The solvatochromic behaviour of 2- and 4-pyridiniophenoxides

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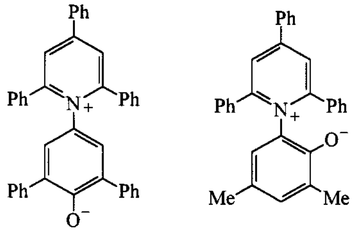
The solvatochromic shifts of the two isomeric title betaines **4** and **5**, built up from the unsubstituted pyridinio acceptor and phenoxide donor fragments, were recorded in twelve solvents and the data compared with results from semi-empirical (AM1) and *ab initio* (HF/6-311G and B3LYP/6-311G) calculations.

Introduction

Pyridiniophenoxide betaines have been the object of sustained interest since Dimroth and Reichardt described their solvatochromic properties in a classic paper nearly thirty years ago.[1] The most conspicuous member of the family, the $E_T(30)$ betaine **1** (Scheme 1), has provided the basis of a polarity scale of wide application.[2]



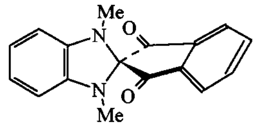
1 **2**

Scheme 1

The highly solvent-sensitive absorption of these compounds in the visible region arises from a charge transfer from the phenoxide donor ring to the pyridinium acceptor fragment. Aryl substituents on the donor and/or acceptor moieties modulate this transfer, shifting the CT absorption to longer wavelength values. The degree of bathochromic shift due to these substituents should depend on the position and nature of the aryl group. This effect is difficult to assess quantitatively, in spite of the large number of different pyridiniophenoxides described so far. Prior to any attempts at correlating such CT shifts with the nature and position of the aryl substituents, a study of the simple, unsubstituted pyridiniophenoxide system is required.

Besides the assessment of the electronic contribution of aryl substituents to the CT transition of the unsubstituted pyridiniophenoxide betaine, a second aspect which remains unexplored in these systems is the importance of donor–acceptor coplanarity in determining the energy of the charge-transfer transition. It is now clear that this coplanarity does not influence the charge-transfer process which takes place in these systems. X-Ray diffraction studies of $E_T(30)$ derivatives have shown that the phenoxide and pyridinium rings in such systems are twisted out of plane by nearly 65°.[3] In addition, compounds which exhibit an even greater degree of orthogonality have been synthesized and shown to possess remarkable solvatochromic properties. This is, for example, the case for compound **2**, with a CT band in the visible region which spans nearly 240 nm when going from nonpolar solutions in benzene to solutions in aqueous ethanol.[4]

More recently, the question of donor–acceptor orthogonality with respect to charge-transfer transitions has been addressed by the synthesis and spectroscopic studies of spiro compounds like **3** (Scheme 2), which have been shown to be solvatochromic.[5]



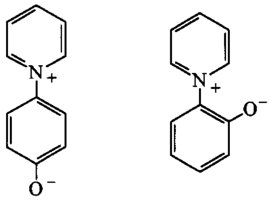
3

Scheme 2

However, the question still remains as to the relative importance of the donor–acceptor coplanarity in these systems, as compared to purely electronic effects due to ring substituents, in determining the position of the charge-transfer band of these compounds. We endeavoured to tackle this problem by synthesizing a family of N-substituted vinylogous α-pyridones and comparing their solvatochromic behaviour in different media, but our results were far from conclusive, because we could not separate steric from electronic effects in these systems.[6]

Reports of λ_{max} shifts of solvatochromic dyes with changes in the dihedral angle between donor and acceptor fragments[7] raise the question of the relative contributions of electronic and steric factors to the solvatochromic behaviour of betaines like **2**.

The above considerations led us to carry out a study of the solvatochromic properties of betaines **4** and **5** (Scheme 3).



4 **5**

Scheme 3

These interesting molecules are essentially donor–acceptor skeletons of more complex, highly substituted pyridiniophenoxide systems like the $E_T(30)$ **1** or **2**. In comparing these two isomers, we are not confronted with the problem of electronic contributions by substituents, which tend to mask purely steric effects. In addition, such small systems are amenable to more elaborate theoretical treatments, which are generally precluded by the size of larger molecules like **1**. As an example, a theoretical paper dealing with the solvatochromic properties of the $E_T(30)$ probe had to rely on a semi-empirical method (ZINDO-CIS) and a supramolecular approach to describe the spectroscopic behaviour of this compound in different media.[8]

In the present paper the solvatochromic behaviour of compounds **4** and **5** is described and compared with that of their substituted analogues **1** and **2**. The McRae treatment was applied to the experimental solvatochromic shifts of the more soluble betaine **5** in media of low polarity. Semi-empirical (AM1) and *ab initio* (HF/6-311G and B3LYP/6-311G) methods were then utilized to reproduce the geometry of this betaine, and the results compared with related parameters available in the literature. Finally, the variation of the charge-transfer transition energy of **5** in four solvents was simulated by means of the semi-empirical AM1 hamiltonian and these results compared with the corresponding HOMO–LUMO gaps in the same media, calculated with the hybrid B3LYP/6-311G method and the application of the Onsager model.

Experimental

Melting points were obtained with a Koffler hot-stage apparatus and were not corrected. NMR spectra were recorded with a Bruker WH 90/DS equipment, utilizing hexamethyldisiloxane as internal reference; *J* values are in Hz. UV-Visible spectra of both phenoxides in various solvents were obtained with a Spectronic Genesys 5 spectrophotometer.

Calculations were performed with the MOPAC options of the ChemDraw package and with the Gaussian94w package. Full geometry optimizations were performed with the AM1 hamiltonian and with the HF/6-311G and B3LYP/6-311G methods. For the calculations of the excitation energies in solution the COSMO option was utilized. Starting from the AM1-optimized structure, single-configuration-interaction calculations were performed with the appropriate relative permittivity of the medium (ε) and a total of 10 molecular orbitals (5 occupied and 5 unoccupied) with the keywords CIS C.I. = 5 MECI EPS = ε. A second set of excitation energies was obtained by calculating the energy gaps between the highest occupied and the lowest virtual orbitals of molecule **5** in different media, by the B3LYP/6-311G method. The cavity radius a_o of **5** was obtained form a volume calculation with this hybrid DFT method. This value was then fed, together with the corresponding relative permittivity of the medium, into SCRF calculations with the same method, based on the Onsager model.

N-(4-Hydroxyphenyl)pyridinium perchlorate 6

A solution of 4-aminophenol (4.36 g, 0.04 mol) and *N*-(2,4-dinitrophenyl)pyridinium chloride (11.26 g, 0.04 mol) in absolute ethanol (100 ml) was refluxed for 48 h. The initially deep red solution changed to a red–brown colour. The solution was then cooled, filtered and rotary evaporated. The brown resinous residue was boiled in water (450 ml) for 10 min and the aqueous solution was cooled, filtered and sodium perchlorate (6.13 g, 0.05 mol) was added, to precipitate the crude brown–yellow pyridinium perchlorate (4.3 g, mp 182–186 °C). After two recrystallizations from dilute perchloric acid (3%, 15 ml of acid solution per gram of salt, activated charcoal added), the pure light yellow perchlorate **6** (2.6 g, 24% yield) melted at 217–219 °C (Found: Cl, 13.30. $C_{11}H_{10}ClNO_5$ requires Cl, 13.05%); ν_{max}(paraffin oil)/cm^{-1} 3270, 1620, 1595 and 1500; δ_H(DMSO-d_6) 10.34 (s, OH), 9.17 (d, 2 H, *J* 7, Py-2,6), 8.68 (t, 1 H, *J* 7, Py-4), 8.17 (t, 2 H, *J* 7, Py-3,5), 7.67 (d, 2 H, *J* 9, Ph-3,5), 7.06 (d, 2 H, *J* 9, Ph-2,6).

4-Pyridiniophenoxide dihydrate 4

To a solution of pyridinium perchlorate **6** (0.27 g, 1.0 mmol) in methanol (10 ml) at 30–35 °C was added a 2 M solution of potassium hydroxide in methanol (0.6 ml). The orange solution was filtered and the filtrate evaporated. The residue was crystallized once from water (10 ml, activated charcoal added) and then from acetonitrile–water (10 ml H_2O and 12 ml MeCN) to give 0.12 g (60% yield) of the 4-pyridiniophenoxide **4** in the form of long, bright yellow needles (Found: C, 63.26; H, 6.34; N, 6.78. $C_{11}H_9NO{\cdot}2H_2O$ requires C, 63.76; H, 6.32; N, 6.76%); $\delta_H(CD_3OD)$ 8.96 (d, 2 H, *J* 7, Py-2,6), 8.45 (t, 1 H, *J* 7, Py-4), 8.07 (t, 2 H, *J* 7, Py-3,5), 7.29 (d, 2 H, *J* 9, Ph-3,5), 6.67 (d, 2 H, *J* 9, Ph-2,6).

N-(2-Hydroxyphenyl)pyridinium perchlorate 7

A solution of 2-aminophenol (22 g, 0.2 mol) and *N*-(2,4-dinitrophenyl)pyridinium chloride (28.2 g, 0.1 mol) in absolute ethanol (300 ml) was refluxed for 15 h. The solution was then concentrated to a volume of 150 ml. Water (1000 ml) was added and the 2,4-dinitroaniline that precipitated after 24 h was removed by filtration. The filtrate was treated with activated charcoal, filtered and concentrated to a volume of 50–70 ml, to which perchloric acid was added until the pH reached 1–2. The precipitated crude product was filtered and purified by dissolution in acetone and reprecipitation by addition of diethyl ether to give 6.5 g (24% yield). The obtained *N*-(2-hydroxyphenyl)pyridinium perchlorate **7** weighed 6.5 g (24% yield), decomposing (**CAUTION**: explosive!) at temperatures higher than 200 °C (Found: N, 4.88; Cl, 13.17. $C_{11}H_{10}ClNO_5$ requires N, 5.16; Cl, 13.05%).

2-Pyridiniophenoxide dihydrate 5

To a solution of the pyridinium perchlorate **7** (0.54 g, 2.0 mmol) in warm methanol (25 ml) was added a 1 M solution of potassium hydroxide in methanol (2.0 ml). The red–orange solution was evaporated, the residue redissolved in boiling chloroform (50 ml), the precipitated potassium perchlorate filtered, and the filtrate concentrated to 5–10 ml and stored overnight in the refrigerator. The precipitated product was solubilized in ethanol (2 ml); to this solution was added diethyl ether (2 ml), the mixture was filtered and the filtrate was diluted with 4 ml of diethyl ether. The red–yellow oil, which separated by stirring and rubbing, crystallized to give 0.2 g (48% yield) of the hydrated yellow 2-pyridiniophenoxide **5**. By heating to 65 °C the yellow product was dehydrated to the orange anhydrous betaine which started to darken at 95 °C, finally melting with decomposition at 183 °C (Found: C, 63.60; H, 6.05; N, 6.70. $C_{11}H_9NO{\cdot}2H_2O$ requires C, 63.76; H, 6.32; N, 6.76%); $\delta_H(CDCl_3)$ 9.02 (d, 2 H, *J* 7, Py-2,6), 8.16 (t, 1 H, *J* 7, Py-4), 7.82 (t, 2 H, *J* 7, Py-3,5), 7.2–6.9 (m, 4 H, Ph-H).

Results and discussion

The 4-pyridiniophenoxide **4** was prepared by treating with potassium hydroxide the corresponding *N*-(4-hydroxyphenyl)-pyridinium perchlorate **6**. The latter compound was obtained from reaction of 4-aminophenol with *N*-(2,4-dinitrophenyl)-pyridinium chloride, following a procedure described previously.[9]

The 2-pyridiniophenoxide **5** was obtained in an analogous way, as shown in Scheme 4.

The solvatochromic longest wavelength band of the two betaines was recorded in different solvents and the corresponding λ_{max} values are given in Table 1.

Betaine **4** was sparingly soluble in media of low polarity. This fact precluded the comparison of the solvatochromic behaviour of the two isomers in such media. In protic solvents betaine **4** absorbs, in general, at smaller λ_{max} values than compound **5**, also spanning a larger solvatochromic shift (77 nm), when changing from propan-2-ol to water, than its isomer **5** (57 nm). This greater sensitivity to the acidity of the solvent reflects the

Table 1 Variations of the charge-transfer band of pyridiniophenoxides **4** and **5** in the visible region with solvent

Solvent	E_T^N value[a]	λ_{max}/nm **4**	λ_{max}/nm **5**
Water	1.00	365	378
Methanol	0.76	394	409
Ethanol	0.65	413	418
Propan-1-ol	0.62	427	435
Propan-2-ol	0.55	442	435
Acetonitrile	0.46	464	477
Dimethyl sulfoxide	0.44	486	482
Acetone	0.36	insol.	486
Dichloromethane	0.31	insol.	499
Chloroform	0.26	insol.	517
Benzene	0.11	insol.	528
Toluene	0.10	insol.	529

[a] Polarity values taken from ref. 2(*a*), pp. 365–371.

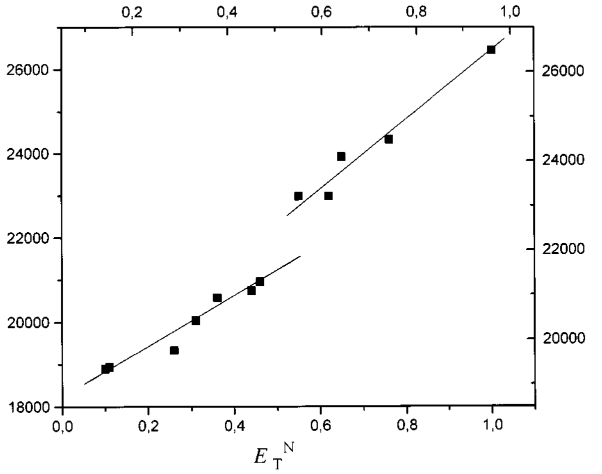
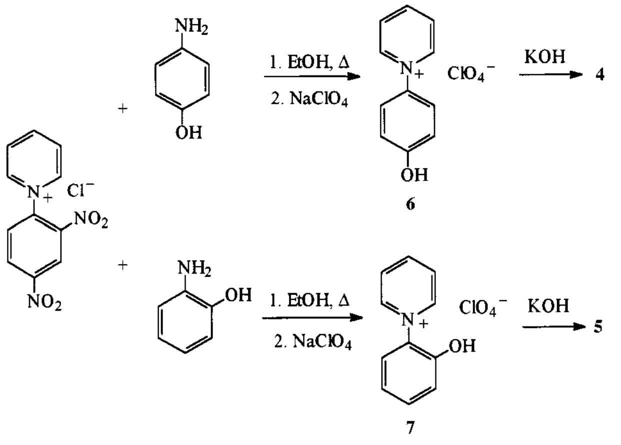


Fig. 1 Solvatochromic shifts in wavenumber values ν of pyridiniophenoxide **5** as a function of the normalized polarity value E_T^N of the solvent.



Scheme 4

fact that the phenoxide oxygen in **4** is more exposed to hydrogen-bonding with the solvent than that in **5**.

Neither of the two betaines should be expected to yield perfect linear correlations in a plot of their CT transition energies *vs.* E_T^N values, when the full range of employed solvents is considered. This is because the solvatochromic shifts of pyridiniophenolate betaines results from a blend of dipolarity/polarizability and acidity contributions, whose proportions are, in a way, unique for each compound. Fig. 1 illustrates this fact in a plot of the transition energies of compound **5**, expressed in wavenumber values, as a function of the E_T^N values of the solvent. Two straight lines could be drawn, which corresponded to solvatochromic shifts in protic and non-protic solvents. It is seen that betaine **5** is more sensitive than the $E_T(30)$ probe to the acidity of the protic solvents, a result of the greater steric shielding of the phenoxide oxygen by the two adjacent phenyl substituents in the latter compound.

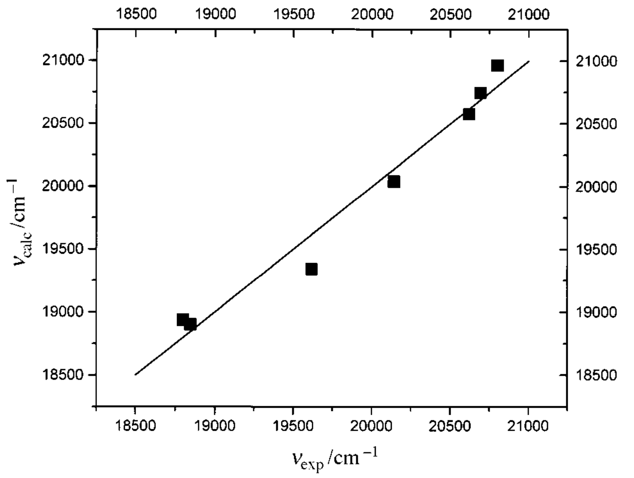


Fig. 2 Comparison of the experimental wavenumber values ν_{exp} of betaine **5** with ν_{calc} values obtained from data fitted to the McRae equation.

The solvatochromic shifts of the *ortho* betaine **5** were fitted to the McRae equation[10] [eqn. (1)], which relates the frequency

$$\nu_{max} - \nu_o = A(n^2 - 1)/(2n^2 + 1) + B[(\varepsilon - 1)/(\varepsilon + 2) - (n^2 - 1)/(n^2 + 2)] \quad (1)$$

of transition of the dye in a solvent ($\nu_{max} = 1/\lambda_{max}$) with its refractive index (n) and relative permittivity (ε). A and B are constants, obtained by linear regression of the data, and ν_o is the frequency of transition in vacuum. Constant B is related to the dipole moment change upon excitation ($\mu_g - \mu_e$), where the subscripts g and e refer to ground and excited states respectively, by eqn. (2).

$$B = 2\mu_g(\mu_g - \mu_e)/4\pi a^3 h\varepsilon_o \quad (2)$$

Here a is the cavity radius of the dye in the solvent, h is Planck's constant and ε_o is the permittivity in the vacuum.

Since the derivation of eqn. (1) was based on a simple electrostatic model that excluded all specific interactions between the betaine and the solvent, data from protic solvents in Table 1 were left out of the fitting.

A regression analysis of the data of Table 1 for the seven aprotic, non-polar solvents (toluene, benzene, chloroform, dichloromethane, acetone, dimethyl sulfoxide and acetonitrile) yielded values of 18509 cm^{-1}, 1204 and 2922 respectively, for ν_o, A and B of eqn. (1), with a regression coefficient $r = 0.984$. Fig. 2 compares the experimental wavenumber values for these solvents with those calculated with the regression values of ν_o, A and B. The obtained value of B is of the same order of magnitude as the constant obtained from data for compound **2** (2500),[4] suggesting for compound **5** an equally significant dipole moment change upon excitation, with a less polarized excited state than the zwitterionic ground state. The obtained value of 18509 ± 1266 cm^{-1} for ν_o, the frequency of the charge-transfer transition in the vacuum, should be treated with caution, as it was obtained from a regression curve with deviations which are not negligible.

We next proceeded to calculate the charge-transfer transition frequency of betaine **5** in various solvents.

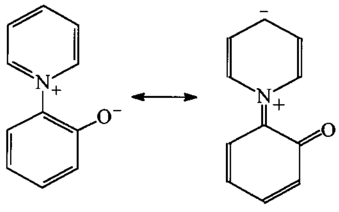
We first decided to compare the optimized structures of this betaine employing different semiempirical (AM1) and *ab initio*

Table 2 Calculated parameters for betaine **5**, from geometry optimizations employing different semiempirical and *ab initio* methods

Method	Torsion angle θ (°)	C=O bond length/Å	C–N bond length/Å	Dipole moment/D	Net charge on atom O	Net charge on atom N
AM1	31.1	1.257	1.406	6.56	−0.43	0.15
HF/6-311G	44.0	1.280	1.451	9.17	−0.72	−0.86
B3LYP/6-311G	27.0	1.293	1.431	6.82	−0.51	−0.73

(HF/6-311G and B3LYP/6-311G) methods. Some significant features of the obtained structures are listed in Table 2.

Comparison of the data shows that the AM1 method emphasizes the contribution of the *o*-quinonoid canonical form of the hybrid betaine structure (Scheme 5). This is indicated by the shorter C=O and C–N bond distances, the smaller dipole moment and the smaller negative change on the oxygen atom, when compared with the *ab initio* methods. The latter yield structures with a larger zwitterionic character. The extreme case is the HF/6-311G method, with the largest torsion angle θ between both rings, and the largest C–N bond length, dipole moment and negative charge on the oxygen atom. The hybrid DFT method B3LYP/6-311G does not deviate so much from the AM1 results, with comparable torsion angles, dipole moments and C=O/C–N bond lengths.



Scheme 5

Although a direct comparison of the calculated parameters with experimental data is as yet not feasible, the reported structure of analogous betaine **2** by X-ray diffraction analysis[4] may provide us with some degree of comparison for the calculated results. The torsion angle of **2** should inevitably be larger than that of **5**, because of the steric repulsion arising from the phenyl and the methyl substituents in the former betaine, which are absent in **5**. In fact, the pyridinium and the phenoxide rings are fully perpendicular in compound **2**. This difference may also account for the rather large C–N bond length (1.47 Å), larger than any of the calculated values (1.41–1.45 Å). The reported C=O bond length (1.29 Å) in **2** is the same as that calculated by the B3LYP/6-311G method. One may speculate that, in a more coplanar structure, both C=O and C–N bond lengths should be smaller, and betaine **5** should exhibit a more reduced zwitterionic character than **2**.

We next tried to simulate the solvatochromic behaviour of betaine **5** by means of the COSMO option of the MOPAC package. This rather cheap alternative to the much more costly *ab initio* calculations proved rather good, when applied to five different non-protic solvents (benzene, chloroform, dichloromethane, acetone and acetonitrile). Starting from the initially AM1-optimized structure, we calculated the first singlet transition energy of the molecule in media of different relative permittivity, taking into account configuration interactions arising from monoelectronic transitions from the five highest occupied to the five lower unoccupied molecular orbitals. The results are compared with the experimental λ_{max} values in Table 3. Agreement is very good, especially for the non-planar solvents (benzene, chloroform and dichloromethane), departing somewhat more from the experimental values in the more polar media (acetone and acetonitrile).

The negative solvatochromic behaviour of the betaine in the five solvents was very well reproduced by these calculations. Agreement in individual solvents was also good, especially in non-polar media (benzene, chloroform and dichloromethane). In more polar solvents, like acetone and acetonitrile, the calculated λ_{max} values departed more from the experimental values, being, however, still acceptably good.

Table 3 Experimental and calculated charge-transfer transition wavelengths and energies of betaine **5** in various solvents

	λ_{max}/nm (transition energies/eV)		
Solvent	Experimental	Calculated[a,b]	Calculated[b,c]
Benzene	528 (2.348)	523 (2.371)	490 (2.530)
Chloroform	517 (2.398)	481 (2.579)	478 (2.594)
Dichloromethane	499 (2.485)	456 (2.719)	—
Acetone	486 (2.551)	437 (2.835)	466 (2.661)
Acetonitrile	477 (2.599)	431 (2.875)	464 (2.672)

[a] Values from AM1-optimized, single-excitation CI calculations with the COSMO option of the MOPAC package. [b] Employed relative permittivities (ε) at 25 °C: 2.28 (C_6H_6), 4.81 ($CHCl_3$), 8.93 (CH_2Cl_2) 21.01 [$(CH_3)_2CO$] and 36.64 (CH_3CN) (from ref. 13). [c] HOMO–LUMO energy gaps, with the B3LYP/6-311G method, employing the Onsager method with a calculated cavity radius of 4.83 Å.

Although we were satisfied with the good agreement achieved with the cheaper semiempirical approach, we decided to test the hybrid *ab initio* DFT method B3LYP/6-311G in the calculation of transition energies of **5** in different solvents. This approach was admittedly not rigorous. DFT methods have traditionally been regarded as inappropriate for calculations of excited states, since the Kohn–Sham orbitals do not have any physical significance, as in Hartree–Fock methods.[11] This view however has been the object of increasing debate. Recent publications have appeared comparing Kohn–Sham and Hartree–Fock orbital energies. A recent review refers to the long-known empirical observation that energy differences between virtual and occupied Kohn–Sham orbitals are good approximations to excitation energies.[12]

We therefore found that the solvatochromic behaviour of betaine **5** offered a good opportunity of testing the method and providing more topics for discussion in this theoretical controversy.

We calculated the energy gaps between the highest occupied and the lowest virtual orbitals of compound **5** in four different solvents, characterized by their relative permittivities ε.[13] We employed the crudest and cheapest alternative for calculations in solution, the Onsager model, that position the molecule in a round cavity of radius a_o, surrounded by a continuum of permittivity ε. We obtained a radius a_o of 4.83 Å, after we performed a volume calculation on the B3LYP/6-311G-optimized structure. Next we performed SCRF calculations with the same method and radius a_o, employing different relative permittivities for the various solvents. The results are given in Table 3.

In spite of all approximations, the obtained results are rather good, adequately reproducing the negative solvatochromic behaviour of the betaine in these solvents. A graph (not shown) of the calculated λ_{max} values *vs.* the experimental values yielded a straight line with a correlation coefficient $r = 0.97$. These results therefore confirm Baerends and Gritsenko's observations that the use of DFT methods for the calculation of excitation energies, though not yet validated by theory, yield 'empirically' good approximations to experimental values.[12]

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