X = I) is reported which afford more insight in to the position of the iodide ion and the disposition of both phenyl and pyridyl ring planes.



## Experimental Section

1-Methyl-4-(4-*N,N*-dimethylamino)styryl pyridinium iodide **1** was synthesized by condensation of 1,4-dimethyl pyridinium iodide with 4-*N,N*-dimethylamino benzaldehyde in presence of piperidine. The red coloured compound obtained was crystallized from absolute ethanol (mp. 253°). The

single crystal of desired size was grown in a dilute solution during a period of 4 months. The three dimensional intensity data was collected on an Enraf-Nonius CAD-4 (1977) diffractometer. Cell constants were obtained from least square refinement using 25 reflection in the range of 15° < *T* < 17°. Data were collected via the ω-2θ scan mode (*h* = -9 to 0, *k* = 0 to 10 and *l* = -45 to 45 ω/2θ). 4707 unique reflections were measured out of which 3959 observations were recorded with *I* > 1.0σ(*I*). The structure was solved by using direct method programme (SIR, Burla *et al.* 1989). LSFM-MOJEN (Fair, 1990) was used for full matrix least square refinement. The hydrogen atoms were not refined properly. The crystal data with detail refinement are given in **Table I**. The detail positional parameters, the bond length, bond angles and torsion angles are given in **Tables II, III, IV and V** respectively. Molecular graphics were computed on ORTEP (Johnson, 1976). Atom scattering factors were taken from international tables for X-ray crystallography (1974).

## Results and Discussion

The perspective structural view with atomic numbering is shown in Fig. 1. The stereoscopic packing view is depicted in Figure 2. The interesting feature in the molecule is the position of the iodide ion relative to the N-atom in the compound. The iodide ions are situated in the crystal lattice such that they are 0.216 Å closure to N1 than to N2; N1-I, 5.257 versus N2-I, 5.473 Å. This is in agreement with the theoretical study of Cao *et al.*<sup>6</sup> on this dye **1** which has revealed that the positive charge is concentrated with pyridyl nitrogen in the ground state.

The dimethyl amino phenyl group is coplanar with C8=C7, as indicated by C8-C7-C4-C5 torsion angle of 179.93(3)°. The torsion angles of C16-N2-C1-C6 and C15-N2-C1-C2 [172.98(2)° and 172.9(2)° respectively] show that the amino group is not significantly distorted both from planarity and from coplanarity with the phenyl ring; N2, C15 and C16 deviate from the mean phenyl ring plane by -0.055(2), 0.083(3) and -0.230(3) Å respectively.

The entire molecule is approximately planar. The dihedral angle between the phenyl ring plane [C1, C2, C3, C4, C5, C6; Σ (Δ/σ)<sup>2</sup> = 96.6] and pyridine ring plane

**Table I**—Crystallographic data of dye **1**

Formula	C <sub>16</sub> H <sub>19</sub> N <sub>2</sub> I	No. of intensity controls	3
FW	366.3	Mode of data collection	$\omega/2\theta$
Space group	Monoclinic, P2 <sub>1</sub> /c	Maximum scan time/s	120
Radiation used	MoK $\alpha$	Maximum transmission/%	99.89
Crystal size/mm	0.4 × 0.3 × 0.3	Average transmission/%	91.66
Colour fragment	Red	Minimum transmission/%	80.98
Z	4	R (obs. data)	0.032
F <sub>(hkl)</sub>	728	R (all data)	0.046
a/Å	6.331(8)	R <sub>w</sub>	0.036
b/Å	7.699(2)	Unique reflections	4707
c/Å	32.119(7)	Observed reflection	3959
$\beta$ /°	90.39(1)	GOF	1.878
V/Å <sup>3</sup>	1565.6(9)	Cutoff	$I > 1\sigma(I)$
$\lambda$ /Å	0.71073	Weighing function(w)	$4.0/\sigma^2 + 0.0004F_o^2$
$\mu$ /cm <sup>-1</sup>	20.12	Maximum shift	0.01 $\sigma$
D <sub>c</sub> /gcm <sup>-3</sup>	1.554	Variables	173
T/°K	298	Fudge	0.02
$\theta$ /°	1-30.4	Maximum Residual/eÅ <sup>2</sup>	0.78
R <sub>int</sub>	0.019	Minimum Residual/eÅ <sup>2</sup>	-0.27

**Table II**—Positional parameters and temperature factor of **1** with their estimated standard deviations in parentheses

Atom	X	Y	Z	B(Å <sup>2</sup> )	Atom	X	Y	Z	B(Å <sup>2</sup> )
I	0.68474(3)	0.60135(2)	0.57586(1)	4.28(3)	H2	0.5453	0.0278	0.7800	4
N1	-0.0902(3)	0.1870(3)	0.52726(6)	3.88(4)	H3	0.3700	0.0264	0.7174	4
N2	0.8958(3)	0.1876(3)	0.80032(6)	3.71(4)	H5	0.8217	0.3304	0.6673	4
C1	0.7948(3)	0.1830(3)	0.76285(7)	3.08(4)	H6	1.0048	0.3294	0.7294	4
C2	0.6025(3)	0.0906(3)	0.75732(7)	3.47(4)	H7	0.5214	0.2607	0.6250	4
C3	0.4980(4)	0.0901(3)	0.71997(8)	3.51(4)	H8	0.2171	0.0367	0.6564	4
C4	0.5741(3)	0.1809(3)	0.68519(7)	3.19(4)	H10	0.3470	0.3136	0.5686	5
C5	0.7650(4)	0.2688(3)	0.69035(7)	3.44(4)	H11	0.1395	0.3495	0.5105	5
C6	0.8740(3)	0.2696(3)	0.72752(7)	3.46(4)	H12	-0.2840	0.0198	0.5542	5
C7	0.4995(4)	0.1916(3)	0.64625(7)	3.44(4)	H13	-0.0855	-0.0243	0.6129	5
C8	0.2746(4)	0.1146(3)	0.63655(8)	3.84(5)	H14a	-0.1465	0.2114	0.4662	6
C9	0.1563(4)	0.1405(3)	0.59846(8)	3.48(4)	H14b	-0.2811	0.3369	0.4929	6
C10	0.2177(4)	0.2518(3)	0.56636(8)	4.06(5)	H14c	-0.3397	0.1415	0.4904	6
C11	0.0946(4)	0.2728(4)	0.53186(8)	4.24(5)	H15a	1.1632	0.2340	0.8305	5
C12	-0.1537(4)	0.0795(3)	0.55742(9)	4.44(5)	H15b	1.0910	0.3880	0.8027	5
C13	-0.0364(4)	0.0538(4)	0.59230(8)	4.41(5)	H15c	1.1912	0.2245	0.7826	5
C14	-0.2264(5)	0.2223(4)	0.49103(9)	5.25(6)	H16a	0.6793	0.1799	0.8444	6
C15	1.1031(4)	0.2652(4)	0.80442(8)	4.11(5)	H16b	0.9003	0.1190	0.8597	6
C16	0.8014(4)	0.1148(4)	0.83738(8)	4.82(6)	H16c	0.7625	-0.0024	0.8322	6

**Table III**—Bond distances of **1** with esds in parentheses

Atom	Distance/Å	Atom	Distance/Å
N1-C11	1.352(3)	C4-C5	1.394(3)
N1-C12	1.338(3)	C4-C7	1.444(3)
N1-C14	1.469(3)	C5-C6	1.375(3)
N2-C1	1.360(3)	C7-C8	1.347(3)
N2-C15	1.448(3)	C8-C9	1.444(3)
N2-C16	1.448(3)	C9-C10	1.398(3)
C1-C2	1.420(3)	C9-C13	1.404(3)
C1-C6	1.411(3)	C10-C11	1.360(3)
C2-C3	1.366(3)	C12-C13	1.354(4)
C3-C4	1.406(3)		

**Table IV**—Bond angles of **1** with esds in parentheses

Atom	Angle/°	Atom	Angle/°
C11-N1-C12	119.2(2)	C5-C4-C7	120.4(2)
C11-N1-C14	119.9(2)	C4-C5-C6	122.3(2)
C12-N1-C14	120.7(2)	C1-C6-C5	121.2(2)
C1-N2-C15	120.8(2)	C4-C7-C8	127.3(2)
C1-N2-C16	121.5(2)	C7-C8-C9	125.5(2)
C15-N2-C16	117.7(2)	C8-C9-C10	124.4(2)
N2-C1-C2	121.4(2)	C8-C9-C13	119.9(2)
N2-C1-C6	122.1(2)	C10-C9-C13	115.7(2)
C2-C1-C6	116.4(2)	C9-C10-C11	120.9(2)
C1-C2-C3	121.4(2)	N1-C11-C10	121.5(2)
C2-C3-C4	122.0(2)	N1-C12-C13	121.6(2)
C3-C4-C5	116.6(2)	C9-C13-C12	121.2(2)
C3-C4-C7	123.0(2)		

Table V—Torsion angles of dye I

Atom	Angle/ Å	Atom	Angle/ Å
C12-N1-C11-C10	0.28 (0.38)	C3-C4-C5-C6	-0.74 (0.33)
C14-N1-C11-C10	175.56(0.25)	C7-C4-C5-C6	176.59(0.21)
C11-N1-C12-C13	-0.48 (0.38)	C3-C4-C7-C8	-2.91 (0.38)
C14-N1-C12-C13	-175.73(0.25)	C5-C4-C7-C8	179.93(0.33)
C15-N2-C1-C2	172.90(0.21)	C4-C5-C6-C1	-1.20 (0.35)
C15-N2-C1-C6	-7.33 (0.34)	C4-C7-C8-C9	174.44(0.23)
C16-N2-C1-C2	-6.79 (0.34)	C7-C8-C9-C10	-0.75 (0.39)
C16-N2-C1-C6	172.98(0.22)	C7-C8-C9-C13	-179.20(0.24)
N2-C1-C2-C3	178.12(0.21)	C8-C9-C10-C11	-178.17(0.24)
C6-C1-C2-C3	-1.66 (0.32)	C13-C9-C10-C11	0.35 (0.37)
N2-C1-C6-C5	-177.43(0.21)	C8-C9-C13-C12	178.04(0.24)
C2-C1-C6-C5	2.35 (0.32)	C10-C9-C13-C12	-0.55 (0.36)
C1-C2-C3-C4	-0.23 (0.35)	C9-C10-C11-N1	-0.23 (0.40)
C2-C3-C4-C5	1.45 (0.33)	N1-C12-C13-C9	0.63 (0.41)
C2-C3-C4-C7	-175.81(0.22)		

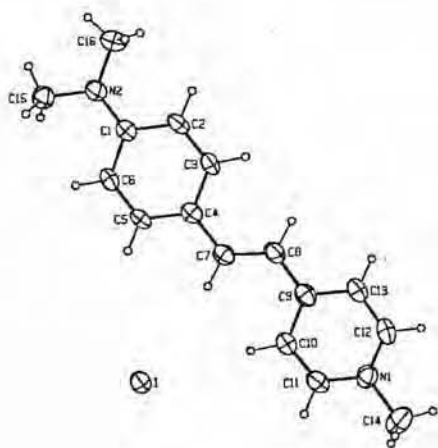


Figure 1—A perspective structural view of the molecule with atomic numbering scheme.

[ N1, C11, C10, C9, C13, C12:  $\Sigma(\Delta/\sigma)^2 = 2.7$ ] is  $10.47(3)^\circ$ . The molecules are packed in the crystal by the possible weak C-H $\cdots$ I intramolecular interaction with C7 and C10 [C7 $\cdots$ I, 4.138(5), H7-I, 3.224(5) Å, C7-H7 $\cdots$ I,  $159.7(5)^\circ$ ; C10 $\cdots$ I, 4.008(5), H10-I 3.076(5) Å, C10-H10 $\cdots$ I,  $164.1(5)^\circ$ ] and intermolecular interaction with C11 of the inverse related molecule [C11 $\cdots$ I, 4.720(5), H11-I, 3.014(5) Å, C11-H11 $\cdots$ I,  $148.6(5)^\circ$ ]. The X-ray model shows that the molecule has trans- configuration.

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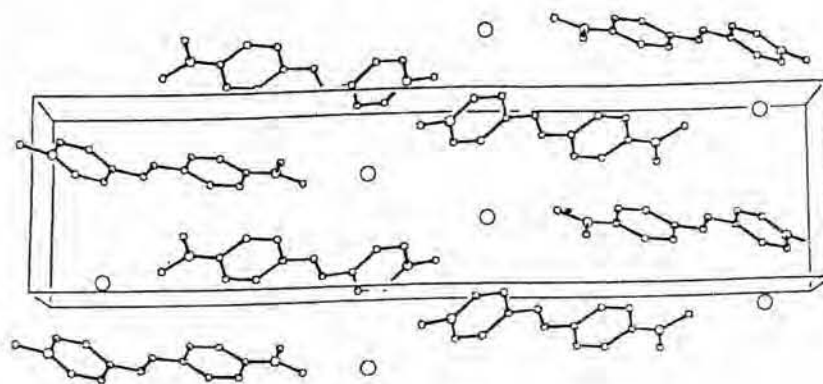


Figure 2—Stereoscopic drawing of the packing of molecule in the monoclinic modification.

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