

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



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

Synthesis, spectroscopic and structural elucidation of 1-butyl-4-[2-(3,5-dimethoxy-4-hydroxyphenyl)ethenyl)]pyridinium chloride tetrahydrate

B.B. Koleva^{a,b}, T. Kolev^{a,*}, M. Lamshöft^a, H. Mayer-Figge^b, W.S. Sheldrick^b, M. Spiteller^a

^a Institut für Umweltforschung, Universität Dortmund, Otto-Hahn-Strasse 6, 44221 Dortmund, Germany

^b Lehrstuhl für Analytische Chemie, Ruhr-Universität Bochum, Universitätsstraße 150, 44780 Bochum, Germany

ARTICLE INFO

Article history: Received 5 December 2008 Received in revised form 21 August 2009 Accepted 12 September 2009

Keywords: 1-Butyl-4-[2-(4hydroxyphenyl)ethenyl)]pyridinium] chloride tetrahydrate Single crystal, X-ray data, Solid-state linear-polarized IR-spectroscopy, UV-vis, MS, TGA and DTA

ABSTRACT

The novel chloride salt of 1-butyl-4-[2-(4-hydroxyphenyl)ethenyl)]pyridine (1), has been synthesized as the tetrahydrate and its structure and properties elucidated in detail spectroscopically, thermally and structurally, using single crystal X-ray diffraction, linear-polarized solid-state IR-spectroscopy, UVspectroscopy and mass spectrometry. Quantum chemical calculations were performed with a view to supporting and explaining the experimental structural and spectroscopic data. The compound (1) crystallizes in triclinic P1 space group and its unit cell contains two independent 1-butyl-4-[2-(3,5dimethoxy4-hydroxyphenyl)ethenyl)|pyridinium] cations, differing with respect to the butyl chain torsion angle for which values of $80.0(9)^{\circ}$ and $173.6(3)^{\circ}$ are observed. The cations and anions are joined into infinite layers, formed by two different dimers and including solvent molecules. Hydrogen bonds OH...OH₂ (2.814 Å), HOH...O(CH₃) (2.960 Å), OH...Cl (2.967 Å), HOH...Cl⁻ (3.034, 3.188, 3.161 and 3.062 Å) and HOH...OH₂ (2.772 Å) are observed. For first time in the literature, we are reporting the crystal structure of the dye with the syring-fragment in the molecule. The spectroscopic properties of the novel compound are compared and with those of the corresponding quinoide form (2). Both the forms (1) and (2) are characterized by 21 and 140 nm solvatochromic effects depending of the type of the solvent. The UV-spectroscopic data in solution confirm the formation of classical H-aggregates in polar protic solvent mixture.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Pyridinium salts have received considerable attention during the past 30 years, due to many of their derivatives possessing large second order molecular hyperpolarisability. Studies of the second harmonic generation (SHG) from powders and Langmuir–Blodgett films of these merocyanine dyes have been performed due to their application in various areas of non-linear optics. Second order nonlinear optical properties of these materials are very sensitive to the symmetry of the structure [1–4]. It has been found that the variation of the counterion in organic salts is a simple and highly successful approach to creating materials with larger χ values. This methodology has been also supported by the obtained crystal structure and properties of DAST [1].

As a part of our systematic study of organic dyes [5–9], we now present a spectroscopic and structural elucidation of the newly synthesized 1-butyl-4-[2-(3,5-dimethoxy4-hydroxyphenyl)ethenyl)]

pyridinium] chloride tetrahydrate and its quinoide form, obtained after deprotonation of the 4-OH group (Scheme 1, Table 1). The relationship between the structure and the spectroscopic properties has been elucidated using the single crystal X-ray diffraction, UV-vis and fluorescence methods, polarized linear-dichroic infrared (IR-LD) spectroscopy of oriented colloid suspensions in a nematic liquid crystal, mass spectrometry, and TGV and DSC methods.

2. Experimental

2.1. Materials and methods

X-ray diffraction intensities were measured in the ω scan mode on a Siemens P4 diffractometer equipped with MoK α radiation ($\lambda = 0.71073$ Å, $\theta_{max} = 25^{\circ}$). The structure was solved by direct methods and refined against F^2 [30,31]. An ORTEP plot illustrates the anion and cation structures at the 50% probability level. Relevant crystallographic structure data and refinement details are presented in Table 2, selected bond distances and angles in Table 3. The hydrogen atoms were constrained to calculated posi-

^{*} Corresponding author. Tel.: +44 0 231 755 7069. *E-mail address:* kolev@orgchm.bas.bg (T. Kolev).

^{1386-1425/\$ -} see front matter © 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2009.09.020



Scheme 1. Chemical diagram of stubazolium salts.

tions and refined using riding models in all cases. The *IR-spectra* were measured on a Thermo Nicolet OMNIC FTIR-spectrometer (4000–400 cm⁻¹, 2 cm⁻¹ resolution, 200 scans) equipped with a Specac wire-grid polarizer. Non-polarized solid-state IR-spectra were recorded using the KBr disk technique. The *oriented samples* were obtained as a suspension in a nematic liquid crystal (MLC 6815, Merck) with the presence of an isolated nitrile stretching IR-band at about 2245 cm⁻¹ additionally serving as an orientation indicator. The theoretical approach as well as the experimental technique for preparing the samples, and procedures for polarized IR-spectra interpretation and the validation of this new linear-dichroic infrared (IR-LD) orientation solid-state method

Table 1

Crystal structures of stubazolium salts with formulae, given in Scheme 1.

for accuracy, precision and the influence of the liquid crystal medium on peak positions and integral absorbances of the guest molecule bands have been presented [32-35]. The nature and balance of the forces in the nematic liquid crystal suspension system, the mathematical model for their clearance, the morphology of the suspended particles and the influence of the space system types on the degree of orientation (*i.e.* ordering parameter) have been demonstrated [35] using five liquid crystals and fifteen compounds. The applicability of the latter approach to experimental IR-spectroscopic band assignment as well as in obtaining stereo-structural information has been demonstrated for a series of organic systems and coordination complexes of heterocyclic ligands, Cu(II) complexes, polymorphs, codeine derivatives, Au(III) peptide complexes and their hydrochlorides and hydrogensquarates [36–39]. The theory of IR-LD spectroscopy and the employed polarized IR-spectra interpretation differencereduction procedure are given in Refs. [40-43]. FAB mass spectra were recorded on a Fisons VG Autospec instrument employing 3nitrobenzylalcohol (Sigma-Aldrich) as the matrix. Ultraviolet (UV-) spectra were recorded on Tecan Safire Absorbance/Fluorescence XFluor 4V 4.40 spectrophotometer operating between 190 and

R ₁	R ₂	R ₃	Х	CCDC code ^a [ref.]
CH ₃	Н	Н	(+)-Camphor-10-sulfonate	BOJWAY [10]
CH ₃	OH	Н	Toluene-p-sulfonate	JOYBEE [11], JOYBEE10 [12]
CH ₃	OCH ₃	Н	Bromobenzenesulfonate	LANLAO [13]
CH₃	Н	Н	Triiodide iodide	LIBZEC [14]
2-Hydroxyethyl		Н	2,4-dihydroxyacetophenone	NUPFUZ ^b [15]
Butyl	OH	Н	Cl-	OMIXAJ [16]
CH₃	OCH ₃	Н	P-toluenesulfonate	OMIXUD [17], VIJPAF [18]
CH₃	OCH ₃	Н	Chlorobenzenesulfonate	WAQNOS [19]
CH₃	OCH ₃		I-	QAWMIK [20]
2-Hydroxyethyl	Н		I-	QIGHET [21]
CH₃	Н			SIFFAO ^b [22]
2-Hydroxyethy	Н			SUJKUD ^b [23]
CH ₃	Н		Tetraphenylborate dimethylsulfoxide solvat	TAQQEI [24]
CH₃	Н		2-Amino-4-nitrophenol	TEBLUH, TEBMAO [25]
2-Hydroxyethy	Н		2,4-Dihydroxybenzaldehyde	TETQAK [26]
CH₃	OCH ₃		I-	TOHGIG [27]
CH₃	Н		Bromide iodide	YIFPIN [28]
CH₃	Н		Hydrogensquarate	[29]
CH₃	Н	Н	Hydrogenphosphate	[9]
Butyl	OCH ₃	OCH ₃	Cl-	(1)

^a CCDC: Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk/).

Table 2

^b Quinoide form (2) in Scheme 2, of the dyes obtained after deprotonation of the 4-OH group.

Empirical formula	$C_{38}H_{48}C_{12}N_2O_6$	
Formula weight	699.68	
Temperature	294(2)K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, P1	
Unit cell dimensions	<i>a</i> = 12.587(8)Å	$\alpha = 97.01(2)^{\circ}$
	<i>b</i> = 12.753(6)Å	$\beta = 115.64(5)^{\circ}$
	c = 14.269(8)Å	$\gamma = 90.61(3)^{\circ}$
Volume	2044(2)Å ³	
Ζ	2	
Calculated density	1.137 mg/m ³	
Absorption coefficient	$0.201 \mathrm{mm^{-1}}$	
F(000)	744	
Crystal size	$0.21mm \times 0.33mm \times 0.12mm$	
θ Range for data collection	1.81-25.00°	
Limiting indices	−1<= <i>h</i> <=14, −15<= <i>k</i> <=15, −16<= <i>l</i> <=15	
Reflections collected/unique	8131/7086 [<i>R</i> (int)=0.0248]	
Refinement method	Full-matrix least-squares on F ²	
Goodness-of-fit on F ²	1.509	
Final R indices $[I > 2\sigma(I)]$	R1 = 0.1035, wR2 = 0.2559	
R indices (all data)	R1 = 0.1794, wR2 = 0.2961	

Table 3

Selected bond lengths (Å) and angles ($^{\circ}$) for (1).

N1 C11 1.316(7)	O3 C12 1.341(6)	C12 C18 1.377(8)	C27 C35 1.395(7)
N1 C9 1.345(7)	O4 C39 1.361(6)	C13 C17 1.376(7)	C28 C29 1.374(8)
N1 C7 1.476(6)	O4 C24 1.431(7)	C14 C17 1.397(8)	C28 C35 1.380(7)
O1 C18 1.379(7)	C4 C7 1.492(9)	C40 C18 1.360(7)	C30 C33 1.301(7)
O1 C5 1.431(8)	O5 C37 1.373(6)	C40 C20 1.394(8)	C30 C34 1.474(7)
N2 C32 1.324(6)	O6 C36 1.365(6)	C16 C19 1.309(7)	C31 C39 1.383(7)
N2 C29 1.326(7)	O6 C25 1.437(6)	C16 C20 1.447(7)	C31 C34 1.391(8)
N2 C26 1.470(6)	C8 C10 1.391(7)	C17 C19 1.445(7)	C33 C35 1.459(7)
O2 C10 1.382(7)	C8 C20 1.393(8)	C21 C22 1.647(12)	C34 C38 1.372(8)
O2 C6 1.415(7)	C9 C14 1.359(7)	C22 C23 1.403(11)	C36 C38 1.392(7)
C2 C3 1.323(14)	C10 C12 1.372(8)	C23 C26 1.505(11)	C36 C37 1.395(7)
C2 C4 1.651(12)	C11 C13 1.344(7)	C27 C32 1.375(7)	C37 C39 1.380(7)
C11 N1 C9 118.4(5)	C12 C10 C8 120.9(6)	C16 C19 C17 126.3(6)	C38 C34 C30 123.8(5)
C11 N1 C7 121.7(5)	O2 C10 C8 124.3(6)	C8 C20 C40 119.5(5)	C31 C34 C30 116.0(5)
C9 N1 C7 119.9(5)	N1 C11 C13 122.7(6)	C8 C20 C16 121.2(6)	C28 C35 C27 116.0(5)
C18 O1 C5 118.4(5)	O3 C12 C10 119.5(6)	C40 C20 C16 119.4(6)	C28 C35 C33 120.1(5)
C32 N2 C29 120.3(5)	O3 C12 C18 121.4(6)	C23 C22 C21 109.5(9)	C27 C35 C33 123.9(5)
C32 N2 C26 119.6(5)	C10 C12 C18 119.1(5)	C22 C23 C26 111.2(8)	O6 C36 C38 126.3(5)
C29 N2 C26 120.1(5)	C11 C13 C17 121.4(6)	N2 C26 C23 111.3(5)	O6 C36 C37 113.6(4)
C10 O2 C6 116.8(5)	C9 C14 C17 120.7(5)	C32 C27 C35 120.7(5)	C38 C36 C37 120.1(5)
C3 C2 C4 111.7(11)	C18 C40 C20 119.8(6)	C29 C28 C35 121.0(5)	O5 C37 C39 117.6(5)
C39 O4 C24 118.0(4)	C19 C16 C20 128.6(6)	N2 C29 C28 121.1(5)	O5 C37 C36 122.1(5)
C7 C4 C2 107.8(7)	C13 C17 C14 115.4(5)	C33 C30 C34 128.7(6)	C39 C37 C36 120.3(5)
C36 O6 C25 117.5(4)	C13 C17 C19 121.0(5)	C39 C31 C34 120.8(5)	C34 C38 C36 119.5(5)
N1 C7 C4 110.3(5)	C14 C17 C19 123.6(5)	N2 C32 C27 120.9(5)	O4 C39 C37 115.4(4)
C10 C8 C20 119.1(6)	C40 C18 C12 121.5(6)	C30 C33 C35 124.9(6)	O4 C39 C31 125.4(5)
N1 C9 C14 121.4(5)	C40 C18 O1 125.1(6)	C38 C34 C31 120.2(5)	C37 C39 C31 119.2(5)
C12 C10 O2 114.7(5)	C12 C18 O1 113.4(5)		

900 nm, using water, methanol, dichloromethane, tetrahydrofuran, acetonitrile, acetone, 2-propanol and ethyl acetal as solvents (all Uvasol, Merck products) at concentrations of 2.5×10^{-5} M, in 0.921 cm quarz cells. Quantum chemical calculations were performed using the GAUSSIAN 98 and Dalton 2.0 program packages [44,45] with visualization being done by the ChemCraft program [46]. The geometries of the cationic and quinoide forms of the dye were optimized at two different levels of theory: Restricted Hartree-Fock (RHF) and density functional theory (DFT) using the 6-311++G** basis set. In the second case the B3LYP method, which combines Becke's three-parameter non-local exchange functional with the correlation function of Lee, Yang and Parr was applied. Molecular geometries of the studied species were fully optimized by the force gradient method using Bernys' algorithm. For every structure the stationary points found on the molecule potential energy hypersurfaces were characterized using standard analytical harmonic vibrational analysis. Absence of imaginary frequencies and negative eigenvalues of the second-derivative matrix confirmed that the stationary points correspond to minima of the potential energy hypersurfaces. The calculations of vibrational frequencies and infrared intensities were checked to establish which kind of performed calculations agreed best with the experimental data. A modification of the results using the empirical scaling factor 0.9614 was performed with a scaling factor of 0.8929 being used in the case of HF calculations. The solvent effects on the absorption bands were studied at the TD [47] DFT level of theory combined with the polarized continuum model (PCM) [48-50]. The thermal analyses were carried out in the 25–300 °C range with a Differential Scanning Calorimeter PerkinElmer DSC-7 and a Differential Thermal Analyzer DTA/TG (Seiko Instrument, model TG/DTA 300). The experiments were performed at a scanning rate of 10 K/min under an argon atmosphere. The *elemental analysis* was carried out according to the standard procedures for C and H (as CO_2 , and H_2O) and N (by the Dumas method).

2.2. Synthesis

1-methyl-4-butylpyridinum The starting compounds, chloride and 4-syringaldehyde, for the synthesis of 1-butyl-4-[2-(3,5-dimethoxy-4-hydroxyphenyl)ethenyl)]piridinium] chloride tetrahydrate were Merck (Germany) products. 2.3500 g (10.0 mmol) of the first compound is mixed with 1.2200 g (10.0 mmol) of the aldehyde in 50.0 ml toluene. 5.00 ml acetic acid and 0.77 g (10.00 mmol) ammonium acetate are then added to the reaction mixture and the resulting suspension is stirring for 24 h at room temperature. Then 0.50 ml c. HI acid and 10.00 ml ethanol are added and the reaction mixture is left to stand for 16h at room temperature. The resulting orange crystalline precipitate is filtered off, washed with C₂H₅OH and dried on P₂O₅ at 298 K. Yields 61%. Found: C, 54.10; H, 7.66; N, 3.31; [C₁₉H₃₂NO₇Cl] calcd.: C, 54.09; H, 7.64; N, 3.31%. TGV and DSC analysis in the range 300–500 K showed that (1) contains four water molecules, on the basis of the observed weight loss of 17.01%. The obtained enthalpy effect of 28.01 kcal/mol, proved



Scheme 2. Scheme for obtaining of quinoide form (2), using the novel compounds (1).

TGA data additionally. The most intensive signal in the mass spectrum of the title compound is that of the peak at m/z 314.71, corresponding to the singly charged cation $[C_{19}H_{24}NO_3]^+$ with a molecular weight of 314.40. 1-Methyl-4-[2-(3,5-dimethoxy-4-oxocyclohexadienylidene)ethylidene]-1,4-dihydropyridine (2) (Scheme 2) can be prepared in the following way: 10.0 mg of the salt (1) are dissolved in 10.00 mmol ethanol and then 5 ml 1.0 M KOH are added. The resulting violet solution is heated for 2 h at a temperature of 70°C and then is left to stand at 4°C for 16h. The resulting violet precipitate is filtered off and dried on P₂O₃ at 298 K. Yield 88%. Found: C, 72.80; H, 7.38; N, 4.47; [C₁₉H₂₃NO₃] calcd.: C, 72.82; H, 7.40; N, 4.47%. TGV and DSC analysis in the range 300-500 K showed that no solvent molecules were included in compound 2. The most intensive signal in the mass spectrum of (2) is that of the peak at m/z 314.27, corresponding to the singly charged cation $[C_{19}H_{24}NO_3]^+$ with a molecular weight of 314.40.

3. Results and discussion

1-Butyl-4-[2-(3,5-dimethoxy-4-hydroxyphenyl)ethenyl)]pyridinium] chloride tetrahydrate crystallizes in the triclinic space group $P\bar{1}$ (Fig. 1). The unit cell contains two crystallographically independent 1-butyl-4-[2-(3,5-dimethoxy4-hydroxyphenyl)ethenyl)pyridinium] cations, which exhibit torsion angles of 80.0(9)° and 173.6(3)°, respectively, in their butyl chains (H₃CCH₂CH₂CH₂) (Fig. 1). The molecules are joined into infinite layers, formed by two different dimers of the cations, anions and included solvent molecules (Fig. 2). The observed hydrogen bonds are $OH \cdots OH_2$ (2.814 Å), $HOH \cdots O(CH_3)$ (2.960 Å), OH...Cl (2.967 Å), HOH...Cl[−] (3.034, 3.188, 3.161 and 3.062 Å) and HOH. OH_2 (2.772 Å), respectively (Fig. 2). The 4-[2-(3,5dimethoxy-4-hydroxyphenyl)ethenyl)]pyridinium] fragment of the cation is effectively flat with a deviation from total planarity of only 0.2°. The bond lengths and angles of the benzene ring and the pyridine fragment are all in accordance with aromatic character, similar to those of previously reported structures of this class of compounds (Table 1). The corresponding values of the geometrical parameters (Table 3) correlate well with those of other merocyanine dyes given in Table 1. The typically observed crystallographic disorder of the double bond in these dyes is due to the presence of tautomers with either a formally single central bond or a formally double central bond. In our case only disorder of the anions is observed. Like other dyes [51,52], this disorder led to the relatively high observed R factor (Table 2).

The theoretical conformational analysis of the cationic form of compound (1) and its neutral form (2) (Scheme 3) shows that



Fig. 1. The molecular structure of 1-butyl-4-[2-(3,5-dimethoxy4-hydroxyphenyl)ethenyl)]pyridinium] chloride tetrahydrate, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.



Fig. 2. Linkage of the molecules of 1-butyl-4-[2-(3,5-dimethoxy-4-hydroxyphenyl)ethenyl)]pyridinium] chloride tetrahydrate.



Scheme 3. 3D graph of the Phi and Psi values vs energy (kJ/mol) for the cationic (1) and quinoide (2) forms of the dye 1-butyl-4-[2-(3,5-dimethoxy4-hydroxyphenyl)]pyridine.

in both cases the conformer with torsion angles of $178.9(1)^{\circ}$ and $179.9(0)^{\circ}$, respectively (Scheme) in the butyl chain is energetically favourable. The corresponding energies are 0.1 and 0.0 kJ/mol. These data suggest that the presence of a conformer in solid state with a torsion angle for the discussed chain of $80.0(9)^{\circ}$ is the result of the steric effects in the condensed phase.

The observed significant degree of macro-orientation in the polarized IR-spectrum of the sample facilitates an adequate interpretation of the polarized IR-data and results from the presence of a pseudo layer structure, which adopts a macro-orientation in the solid phase toward the orientation director (\mathbf{n}) of the liquid crystal. The detailed IR-LD spectroscopic analysis is supported by the theoretical vibrational analysis at the B3LYP/6-311++G** level. The non-polarized IR-spectrum shows a relatively intensive band at 3383 cm⁻¹ corresponding to the stretching v_{OH} vibration of the hydrogen bonded OH-group in the merocyanine dye, thus correlating with the experimental crystallographic data. The band at 3515 cm⁻¹ is caused by the same vibration but belongs to the water molecules of crystallisation. In the 1700–1600 $\rm cm^{-1}$ range aromatic i.p. modes of the benzene and pyridine rings were observed at $1614 \, \text{cm}^{-1} \, (\mathbf{8a}_{(\text{py})})$ and $1584 \, \text{cm}^{-1} \, (\mathbf{8a}_{(\text{Ph})})$. The absorbtion maxima belonging to the out-of-plane (o.p.) bending vibrations $\gamma_{C=C_{1}}$ and 11- γ_{CH} of the benzene ring and the o.p. mode of the pyridine ring are observed at 996, 849 and $734\,cm^{-1}$, respectively. Spectroscopic support of the experimental crystal structure is obtained by application of the reducing difference procedure to polarized IR-spectra, where the elimination of the bands at 1614 and 1584 cm⁻¹ at the same dichroic ratio occurs because the corresponding transition moments are orientated in a co-linear manner. On the other hand, the disappearance of the maxima at 996, 849 and 734 cm⁻¹ at same dichroic ratio (Fig. 3) indicates a mutually co-planar disposition of the aromatic rings and the double bond, also in good agreement with the X-ray crystal structure. This result is in accordance with other derivatives with small R₁-substituents (Table 1).

In the corresponding Raman spectrum of (1) (supplementary material Fig. S1), the series of in-plane vibrations of the benzene and pyridine rings are observed at 1616, 1584, 1561 and 1516 cm⁻¹. The out-of-plane modes at 996 and 739 cm⁻¹ are characterized by relatively low intensity, while the band at 849 cm⁻¹ is absent.

The possible redistribution of the electronic density in these compounds as typical push-pull systems depends on the solvent polarity. As far as the electron transition is connected with intramolecular charge transfer (CT) this leads to a significant difference between the dipole moment in the ground and exited state, i.e. determines their significant solvatochromism, or NLO properties in solution. Depending of the solvent polarity, the CT band in 1-butyl-4-[2-(3,5-dimethoxy-4-hydroxyphenyl)ethenyl)]pyridinium] chloride exhibits a bathochromic shift of 21 nm for λ_{max} (Fig. 4) on going from 1,2-dichloromethane to acetonitrile. The obtained negative solvatochromic effect in these compounds has been explained by both intra and intermolecular charge transfer. In contrast to (1), the quinoide form of the compound (2) is characterized by an observed solvatochromic effect of 140 nm (Fig. 4). In acetone and acetonitrile two bands at about 600 and 640 nm as well as a shoulder at about 560 nm are observed. These maxima as well as the spectral changes and the well-defined isosbestic points provide good evidence for an equilibrium between monomeric and dimeric species [9,53,54]. It is noteworthy that in addition to the very intense hypsochromically shifted absorption band for the H-dimer, a weak band appears at longer wavelength, which can be ascribed to the forbidden transition to the lower energy exciton state. It is interesting to note that these dimers are strongly affected by solvent mixtures like acetonitrile/H₂O with a band at 547 nm.



Fig. 3. Non-polarized IR-(1) and reduced IR-LD (2) spectrum of the 1-butyl-4-[2-(3,5-dimethoxy4-hydroxyphenyl)ethenyl)]pyridinium] chloride tetrahydrate after the elimination of the band at 849 cm⁻¹.



Scheme 4. Molecular orbital surface of the HOMO and LUMO for the ground state of cationic (1) and quinoide form (2) of the dye 1-butyl-4-[2-(3,5-dimethoxy-4-hydroxyphenyl)]pyridine.

The distribution of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals for the ground state is illustrated in Scheme 4. Nearly all of the MOs are substantially localized on the conjugated plane, with only small contributions to the group out of the plane in the case of (1). In contrast, the underlying CT is observed in compound (2).

For the precise investigation of the geometry changes associated with the electronic excitation, to the lowest singlet excited state, the geometry of the studied compounds was optimized at the CIS/6-31++G^{**} level of theory for comparison with the data for the ground state optimized at HF/6-31++G^{**}. The data indicate that the structural shift is predominantly localized on the conjugated plane in (1) and that the groups out of the discussed plane are not changed significantly. The distributions for the HOMO and LUMO of the lowest single exited state show a strong optical emission in case of (2).

The proton chemical shifts of both the compounds (1) and (2) are assigned in the following way (supplementary material Fig.



Fig. 4. UV-vis spectra of 1-butyl-4-[2-(3,5-dimethoxy-4-hydroxyphenyl)-ethenyl)]piridinium] chloride tetrahydrate in different media at a concentration of 2.5×10^{-5} M.

S2A), using the atom numbering Scheme 2. The OCH₃ signals are observed within the 3.75–3.85 ppm range as singlets with intensity 6H. The signals between 0.90 and 2.00 ppm belong to the aliphatic CH₃CH₂CH₂CH₂ protons. The H-2 and H-6 signals are observed at about 7.00 in (**1**) and 6.80 ppm in (**2**), respectively. The AB signals of H-7 and H-8 are at 7.35 and 7.95 ppm (**1**). The analogous signals in (**2**) are observed at 6.51 and 7.55 ppm. The AA'BB' chemical shift signals are within the 8.70–8.00 ppm (**1**) and 7.55–8.00 ppm (**2**) ranges. In the case of (**1**), the peak at 9.20 ppm can be attributed to the OH proton (supplementary material Fig. S2B). The corresponding ¹³C NMR spectra of both the compounds, exhibit OCH₃ signals at about 5.6 ppm. The peaks at about 106.00, 120.00, 122.25, 122.70, 125.60, 138.00, 140.00, 145.00, 149.00 and 152.00 ppm correspond to C-2'/C-6', C-7, C3/C5, C1', C-4', C-8, C-2/C-6, C-3'/C-5' and C-4 carbon chemical shifts, respectively.

4. Conclusion

We are reported the new chloride salt of 1-butyl-4-[2-(4-hydroxyphenyl)ethenyl)]pyridine, crystallizing in triclinic *P*1 space group. Its unit cell contains two independent 1-butyl-4-[2-(3,5-dimethoxy4-hydroxyphenyl)ethenyl)]pyridinium] cations, differing with respect to the butyl chain torsion angle for which values of $80.0(9)^{\circ}$ and $173.6(3)^{\circ}$. The cations and anions are joined into infinite layers, formed by two different dimers and including solvent molecules. Hydrogen bonds OH···OH₂ (2.814 Å), HOH···O(CH₃) (2.960 Å), OH···Cl (2.967 Å), HOH···Cl⁻ (3.034, 3.188, 3.161 and 3.062 Å) and HOH···OH₂ (2.772 Å) are observed. For first time in the literature, we are reporting the crystal structure of the dye with the syringaldehyde-fragment in the molecule.

Supporting information

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 705628 Copies of this information may be obtained from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Raman (supplementary material Fig. S1) as well as ¹H and ¹³C NMR spectra (supplementary material Figs. S2A and S2B), respectively.

Acknowledgements

T.K. and M.S. wish to thank the DAAD for a grant within the priority program "Stability Pact South-Eastern Europe" and DFG under the grant number SP 255/21-1. B.K. thanks the Alexander von Humboldt Foundation for the Fellowship.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2009.09.020.

References

- [1] S. Marder, J. Perry, W. Schaefer, Science 245 (1989) 626.
- [2] S. Marder, J. Perry, B. Tiemann, R. Warsh, W. Schaefer, Chem. Matter 2 (1990) 685
- [3] G. Ashwell, R. Hargreaves, C. Baldwin, G. Bahra, C. Brown, Nature 357 (1992) 393
- [4] D. Lupo, W. Prass, U. Scheunemann, A. Laschewsky, R. Ringsdorf, I. Ledoux, J. Opt. Soc. Am. B 5 (1988) 300.
- [5] T. Kolev, D. Yancheva, S. Stoyanov, Adv. Funct. Mater. 14 (2004) 799.
- [6] T. Kolev, R. Wortmann, M. Spiteller, W. Sheldrick, M. Heller, Acta Crystallogr. E60 (2004) o1449.
- [7] T. Kolev, R. Wortmann, M. Spiteller, W. Sheldrick, H. Maver-Figge, Acta Crystallogr. E61 (2005) o1090.
- [8] T. Kolev, B. Stamboliyska, D. Yancheva, Chem. Phys. 324 (2006) 489.
- [9] T. Kolev, B. Koleva, M. Spiteller, H. Mayer-Figge, W.S. Sheldrick, Dyes Pigments 79 (2008) 7.
- [10] R. Ziolo, W. Günther, G. Meredith, D. Williams, J. Troup, Acta Crystallogr. 38B (1982) 341.
- [11] S. Marder, J. Perry, W. Schaefer, J. Mater. Chem. 2 (1992) 985.
- [12] S. Marder, J. Perry, C. Yakymyshyn, Chem. Mater. 6 (1994) 1137.
- [13] B. Jindawong, S. Chantrapromma, H. Fun, X. Yu, C. Karalai, Acta Crystallogr. 61E (2005) 01340.
- [14] S. Chantrapromma, K. Chanawanno, H. Fun, Acta Crystallogr. 63E (2007) 01554.
- [15] C. Bosshard, M. Wong, F. Pan, V. Gramlich, P. Günter, Adv. Mater. 9 (1997) 554.
- [16] T. Kolev, T. Berends, D. Kleb, H. Preut, M. Spiteller, Acta Crystallogr. 59E (2003) 01788.
- [17] A. Rahman, I. Razak, H. Fun, P. Saenee, B. Jindawong, S. Chantrapromma, C. Karalai, Acta Crystallogr. 59E (2003) o1798.
- [18] S. Okada, A. Masaki, H. Matsuda, H. Nakanishi, M. Kato, R. Muramatsu, M. Otsuka, Japan. J. Appl. Phys. 29 (1990) 1112.
- [19] S. Chantrapromma, B. Jindawong, H. Fun, S. Anjum, C. Karalai, Acta Crystallogr. 61E (2005) o2096.
- [20] T. Zhang, L. Ge, G. Zhang, Y. Zhang, K. Yu, Chin. J. Struct. Chem. 19 (2000) 6.
- [21] P. Lacroix, C. Lepetit, J. Daran, New J. Chem. 25 (2001) 451. [22] D. De, D. Ridder, H. Heijdenrijk, H. Schenk, R. Dommisse, R. Lemiere, J. Lepoivre,
- F. Alderweireldt, Acta Crystallogr. 46C (1990) 2197.
- [23] P. Lacroix, J. Daran, P. Cassoux, New J. Chem. 22 (1998) 1085.
- [24] W. Yang, S. Li, D. Zhang, Acta Crystallogr. 61E (2005) 02461.

- [25] F. Pan, M. Wong, G. Gramlich, C. Bosshard, P. Günter, Chem. Commun. 1996 1557.
- [26] F. Pan, M. Wong, V. Gramlich, C. Bosshard, P. Günter, J. Am. Chem. Soc. 118 (1996) 6315.
- [27] D. Zhang, T. Zhang, Y. Zhang, Z. Fei, K. Yu, Acta Crystallogr. 53C (1997) 364.
- [28] S. Chantrapromma, H. Fun, Acta Crystallogr. 63E (2007) o2882.
- [29] B. Koleva, T. Kolev, H. Mayer-Figge, W. Sheldrick, Anal. Sci., in press.
- [30] G.M. Sheldrick, SHELXTL, Release 5.03 for Siemens R3 Crystallographic Research System, Siemens Analytical X-Ray Instruments, Inc., Madison, USA, 1995.
- [31] G.M. Sheldrick, SHELXS97 and SHELXL97, University of Goettingen, Germany, 1997.
- [32] B. Ivanova, M. Arnaudov, P. Bontchev, Spectrochim. Acta 60A (2004) 855.
- [33] B. Ivanova, D. Tsalev, M. Arnaudov, Talanta 69 (2006) 822.
- [34] B. Ivanova, V. Simeonov, M. Arnaudov, D. Tsalev, Spectrochim. Acta 67A (2006) 66.
- [35] B. Koleva, T. Kolev, V. Simeonov, T. Spassov, M. Spiteller, J. Inclus. Prenome. (2009), doi:10.1007/s10847-008-9425-5.
- [36] B. Ivanova, J. Mol. Struct. 782 (2006) 122.
- [37] B. Ivanova, Spectrochim. Acta 64A (2006) 931.
- [38] B.B. Ivanova, T. Kolev, S. Zareva, Biopolymers 82 (2006) 587.
- [39] T. Kolev, Biopolymers 83 (2006) 39.
- [40] B. Jordanov, B. Schrader, J. Mol. Struct. 347 (1995) 389.
- [41] B. Jordanov, R. Nentchovska, B. Schrader, J. Mol. Struct. 297 (1993) 401.
- [42] J. Michl, E.W. Thulstrup, Spectroscopy with Polarized Light. Solute Alignment by Photoselection, in Liquid Crystals, Polymers, and Membranes, VCH Publishers, NY. 1986.
- [43] E.W. Thulstrup, J. Eggers, Chem. Phys. Lett. 1 (1996) 690.
- [44] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, Ö. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J.J. Dannenberg, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komáromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98, Gaussian, Inc., Pittsburgh, PA, 1998.
- [45] "DALTON", a molecular electronic structure program, Release 2.0, http://www.kjemi.uio.no/software/dalton/dalton.html, 2005.
- [46] G.A. Zhurko, D.A. Zhurko, ChemCraft: Tool for treatment of chemical data, Lite version build 08, 2005.
- [47] D Tozer N Handy Phys Chem Chem Phys 2 (2000) 2117
- [48] J. Tomasi, M. Persico, Chem. Rev. 94 (1994) 2027
- [49] R. Cammi, M. Cossi, J. Tomasi, J. Chem. Phys. 104 (1996) 4611.
- [50] R. Cammi, C. Rossi, B. Bennucci, J. Tomasi, J. Chem. Phys. 105 (1996) 10556.
- [51] S. Benard, P. Yu, J. Audiere, E. Riviere, R. Clement, J. Guilhem, L. Tchertanov, K. Nakatani, J. Am. Chem. Soc. 122 (2000) 9444. [52] Y. Ren, F. Qi, W. Yu, H. Lei, Y. Tian, M. Jiang, Q. Yang, T. Mak, J. Mater. Chem. 10
- (2005) 2025.
- [53] T. Kimura, X. Duan, M. Kato, H. Matsuda, T. Fukuda, S. Yamada, S. Okad, H. Nakanishi, Macromolec. Chem. Phys. 199 (1998) 1193.
- [54] P. Acebal, S. Blaya, L. Carretero, J. Phys. 36 (2003) 2445.