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# Solvatochromism of an Aminobenzodifuranone: An Unprecedented Positive Wavelength Shift

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The nature of the interaction of a solute molecule with its solvent counterparts lies at the heart of problems associated with our understanding of reactivity in solution. Of the phenomena employed to determine (a) the key characteristics of solvents which can influence reactivity, (b) the relative importance of those characteristics for particular solvents, and (c) the importance of those characteristics with respect to individual solutes, solvatochromism has made a spectacular contribution.[3−13] The largest solvatochromic shifts are of the negative variety and involve excitation of molecules from highly dipolar zwitterionic ground states to less dipolar excited states. The results are large hypsochromic shifts with increasing solvent "polarity".[14] Positive solvatochromism in which molecules with donor and acceptor groups, conjugatively linked through a $\pi$-system, have more dipolar excited states leads in general to smaller effects. However, precedent suggests that this phenomenon is of more comprehensive diagnostic value in terms of *specific* solvent properties.[7−9] We herein describe a positively solvatochromic molecule which not only is more sensitive to solvent properties than any hitherto recorded but also promises the potential for even greater sensitivity.

There are clearly two measurable parameters associated with solvatochromic behavior, the $S_0-S_1$ energy gap and the wavelength change $\Delta\lambda_{\max}$ associated with changes in that energy. Since there is essentially no variation in the accuracy of spectroscopic determination of a particular absorption maximum, the principal requisites for a molecule of diagnostic utility (*cf.* ref 13) are

(1) solubility in as wide a range of solvents as possible, stability in solution, a high extinction coefficient, Beer−Lambert behavior, and no solvent-induced change in the electronic nature of the long wavelength transition,

(2) exhibition of a large solvent-induced change in the $S_0-S_1$ energy gap, and

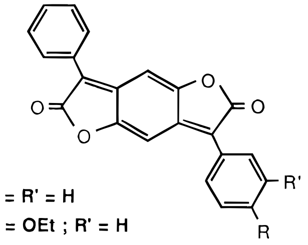
(3) long wavelength absorption maxima as far out to the red as possible in order to maximize the wavelength range of the solvent-derived shifts.

Further consideration of points 2 and 3 and the structures of positively solvatochromic molecules already known[13] indicates the requirement for

(a) an extended chromophore whose absorption characteristics are particularly sensitive to variation in auxochromic substituents and

(b) the inclusion of an auxochrome which not only takes the absorption maximum as far to the red as possible but which also has the functionality to allow the potential general and, in particular, specific solute−solvent interactions to manifest themselves.

The benzodifuranone chromophore[15] would appear to accommodate the first of these requirements since, in crystalline form, the molecules **1**, **2**, and **3** exhibit golden yellow, bright red, and bright blue colors, respectively. In addition, a consideration of the literature shows that 4-nitroaniline exhibits the largest positive solvatochromic shift in terms of transition energy (5855 cm$^{-1}$, 16.8 kcal mol$^{-1}$),[7] although the short-wavelength nature of the transitions results in only a modest wavelength shift of 74 nm in the solvents studied. It is clear that the large energy change is intimately associated with the H-bonding *donating* properties of the NH$_2$ group.[7] These facts suggest solvatochromic potential for an amino-substituted benzodifuranone, and in this work we report that compound **4**[16] fulfills the practical criteria 1−3 listed above and exhibits a positive solvatochromic shift which is larger in terms of both transition energy change and wavelength shift (5876 cm$^{-1}$, 206 nm) than any molecule reported to date.[13,17] A range of 26 solvents gave $\lambda_{\max}$ values ranging from 498 nm in nonafluoro-*tert*-butyl alcohol (NFTB) to 704 nm in HMPA (Table 1).



**1**; R = R' = H
**2**; R = OEt ; R' = H
**3**; R = NEt$_2$ ; R' = H
**4**; R = NH$_2$ ; R' = Me

Positive solvatochromic behavior can be attributed to a number of specific and nonspecific solute/solvent interactions as summarized in the linear solvation energy relationship (LSER) of eq 1[9] where *s*, *a*, and *b* are coefficients and $\pi^*$, $\alpha$, and $\beta$ reflect, respectively, the general solvent dipolarity/polarizability, its specific H-bond donating ability, and its specific H-bond accepting ability, which may or may not oppose one another in terms of solvatochromic contributions. $E_0$ is the

$$E = E_0 + s\pi^* + a\alpha + b\beta \qquad (1)$$

transition energy for a solvent where $\pi^* = \alpha = \beta = 0$ (e.g. cyclohexane). In Figure 1 is shown the excellent correlation

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[1] University of Manchester.
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[14] For instance, the 4-(2,4,6-triphenyl-1-pyridinio)-2,6-diphenylphenolate betaine exhibits the largest published negative shift from water (453 nm) to diphenyl ether (810 nm) corresponding to a transition energy change of 9729 cm$^{-1}$ (27.9 kcal mol$^{-1}$).[11]
[15] Greenhalgh, C. W.; Carey, J. L.; Hall, N.; Newton, D. F. *J. Soc. Dyers Colour.* **1994**, *110*, 178.
[16] European Patent 363034, assigned to ICI plc, Kenyon, R. W.; Newton, D. F.; Thorp, D., investigators; *Chem. Abstr.* **1993**, *113*, 134174v.
[17] According to a recent review,[13] the largest published positive solvatochromic changes, measured in two solvents of maximum difference in solvent polarity, are for a 5-dimethylamino-5′-nitro-2,2′-bithiophene (4710 cm$^{-1}$, 131 nm, highest previous energy change)[18,19] and Brooker's merocyanine (4400 cm$^{-1}$, 185 nm, largest previous wavelength shift).[6] However, as pointed out, a transition energy change of 5855 cm$^{-1}$ has been reported for 4-nitroaniline.[7] Although our range for **4** is 21 cm$^{-1}$ larger, the values are identical within experimental error.
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**Table 1.** Visible Absorption Maxima of Benzodifuranone **4** As a Function of Solvent

| solvent | $\lambda_{max}$/nm | solvent | $\lambda_{max}$/nm |
|---|---|---|---|
| 1 hexamethylphosphoramide | 704 | 14 methanol | 598 |
| 2 tetramethylene sulfoxide | 662 | 15 ethyl acetate | 590 |
| 3 tetramethylurea | 648 | 16 diethyl ether | 588 |
| 4 *N*-methylpyrrolidinone | 647 | 17 acetonitrile | 581 |
| 5 dimethyl sulfoxide | 645 | 18 toluene | 573 |
| 6 *N*,*N*-dimethylformamide | 634 | 19 benzene | 571 |
| 7 pyridine | 625 | 20 dichloromethane | 568 |
| 8 *N*-methylformamide | 620 | 21 chloroform | 568 |
| 9 isopropanol | 617 | 22 tetrachloromethane | 548 |
| 10 ethanol | 615 | 23 cyclohexane | 538 |
| 11 tetrahydrofuran | 606 | 24 trifluoroethanol | 516 |
| 12 $\gamma$-butyrolactone | 605 | 25 hexafluoroisopropanol | 499 |
| 13 acetone | 600 | 26 nonafluoro-*tert*-butyl alcohol | 498 |

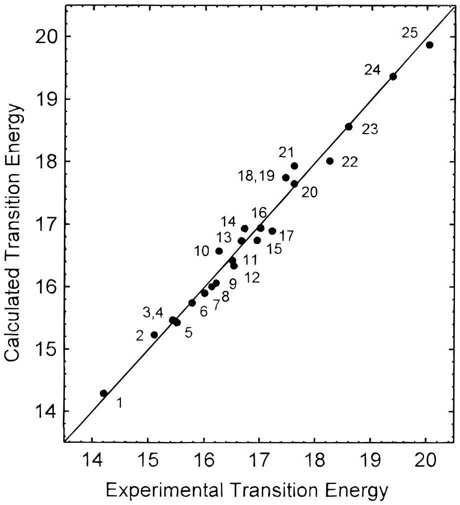


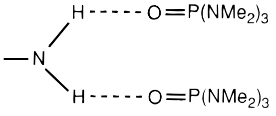
**Figure 1.** Comparison of the experimental transition energy, units of $10^3$ cm$^{-1}$, of **4** as a function of solvent (*cf.* Table 1) with values determined by multilinear regression analysis based on eq 1 (*cf.* eq 2 and ref 20).

resulting from a multilinear regression analysis[20] based on the data in Table 1, eq 1, and published values of $\pi^*$, $\alpha$, and $\beta$.[21,22] The individual form of the LSER for **4** is given by eq 2 (*cf.* eq 1), where energy units are $10^3$ cm$^{-1}$ (kK). Points to be emphasized are as follows.

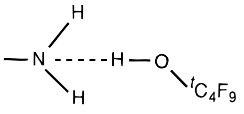
$$E = 18.6 - 0.91\,\pi^* + 0.97\,\alpha - 2.93\,\beta \qquad (2)$$

(1) The value for $E_0$ corresponds to a transition absorption maximum of 538 nm, identical to the experimental value of 538 nm for cyclohexane (*vide supra*).

(2) The huge solvatochromic range is readily understandable in terms of the opposite signs of the coefficients for $\alpha$ and $\beta$ as exemplified below for the two extreme solvents, HMPA and NFTB, in partial structures **5a** and **5b**. Since electronic excitation involves a shift of charge from nitrogen into the cyclic $\pi$-system,[25] the excited states produced will, relative to the ground state, be strongly stabilized by HMPA and destabilized by NFTB.[28]



**5a**



**5b**

(3) In contrast to **4**, 4-nitroaniline shows minimal sensitivity to H-bond donating solvents.[8] The possibility that this reflects a more pyramidal structure of the nitrogen in **4** was examined by estimating the gas phase transition absorption maximum for the latter, using the gas phase value for $\pi^*$ ($-1.1$)[24] and $\alpha = \beta = 0$ in eq 2 and comparing this with values obtained using the PPP-based program *PISYSTEM*.[26] This program gave transition maxima of 543 nm (planar nitrogen)) and 515 nm (pyramidal nitrogen), the latter being virtually identical to the gas phase value of 513 nm determined, as explained, from eq 2.

In conclusion, the aminobenzodifuranone **4** exhibits the largest positive solvatochromic shift in wavelength witnessed to date. This is attributed to the intrinsic nature of the benzodifuranone chromophore, the H-bond *donating* ability of $NH_2$, and the enhanced H-bond *accepting* ability of the latter as a consequence of pyramidalization. Given the two phenyl rings in molecules of this type (*cf.* **1**−**4**) and the potential for introduction of donors and acceptors in different phenyl rings, we anticipate that finer tuning of these systems will provide even greater positive solvatochromic shifts in the future.

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[20] Solvent selection was aided by a hierarchical cluster analysis of solvent parameters.[9,21,22] In all solvents **4** exhibits a single symmetrical absorption band in the visible whose shape is essentially independent of the medium. The LSER model was derived using standard commercial software.[23] Checks for (multiple) colinearities between the solvent parameters showed none to be evident. The degree of statistical fit of the derived model to the experimental data was satisfactory with a standard deviation (0.19 kK) approximately twice the experimental uncertainty and a correlation coefficient of 0.991. The additional polarizability parameter, $\delta$,[24] was invoked but found to be superfluous for the molecule under consideration. Errors in $E_0$, $s$, $a$, and $b$ (*cf.* eqs 1 and 2) are ±0.12 kK, ±0.18, ±0.07, and ±0.13, respectively. The transition energy for NFTB could not be included in the correlation since the appropriate solvation parameters are not available.

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[25] This was supported by calculations at both the PPP and CNDO/S levels of theory, using *PISYSTEM for Windows*[26] and in-house software based on the original CNDO/S model.[27] Details will be included in a full paper.

[26] *PISYSTEM for Windows*, version 3.1, R. Naef, Im Budler 6, CH-4419 Lupsingen, Switzerland.

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[28] That the critical specific interactions are at nitrogen, as opposed to carbonyl oxygen, is demonstrated by the corresponding data for the *N*-ethyl derivative of **4** which shows a significant but much more modest solvatochromic range (1636 cm$^{-1}$; 66 nm) with an individual LSER (eq 3) which demonstrates the critical effect of the H-bond accepting and donating properties of the $NH_2$ group in **4** (*cf.* eqs 1 and 2).

$$E = 16.9 - 1.23\,\pi^* + 0.0\,\alpha - 0.38\,\beta \qquad (3)$$