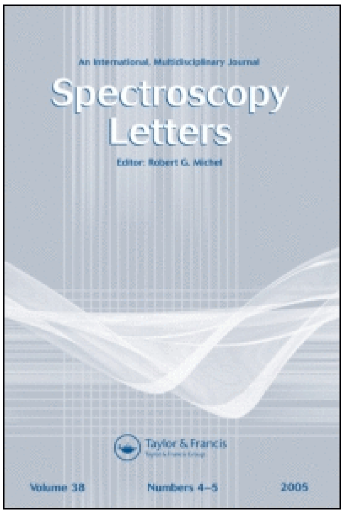

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Solvatochromism and Halochromism of *N*-(4-Oxyphenyl) 5-nitro-2-thiophenecarboxaldimine

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Solvatochromism and Halochromism of *N*-(4-Oxyphenyl) 5-nitro-2-thiophenecarboxaldimine

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ABSTRACT The solvatochromic behavior of the title phenolate **1** was described and interpreted by means of theoretical calculations employing the PCM model and a TD-DFT method. The cationic halochromism of **1** was studied in DMSO and in ethanol solutions of $LiClO_4$ and interpreted by a simple model that reproduced the variation of the charge-transfer transition energy of **1** with the cation concentration in solution.

KEYWORDS cationic halochromism, solvatochromism, TD-DFT calculations, ZINDO/S

INTRODUCTION

We have been interested for some time in the design of new solvatochromic dyes and their behavior in pure solvents,[1,2] in binary solvent mixtures,[3–5] and in the presence of host molecules like cyclodextrins.[6–8]

Solutions of many of these compounds have also been found to be halochromic. The literature defines halochromism as a spectral behavior characterized either by pH-dependent variations in the UV–vis absorptions of a given dye[9,10] or by spectral changes brought about by the addition of salts to a dye solution.[11–14] In this second sense, we have distinguished a cationic and an anionic halochromism in the interpretation of the spectral behavior of various compounds.[15]

In the current communication, we describe the solvato- and halochromic behavior of compound **1** (Scheme 1), where a donor phenolate fragment is conjugated with a nitrothienyl acceptor group.

Phenol **2** has been described as an antiprotozoal agent[16] and as a precursor of antibacterial compounds,[17] but the spectral response of the corresponding phenolate **1** to solvent changes has never been investigated. The solvatochromism of this new dye in different solvents and its halochromic behavior in DMSO and in ethanol solutions of lithium perchlorate were recorded and the experimental data interpreted by means of theoretical calculations and a simple model recently developed by us for other halochromic phenolates.[18]

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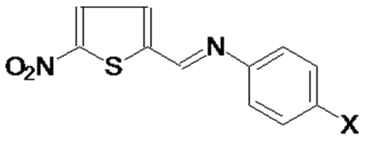


1, X = O⁻
2, X = OH

SCHEME 1

MATERIALS AND METHODS

The melting point of compound **2** was recorded with a Microthermal capillary apparatus and was not corrected. Its ^{1}H NMR spectrum was obtained with a Bruker 400 MHz Avance instrument, employing tetramethylsilane as internal reference. UV–visible spectra of the phenolate **1** were recorded with a Hewlett-Packard TU-1800 spectrophotometer.

All analytically pure solvents were purchased from Merck and were used without any further purification. Reagents 5-nitro-2-thiophenecarboxaldehyde and 4-aminophenol were purchased from Aldrich.

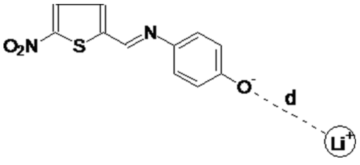
5-Nitro-2-(4-hydroxyphenylimino)methylthiophene (**2**) was prepared in 85% yield by refluxing for 20 min equimolar amounts of 5-nitro-2-thiophenecarboxaldehyde (1.6 g, 10 mmol) and 4-aminophenol (1.1 g, 10 mmol) in ethanol (50 mL) to which 10 drops of concentrated HCl were added. The solution was concentrated to 15 mL, and the crude product that separated upon cooling was filtered and recrystallized from ethanol in the form of red crystals: m.p. 219–220°C, lit.[17] m.p. 220°C. ^{1}H NMR [$(CD_3)_2CO$] δ 6.90 (2H, d, $J = 8$ Hz, Ph-H *ortho* to OH), 7.34 (2H, d, J=Hz, Ph-H *meta* to OH), 7.61 (1H, d, $J = 4$ Hz, 3-ThH), 8.06 (1H, d, $J = 4$ Hz, 4-ThH), 8.85 (1H, s, CH = N).

Solutions of the phenolate **1** were prepared *in situ* by treating 3–5 mL solutions of phenol **2** (*ca.* 2.5×10^{-5} M) with 1–2 μL of methanolic 1 M tetrabutylammonium hydroxide (Aldrich).

Theoretical Calculations

All theoretical calculations were made with the Gaussian 03w package.[19]

The structure of compound **1** was generated by means of Gaussview 3.0 and then optimized at the B3LYP/6-31G* level theory in the gas phase. For calculations in solution, the PCM solvent model was employed. The molecule was first optimized with the AM1 method, and then single-point calculations employing a TD-DFT method at the B3LYP/6-31G* level and the same solvent model were performed to estimate the transition energies of **1** in solution.



SCHEME 2

For the calculations of the halochromism of **1**, a Li$^+$ cation was positioned at variable distances from its oxygen atom, collinearly with its C–O bond (Scheme 2). For each of these structures, the O−Li$^+$ distance was kept constant, and the remaining molecule was optimized at the RHF/6-31G level theory. Transition energies were then obtained by single-point calculations, with the Gaussian03 ZINDO/Soption and configuration interactions involving singly excited transitions among the 10 highest occupied and the 10 lowest unoccupied molecular orbitals of the system.

RESULTS AND DISCUSSION

Solvatochromism and Halochromism of 1

The longest wavelength band of dye **1** showed hypsochromic shifts with the increasing polarity of the medium, with a negative solvatochromic behavior (Fig. 1). The λ_{max} value of the longest wavelength band of dye **1** in various HBD and non-HBD solvents is given in Table 1. Though **1** was sufficiently soluble in water, protonation in basic solutions decreased drastically the intensity of its CT band and prevented a reliable λ_{max} value to be recorded in that solvent.

A plot of the charge-transfer (CT) transition energy, expressed in wavenumber values ν, against the solvent polarity, estimated by the corresponding $E_T(30)$ values,[20] yielded a straight line with a correlation coefficient of 0.98 (Fig. 2). This good correlation is an indication that the solvatochromic behavior of dye **1**, like that of the $E_T(30)$ betaine, reflects to a large extent solvent interactions with the donor phenolate group.

A multiple regression analysis of the CT transition energies, ν_{exp}, in terms of the hydrogen-bond-donor

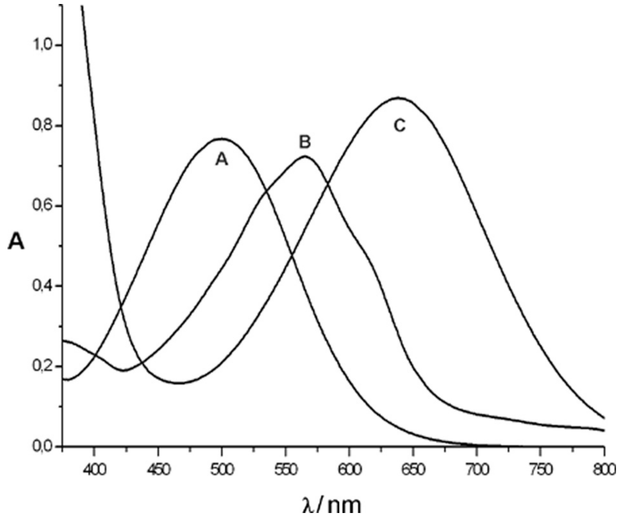


FIGURE 1 UV–vis spectra of dye 1 ($c = 2.9 \times 10^{-5}$ M) in (A) methanol, (B) DMSO, and (C) THF.

strength of the solvent, expressed as the SA parameter,[21] and its dipolarity-polarizability, expressed as the SPP^{N} parameter,[22] yielded relationship (1)

$$\nu_{\text{exp}} = 11,886.4 + 6602\ \text{SA} + 5141\ \text{SPP}_{\text{N}} \qquad (1)$$

indicating that the solvatochromic behavior of dye **1** is equally determined by the HBD strength, or acidity of the solvent, and its dipolarity-polarizability.

Like other solvatochromic phenolates,[11,12,14,15,23] dye **1** exhibited a cationic halochromism in solutions of alkali salts. Figure 3 illustrates this behavior, with the variation of the charge-transfer transition-energy of solutions of compound **1** in ethanol and in DMSO, in the presence of increasing concentrations of lithium perchlorate. Halochromic shifts were larger in ethanol than in DMSO, a result that reflects the distinct abilities of cation-solvation by the two solvents. In DMSO, a strong donor solvent, dye-cation association is rendered more difficult by the competing solvation ability of the solvent, leading to a smaller increase of the transition energy ν with the addition of the salt. In ethanol, where dye-cation association is greater than in DMSO, values of transition energy ν rise more steeply with the increasing salt concentration.

TABLE 1 Variation of the λ_{max} Values of the Longest-Wavelength Band of Compound 1 in Different Solvents

Solvent	λ_{max} values (nm)	$E_T(30)$ values[a] (kcal. mol^{-1})
Methanol	503	55.4
Ethanol	518	51.9
1-Propanol	534	50.7
1-Butanol	531	49.7
3-Methylbutanol	533	49.0
2-Propanol	554	48.4
Dimethylsulfoxide	564	45.1
2-Methylpropanol	580	43.3
1,2-Dichloroethane	603	41.3
Dichloromethane	611	40.7
Chloroform	600	39.1
Ethyl acetate	624	38.1
Tetrahydrofuran	644	37.4
Chlorobenzene	614	36.8

[a] See Ref.[20].

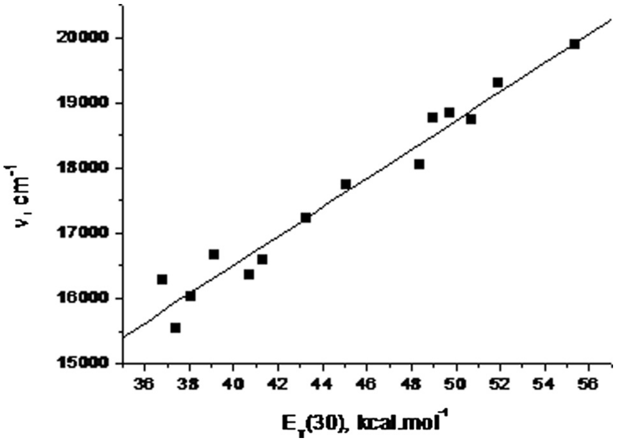


FIGURE 2 Variation of the longest wavelength band transition energy of dye 1, expressed in wavenumber values $\nu = 1/\lambda_{\text{max}}$, with the $E_T(30)$ polarity value of the solvent. Conversion factor: 1 cm^{-1} = 2.859×10^{-3} kcal. mol^{-1}.

Theoretical Results and Discussion

The origin of the solvatochromic absorption band of dye **1** was investigated in more detail with the aid of theoretical calculations, considering the molecule in the gas phase and in solvents of different polarity ($CHCl_3$ and MeOH). For calculations in solution, we employed the PCM and a TD-FDT method, with the hybrid B3LYP/6-31 G* option. The calculated transition energies of the solvatochromic charge-transfer band corresponded with λ_{max} values of 610 and 598 nm in $CHCl_3$ and methanol, respectively. This variation agrees with the observed negative solvatochromism of compound **1**, but the calculated solvatochromic shift of 12 nm is clearly too small if compared with the experimental value of nearly 100 nm. This is a consequence of the continuum model of the PCM option, which overlooks specific

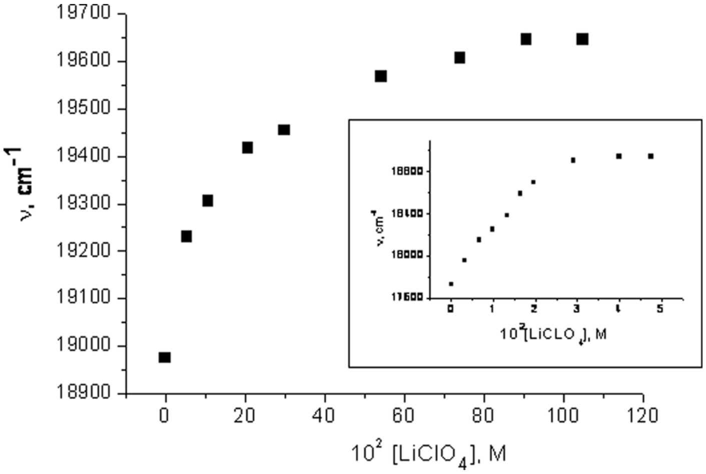


FIGURE 3 Variation of the longest wavelength band transition energy, expressed in wavenumber values $\nu = 1 / \lambda_{max}$, of solutions of dye 1 in ethanol and in DMSO (inset) in the presence of increasing concentrations of $LiClO_4$. Conversion factor: $1\,cm^{-1} = 2.859 \times 10^{-3}$ kcal. mol^{-1}.

solute–solvent interactions like hydrogen bonds. These interactions are reflected in the acidity of the solvent, one of the two determining contributions to the solvatochromism of **1**. Thus, whereas the calculated transition energy is reasonably close to the experimental value in a solvent like chloroform, where these interactions are practically absent, it grossly underestimates the hypsochromic shift caused by hydrogen bonds of the dye phenolate with the solvent in methanol.

The HOMO and LUMO of compound **1** in chloroform are shown in Fig. 4. The internal charge-transfer that takes place during this transition, from the donor phenolate to the acceptor nitrothienyl fragment, is discernible in the figure.

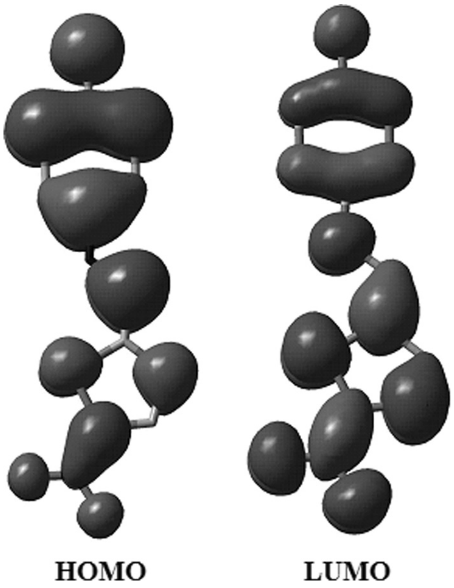


FIGURE 4 HOMO and LUMO densities of compound 1 in chloroform, calculated with a PCM TD-DFT (B3LYP/6-31 G*) method.

The ground and excited dipole moments of the molecule could be obtained from the Lippert–Mataga equation (2)[24–26]:

$$\nu = \nu_0[2\mu_g(\mu_e - \mu_g)/hca^3] \cdot \{[(\varepsilon - 1)/(2\varepsilon + 1)] - 0.5[(n^2 - 1)/(2n^2 + 1)]\} \qquad (2)$$

where ν and ν_0 are transition energies in a given solvent and in vacuum, respectively, μ_g and μ_e are the dipole moments in the ground and excited states, a is the molecular radius, h is Planck's constant, c is the speed of light, ε is the static dielectric constant of the medium and n its refractive index.

A plot of the transition energies ν in the most nonpolar solvents, where specific solute–solvent interactions are absent, against the solvent polarity parameter

$$f = \{[(\varepsilon - 1)/(2\varepsilon + 1)] - 0.5[(n^2 - 1)/(2n^2 + 1)]\} \qquad (3)$$

yielded a straight line (graph not shown) with a slope equal to $-[2\mu_g(\mu_e\text{-}\mu_g)/hca^3]$. The values of μ_g(5.33 D) and a^3 (4.51 Å^3) were obtained after optimization of structure **1** at the B3LYP/6-31G level. Thus, we obtained a value of 2.66 D for the dipole moment of the excited state of dye **1**.

We next tried to mimic the halochromic behavior of compound **1** in the presence of $LiClO_4$ by means of a recently developed simple theoretical model successfully applied to halochromic phenolates.[18]

The model employs metal cations at a variable distance from the halochromic compound to polarize the molecule. A similar approach, based on the use of point charges or sparkles, had been employed by us[1] and others[27] to mimic a solvent of variable polarity. However, contrary to the results obtained by others,[27] which were at variance with experimental data and with previous calculations incorporating solvent parameters,[28,29] our model adequately reproduced the experimental solvatochromic trends.

By positioning a lithium cation at variable distances from the oxygen atom of the phenolate donor, collinearly with the C–O^- bond, we generated variable polar environments, and variable transition energies for the molecule.

The problem of relating the variable distance d with the electrolyte concentration was circumvented by treating the cationic media as a large cubic grid with the vertices occupied by Li^+ cations. Assuming an electrolyte concentration (10^{-2} to 10^{-1} M) much larger than that of the dye (*ca.* 10^{-5} M), a relatively small number of these cations are replaced by the charged oxygen atoms of the phenolate donor. In this purely geometric arrangement, for an average cation–oxygen distance d, the number of cations present in a cubic volume V of side a is given by $N = a^3/d^3$, and the molar cation concentration $[Li^+]$ is given by $[Li^+] = N/N_A = a^3/N_A d^3$, where N_A is the Avogadro's constant. This simple relationship allows us to write that the cation concentration is proportional to d^{-3}, $[Li^+] \propto d^{-3}$, and we may employ the variable d^{-3} in our theoretical plot as an equivalent of $[Li^+]$.

Calculations employing a TD-DFT method, as described above for the estimation of transition energies of **1** in solution, yielded too small values, with transition energies in the IR region. This severe departure from the experimental values was probably due to the additional polarization of **1** by the vicinity of the charged cation. TD-DFT methods are known to drastically underestimate charge-transfer excitations of large molecules with considerable charge separation.[30] This in part may be the cause of the observed difference between the calculated and the experimental $\lambda_{\max}$ values of the CT absorption band of **1** in methanol, referred to above.

We therefore employed the CIS ZINDO/S option of the Gaussian03 package[19] for estimating the excitation energies of **1** in the gas phase, polarized by the vicinity of the lithium cation. Figure 5 depicts the variation of the theoretically calculated transition energy of **1** with the lithium cation concentration $[Li^+]$, assumed proportional to d^{-3}.

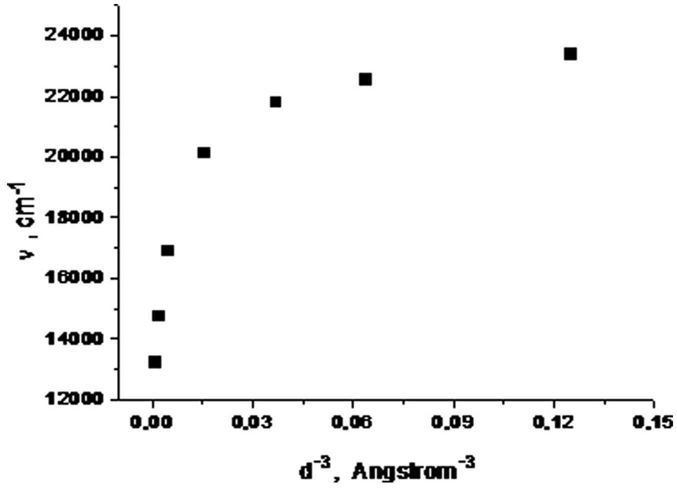


FIGURE 5 **Variation of the theoretically calculated CT transition energy of 1 with the lithium cation concentration, assumed proportional to d^{-3}, where d is the Li^+–O^- distance. Conversion factor: 1 cm^{-1} = 2.859×10^{-3} kcal. mol^{-1}.**

Figure 5 should be compared with the experimental curve of transition energies ν versus $[LiClO_4]$ in ethanol, shown in Fig. 3. Although the experimental and theoretically predicted absolute values of the transition energies and of the halochromic shifts differ, the experimental plot is adequately reproduced by the theoretical curve. The larger halochromic shift predicted by the theoretical model is a consequence of the fact that we neglected the solvent in our calculations. By solvating the phenolate moiety, ethanol should reduce the group sensitivity to the lithium cation. As a result, the experimental halochromic shift is much smaller than what our gas-phase model predicts.

CONCLUSIONS

The phenolate **1** is a simple, easily prepared compound that exhibits an interesting negative solvatochromic shift. Its solvatochromism correlates with the behavior of the $E_T(30)$ betaine in solution. Like the latter, it is determined by the acidity and the dipolarity-polarizability of the medium. Theoretical calculations confirmed that the transition energy of the solvatochromic band is associated with an internal CT from the phenolate donor to the acceptor nitrothienyl group.

Like other solvatochromic phenolates, compound **1** exhibited a halochromic behavior, illustrated in

DMSO and in ethanol solutions of $LiClO_4$. The observed halochromic shifts in ethanol were reproduced with the aid of a simple theoretical model, based on the effect of a variable electric field on the excitation energies of **1**, generated by a Li^+ cation positioned collinearly with the dye $C–O^-$ bond, at a variable distance from the oxygen atom.

ACKNOWLEDGMENTS

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