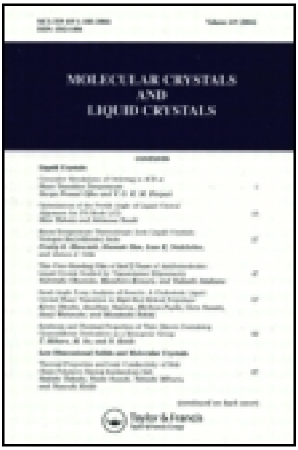

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The crystal structure and spectroscopic characterization of 1-(N-ethyl-1-sulphonate-4-pyridinio)-2-[N-methylpyrrol-2-yl]ethene

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The crystal structure and spectroscopic characterization of 1-(*N*-ethyl-1-sulphonate-4-pyridinio)-2-[*N*-methylpyrrol-2-yl]ethene

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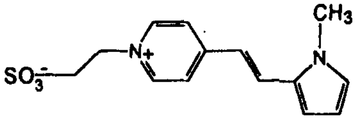
The X-ray structure of 1-(*N*-ethyl-1-sulphonate-4-pyridinio)-2-[*N*-methylpyrrol-2-yl]ethene • H_2O is reported. The molecule belongs to the spatial group $P2_1/n$ with unit cell constants $a = 6.841(5)$, $b = 21.259(5)$, $c = 10.195(5)$, $\beta = 110.262(15)°$. The compound was characterized by means of UV-vis and steady-state fluorescence spectroscopies. In the visible region the powder shows a blue shift of the main absorption band with respect to the solution. Analogously a marked red shift and decrease of intensity is observed in the fluorescence spectra. Packing effects are most likely at the origin of the difference. The molecule is expected to have promising proprieties for two-photon pumped (TPP) frequency-upconversion lasing experiments.

Keywords: Dye; H-aggregate; Solid State; X-Ray structure; TTP

INTRODUCTION

Devices for the upconversion of the laser frequencies from longer wavelengths in the IR region to shorter ones in the UV-vis region have been succesfully developed in recent years. Some organic dyes exhibit large two-photon absorption (TPA) cross-section and strong frequency-upconversion emission [1–5]; by promoting two-photon excitation in these dyes, it is possible to observe two-photon pumped (TPP) cavity lasing effect with high efficiency. The dye that has been studied in this work, 1-(*N*-ethyl-1-sulphonate-4-pyridinio)-2-[*N*-methylpyrrol-2-yl]ethene (CH_3-ESPPE), **1**, may be considered a zwitterionic derivative of the cation 1-(*N*-methyl-4-pyridinio)-2-(*N*-methylpyrrol-2-yl)ethene. A previous study of the latter has shown that in DMSO solutions a low lasing threshold and high lasing efficiency is observed upon pumping with a 800 nm laser beam for TPP cavity lasing at 543 nm [1]. Nevertheless, interesting optical properties which appear in solution have not been tested as yet in anisotropic environment like thin solid films [6] and single crystals of the dyes. TPP cavity lasing experiments on single crystals could permit better understanding of the molecular mechanisms at the origin of the important optical properties. In particular possible relationships with the molecular packing, and indirectly with the electronic density distribution, within the crystal, could be found. Having this goal in mind, the crystal structure analisys of **1** has been determinated and is reported in this work, together with the absorption and emission properties of the dye, both in solution and in powder samples.



SCHEME 1

EXPERIMENTAL DETAILS

The compound 1-(*N*-ethyl-1-sulphonate-4-pyridinio)-2-[*N*-methylpyrrol-2-yl]ethene ($C_{16}H_{33}$-ESPPE), **1**, was synthesized according to the procedure described elsewhere [7]. The compound was handled by avoiding as much as possible the exposure to the visible light in order to prevent the dimerization reaction between the ethene groups of the molecules. Photoinduced production of cyclobutane adduct has been already reported for similar compounds [8–10]. Organic solvents were of analytical grade and supplied by Fluka.

UV-vis absorption spectra were recorded using a Perkin Elmer Lambda 5 spectrophotometer. Steady-state fluorescence spectra were obtained using a Perkin Elmer LS50 spectrofluorimeter.

Diffraction data were collected at room temperature on a Philips PW1100 diffractometer. The cell dimensions were refined by the least-squared fitting of 25 reflections in the θ range of 6–15°. The intensity data were corrected for Lorentz and polarization effects. Atomic scattering factors are taken from ref. [11]. The structure was solved by combined Patterson and Fourier methods. All computational work was carried out on a Digital DEC 2000 AXP workstation using the program SHELX96[12]. The program ZORTEP was also used for molecular drawings [13]. Refinement was carried out by means of full matrix least-square calculations, initially attributing isotropic thermal parameters to all atoms. In the final least-squared cycles of the refinement, anisotropic thermal parameters were used for all non-hydrogen atoms. The hydrogens atom positions with the exception of the hydrogen atoms of the water molecule were localized from ΔF Fourier syntheses and refined with the isotropic thermal parameters. No unusual trend in ΔF vesus F_0 or (sinθ/λ) was observed. A final difference syntheses showed no significant electron density residues. Listing of fractional atomic coordinates, anisotropic thermal parameters of all atoms and structure factors are provided as supplementary material. The crystal data and data-collection details are reported in table I.

TABLE I Crystal data and structure refinement for **1**

Empirical formula	C14 H18 N2 04 S
Formula weight	310.37
Temperature	293(2) K
Wavelength	1.54180 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 6.841(5) Å alpha = 90.000(15) deg
	b = 21 259(5) Å beta = 100 262(15) deg
	c = 10.195(5) Å gamma = 90.00(3) deg
Volume	1459.0(13) $Å^3$
Z	4
Density (calculated)	1.404 Mg/m^3
Absorption coefficient	2.139 mm^{-1}
F(000)	648
Crystal size	0.2 × 0. 1 × 0.04 mm
Theta range for data collection	4.16 to 60.01 deg
Index ranges	−7<=h<=7, −3<=k<=23, −2<=l<=11
Reflections collected	2305
Independent reflections	2172 [R(int) = 0.0204]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2172/0/254
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0586, wR2 = 0.1580
R indices (all data)	R1 = 0.0660, wR2 = 0.1690
Largest diff. peak and hole	0.431 and −0.522 e Å −3

RESULTS AND DISCUSSION

X-Ray Structure

Fig. 1 shows a perspective view of the zwitterion 1. Selected bond distance and angle are given in Table II. The pyridinium, pyrrol, and ethene fragments are almost coplanar with torsion angles in the range of 5–12 degree. The torsion angle of the chain connecting the two rings [C(5), C(8), C(9), C(10)] is 178°. The bond distances C(5)-C(8) and C(9)-C(10) are 1.44 Å and 1.45 Å respectively and support the idea of π–conjugation between the pyridinium and pyrrol rings. Hydrogen bonding between the water of crystallization [atom O(4)] and the atoms O(1) and O(2) of the sulphonate group is shown by the short contacts of 2.918 Å and 2.919 Å respectively. The picture in Fig. 2 shows evidence that the π–conjugated planes of the dyes are stacked in a deck-of-cards fashion [14]. The stacking is of ABAB type: the pyriolinium ring of molecule A stacks above the pyrrol ring of the molecule B along the a-axis. The third molecule is closely aligned to the first one. The angle between the molecule's axis and that through of centers of the stacked molecules is 84°. The distance between the plane A and B is 3.42 Å. The shortest intermolecular contacts of about 3.35 Å are between the atoms N(2) – C(6) and C(13) - C(7). This packing can be ascribed to the so-called H-aggregates. [14]

TABLE II Selected bond lengths [Å] and angles [deg] for 1

C(2)-N(1)	1.476(4)
N(1)-C(3)	1.339(4)
N(1)-C(7)	1.359(4)
N(2)-C(13)	1.351(4)
N(2)-C(10)	1.380(4)
N(2)-C(14)	1.460(4)
C(3)-C(4)	1.364(4)
C(4)-C(5)	1.412(4)
C(5)-C(6)	1.399(4)
C(5)-C(8)	1.445(4)
C(6)-C(7)	1.365(4)
C(8)-C(9)	1.344(4)
C(9)-C(10)	1.445(4)
C(10)-C(11)	1.380(4)

C(11)-C(12)	1.398(5)
C(12)-C(13)	1.367(5)
C(3)-N(1)-C(2)	121.5(3)
C(13)-N(2)-C(10)	108.8(2)
N(1)-C(3)-C(4)	121.3(3)
N(1)-C(7)-C(6)	121.1(3)
C(9)-C(8)-C(5)	123.1(3)
C(8)-C(9)-C(10)	124.5(3)
N(2)-C(10)-C(11)	107.0(3)
N(2)-C(10)-C(9)	121.3(3)
C(11)-C(10)-C(9)	131.7(3)

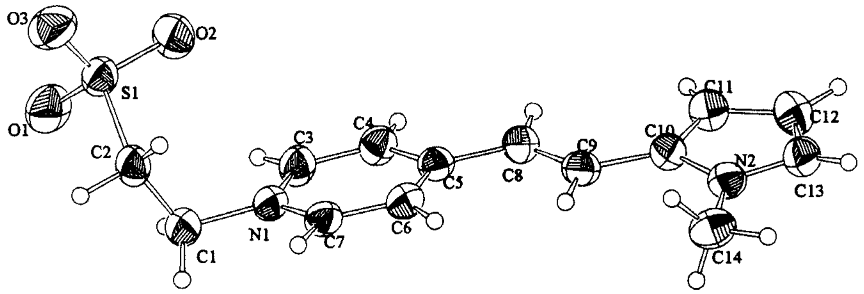


FIGURE 1 Perspective view of **1**. ZORTEP drawing with 30% probability ellipsoid

Uv-Vis Characterization

The UV-vis spectra of **1** show a high intensity absorption band ($\varepsilon = 2.7 \pm 0.4 \cdot 10^4$ $M^{-1}cm^{-1}$) in solution (fig. 3). This band is negatively solvatochromic, namely it is hypsochromically shifted with the increasing polarity of the solvent: in DMSO, for example, it appears at $\lambda_{max} = 438$ nm, while is at $\lambda_{max} = 447$ in ethanol. This behavior is consistent with a transition from a polar ground-state to a less dipolar excited state. These features make the compound an interesting candidate for studies in the field of the non-linear optics. Fig. 3 reports the electronic spectrum of a powder sample of **1**. An absorption band is present at λ_{max}= 413 nm that corresponds to the 438 nm band found in the DMSO solution; As suggested [15–19] the blue-shift of the band in the visible region can be attributed to intermolecular interactions such as those observed in the packed structure of the solid.

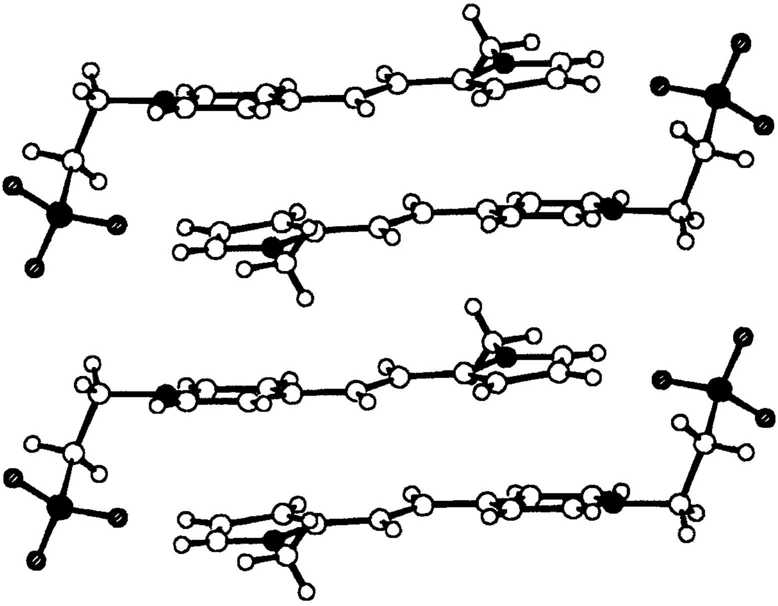


FIGURE 2 Perspective view of the packing of **1**

Fluorescence Measurements

The fluorescence emission spectra of both the powder and the DMSO solution of compound **1** are shown in fig. 4. The emission band presents its maximum at about 524 nm for the solution; the powder sample of **1** presents an emission band with λ_{max} = 595 nm, markedly red shifted with respect to the solution; moreover, although a quantitative determination of fluorescence intensity has not been performed, the fluorescence emission of the powder is strongly quenched with respect to that of the solution. These emission features are also consistent with the packing mode of the chromophore in the powder; similar results were obtained for Langmuir-Blodgett films of the amphiphilic derivative of the same chromophore[6]; a detailed investigation of the emission behavior of this compound by means of time-resolved fluorescence spectroscopy is in progress. The emission features of **1** in solution are almost identical to those of 1-(*N*-methyl-4-pyridinio)-2-(*N*-methylpyrrol-2-yl)ethene, which were the shown to be very efficient for TPP frequency upconversion of 800 nm light [1]; the usage of LB films of **1** could show some new opportunities for other applications in this relatively new field of applied optics.

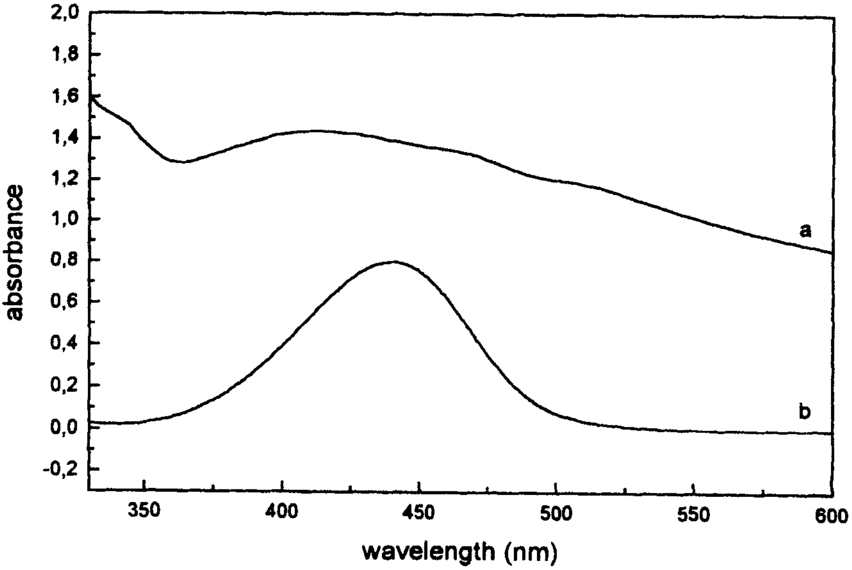


FIGURE 3 UV-vis absorption spectra of **1** as a powder (a) and in DMSO solution (b)

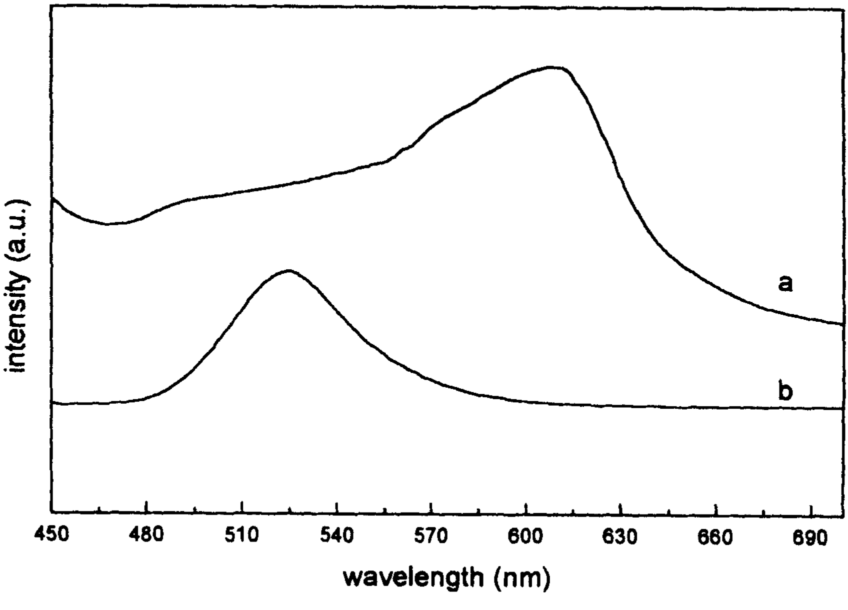


FIGURE 4 Fluorescence emission spectra (λ_{exc} = 410 nm) of : (a) powder of **1**; (b) DMSO solution of **1**

CONCLUSIONS

The X-ray analisys of single crystal of 1 clearly shows that in the solid state the pyridinium ring portion of the dye stacks above the pyrrol ring of the next molecule according to ABAB packing along the a axis of the cell. The π-conjugated planes of the molecules are parallel to each other. This packed structure can be ascribed to the so-called H-aggregates[14–19]; the blue-shift of the visible absorption band, and the corresponding red-shift of the fluorescence emission band of the powder with respect to that of the solution, seem to confirm this hypothesis. Further investigation is in progress in order to find a close correlation between the packed structure and the UV-vis and fluorescence emissions of the crystal. This compound is very promising for two-photon pumped (TPP) frequency up-conversion of 800 nm laser light. The comparison of TPP data from crystals, thin solid organized films like Langmuir-Blodgett films [6], and isotropic solutions could help in interpreting this peculiar optical effect, possibly through the correlation of the optical properties of the compound with its electronic structure.

SUPPLEMENTARY MATERIAL

Tables of fractional coordinates and isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters, and hydrogen coordinates and isotropic displacement parameters for **1** (10 pages) are available from the authors on request.

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