# Unusual solvatochromic behaviour of the 4-hydroxy-7-nitrobenzofurazan conjugated anion in protic solvents

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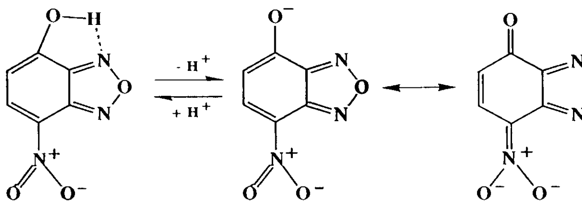
**The absorption spectrum of 4-hydroxy-7-nitrobenzofurazan (NBDOH) and its conjugate anion has been recorded in 23 solvents. The data has been analysed according to the Taft and Kamlet treatment and compared with that of some parent compounds: 4-methoxy-, 4-propylamino- and 4-diethylamino-7-nitrobenzofurazan. The phenolate anion NBDO$^-$ has been shown to exhibit the solvatochromic behaviour characteristic of this NBD series in aprotic media, although in protic media hydrogen bonding had a drastic effect on the UV–VIS spectrum. Such a sensitivity to protogenic solvents was not encountered for other phenoxide anions such as picrate. This difference of behaviour is discussed on the basis of electrostatic potentials obtained by MNDO calculations. Evidence is given of strong negative charges located on the C(5) and C(7) atoms of NBDO$^-$, indicating that strong hydrogen bonding may take place with solvent molecules. However, this stabilization of the anion by hydrogen bonding does not seem to influence the dissociation equilibrium, the acidity of NBDOH being perfectly in line with that of other nitrophenols whatever the solvent.**

## Introduction

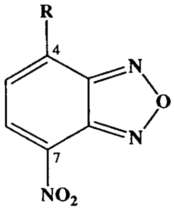
In the course of an investigation of phenols, we have tried to understand the origin of the well known discrepancy which appears between spectroscopically and conductimetrically determined dissociation constants.[1] Thus, the dissociation of 4-hydroxy-7-nitrobenzofurazan (4-hydroxy-7-nitrobenzoxadiazole, NBDOH, **1**) into the corresponding phenolate **2** (Scheme 1) was studied in organic solvents by UV–VIS spectroscopy and conductimetry. It was concluded on the one hand that the presence of water traces was absolutely necessary for this acid to dissociate and on the other hand that basic impurities remaining after standard purification of the solvent could drastically interfere with the measurement and were responsible for the observed discrepancy. Throughout this study, the system NBDOH/NBDO$^-$ proved to be a particularly good tool because its dissociation equilibrium was highly sensitive to the surrounding medium and because the two forms displayed interesting spectral properties.



NBDOH (1) NBDO$^-$ (2)

Scheme 1

The aim of the present work was to investigate more thoroughly the solvatochromic behaviour of NBDOH **1** and NBDO$^-$ **2** from absorption data recorded in 23 different solvents. The results have been compared with those obtained for the parent compounds 4-methoxy- (NBDOMe, **3**), 4-n-propylamino- and 4-diethylamino-7-nitrobenzofurazan (nPA-NBD **4** and DEA-NBD **5**) (Scheme 2), allowing a distinction to be made between the solvatochromic behavioural characteristics of the NBD series and that specific to the phenolate anion.



| R = | | |
|---|---|---|
| OH | NBDOH | 1 |
| $O^-$ | NBDO$^-$ | 2 |
| $OCH_3$ | NBDOMe | 3 |
| $HNCH_2CH_2CH_3$ | nPA-NBD | 4 |
| $N(CH_2CH_3)_2$ | DEA-NBD | 5 |

Scheme 2

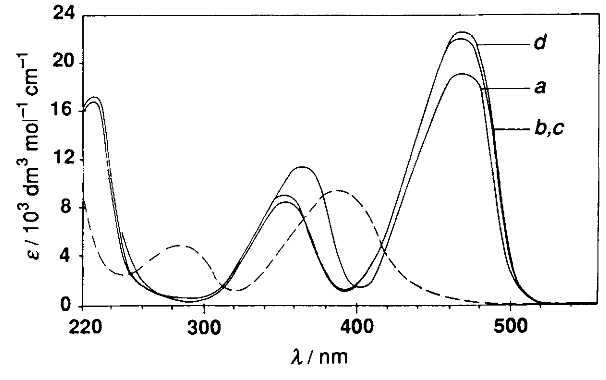


**Fig. 1** Absorption spectra of NBDOH **1** (dotted line) and conjugated anion NBDO$^-$ **2** (solid line) in (*a*) DMF, (*b*) propan-2-ol, (*c*) methanol and (*d*) water

In the second part, a parallel was established between the solvatochromic behaviour of NBDO$^-$ **2** and that of closely related nitrophenolates such as 2,4-dinitrophenolate and picrate. Finally, a link between the properties shown by the solvatochromic behaviour of NBDO$^-$ and the dissociation equilibrium of the NBDOH/NBDO$^-$ system was tentatively researched.

## Results

The 4-substituted derivatives of 7-nitrobenzofurazan display common spectroscopic features, namely the presence of three distinct absorption bands in the UV–VIS region (Fig. 1). According to the assignments given by Heberer and

**Table 1** $\pi^*$ Scale of solvent polarity (from ref. 5), $\alpha$ scale of solvent hydrogen-bond donor acidities, $\beta$ scale of solvent hydrogen-bond acceptor basicities and polarizability correction term $\delta$ (from ref. 4) and maximum absorption wavenumber $\bar{\nu}_{CT}$ of the charge transfer band for compounds **1**–**5**

| | | | | | | $\bar{\nu}_{CT}/10^3\ cm^{-1}$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| No. | Solvent | $\pi^*$ | $\alpha$ | $\beta$ | $\delta$ | NBDOH | NBDO$^-$ | NBDOMe | nPA–NBD | DEA–NBD |
| 1 | n-Hexane | −0.11 | 0.00 | 0.00 | 0.00 | 26.88 | — | 29.59 | 23.69 | 22.32 |
| 2 | Cyclohexane | 0.00 | 0.00 | 0.00 | 0.00 | 26.88 | — | 29.41 | 23.53 | 22.22 |
| 3 | Carbon tetrachloride | 0.21 | 0.00 | 0.00 | 0.50 | 26.67 | 22.03 | 29.07 | 23.25 | 21.83 |
| 4 | Diethyl ether | 0.24 | 0.00 | 0.47 | 0.00 | 26.52 | 21.98 | 29.32 | 22.42 | 21.55 |
| 5 | Ethyl acetate | 0.45 | 0.00 | 0.45 | 0.00 | 26.60 | 21.83 | 28.98 | 22.07 | 21.23 |
| 6 | Trichloroethylene | 0.48 | 0.00 | 0.00 | 0.50 | 26.59 | 21.79 | 28.73 | 22.73 | 21.41 |
| 7 | Toluene | 0.49 | 0.00 | 0.11 | 1.00 | 26.60 | 21.93 | 28.09 | 22.52 | 21.37 |
| 8 | 1,4-Dioxane | 0.49 | 0.00 | 0.37 | 0.00 | 26.45 | 21.93 | 28.49 | 22.17 | 21.28 |
| 9 | Tetrahydrofuran | 0.55 | 0.00 | 0.55 | 0.00 | 26.18 | 21.69 | 28.73 | 21.88 | 21.10 |
| 10 | Benzene | 0.55 | 0.00 | 0.10 | 1.00 | 26.45 | 21.79 | 28.09 | 22.47 | 21.28 |
| 11 | Dimethylformamide | 0.88 | 0.00 | 0.69 | 0.00 | 25.38 | 21.55 | 28.17 | 21.27 | 20.45 |
| 12 | Dimethylsulfoxide | 1.00 | 0.00 | 0.76 | 0.00 | — | 21.46 | 28.01 | 20.92 | 20.24 |
| 13 | *tert*-Butanol | 0.41 | 0.68 | 1.01 | 0.00 | 25.77 | 21.55 | 29.07 | 21.55 | 21.10 |
| 14 | Butan-1-ol | 0.47 | 0.79 | 0.88 | 0.00 | 25.77 | 21.50 | 29.07 | 21.55 | 20.83 |
| 15 | Propan-2-ol | 0.48 | 0.76 | 0.95 | 0.00 | 25.77 | 21.55 | 29.07 | 21.55 | 21.01 |
| 16 | Ethanol | 0.54 | 0.83 | 0.77 | 0.00 | 25.91 | 21.55 | 28.98 | 21.55 | 20.83 |
| 17 | Methanol | 0.60 | 0.93 | 0.62 | 0.00 | 25.91 | 21.55 | 28.90 | 21.55 | 20.57 |
| 18 | Acetone | 0.62 | 0.08 | 0.48 | 0.00 | 26.38 | 21.64 | 28.57 | 21.69 | 20.83 |
| 19 | Acetonitrile | 0.66 | 0.19 | 0.31 | 0.00 | 26.32 | 21.55 | 28.57 | 21.64 | 20.70 |
| 20 | Chloroform | 0.69 | 0.44 | 0.00 | 0.50 | 26.04 | 21.64 | 28.57 | 22.27 | 20.92 |
| 21 | Dichloromethane | 0.73 | 0.30 | 0.00 | 0.50 | 26.11 | 21.55 | 28.41 | 22.07 | 20.75 |
| 22 | Ethylene glycol | 0.92 | 0.90 | 0.52 | 0.00 | 25.64 | 21.46 | 28.41 | 21.01 | 20.24 |
| 23 | Water | 1.09 | 1.17 | 0.18 | 0.00 | 25.38 | 21.50 | 28.41 | 20.75 | 19.88 |

**Table 2** Calculated values of the vapour phase wavenumber $\bar{\nu}_0$ and solvatochromic coefficients $s$, $a$ and $b$ expressed in $10^3\ cm^{-1}$, maximum variation, standard deviation, multiple correlation coefficient $r$ and number of data points used in the calculation

| | $\bar{\nu}_0$ | $s$ | $a$ | $b$ | mv | sd | $r$ | Data points |
|---|---|---|---|---|---|---|---|---|
| NBDOH[a] | 27.0 | −0.90 | −0.37 | −0.46 | 0.44 | 0.16 | 0.937 | 23 |
| NBDO$^-$[b] | 22.0 | −0.45 | −0.21 | — | 0.18 | 0.10 | 0.833 | 21 |
| NBDO$^-$[c] | 22.2 | −0.72 | — | — | 0.18 | 0.06 | 0.945 | 10 |
| NBDOMe[d] | 29.4 | −1.45 | +0.38 | — | 0.40 | 0.09 | 0.972 | 21 |
| nPA-NBD[a] | 23.5 | −1.91 | −0.27 | −1.01 | 0.77 | 0.11 | 0.989 | 23 |
| DEA-NBD[b] | 22.1 | −1.79 | −0.36 | — | 0.59 | 0.11 | 0.981 | 23 |

Calculations were performed using [a] eqn. (1) or [b] eqn. (2) to treat the whole set of data, [c] eqn. (3) to treat the data obtained with non-hydrogen-bond donor solvents only, [d] eqn. (2) to treat the data obtained in all solvents except benzene and toluene. Treatment of the whole set of data for NBDOMe, taking the $\delta$-scale into account led to $\bar{\nu} = 29.5 - 1.44\,(\pi^* + 0.34\,\delta) + 0.37\,\alpha\ (10^3\ cm^{-1})$. mv:0.43, sd:0.117, $r$ = 0.962.

Matschiner[2] for amino derivatives, the short-wavelength band may be related to the aromatic system of the molecule, the intermediate band to a $\pi,\pi^*$ transition polarized along the major axis of the heterocycle, and the intense low energy band to a charge transfer (CT) taking place between the donor group and the nitro acceptor group situated in the 4 and 7 positions respectively.

It has been shown previously for amino-NBD derivatives[3] that the nature of the solvent strongly affects the position of the absorption bands, especially the charge transfer band. That is the reason why measurements were hereafter carried out on the latter. The wavenumber of the absorption maximum $\bar{\nu}$ was recorded in 23 solvents for each of the five compounds studied (Table 1). The data relative to the amino compounds has already been partially published[3] and has been completed in the present work for the sake of comparison. A correlation was then established with the classical Taft and Kamlet treatment. Among the recent compilations of solvatochromic values,[4–6] the scales which gave the best fits have been retained. This treatment enables the solvatochromic shift attributable to hydrogen bonding to be disentangled from that attributable to non-specific solvent effects. In the general expression (1), $\bar{\nu}_0$ is the

$$\bar{\nu} = \bar{\nu}_0 + s(\pi^* + d\delta) + a\alpha + b\beta \qquad (1)$$

vapour phase wavenumber and the empirical parameters $\pi^*$, $\alpha$ and $\beta$ are a measure of the polarity/polarizability character of the solvent and of its hydrogen-bond donor (HBD) and hydrogen-bond acceptor (HBA) capacity, respectively. The coefficients $s$, $a$ and $b$ indicate the susceptibility of $\bar{\nu}$ to a change in the corresponding parameter. The $\delta$ parameter is a 'polarizability correction term', whose coefficient $d$ is zero for all electronic spectra that are shifted bathochromically with increasing solvent dipolarity, as is the case for the NBD derivatives investigated here. The coefficients $s$, $a$ and $b$ have been determined using a multivariable linear regression program and the results are gathered on Table 2. For compounds which are not hydrogen-bond donors, namely NBDO$^-$ **2**, NBDOMe **3** and DEA-NBD **5**, using the $\beta$-scale was irrelevant, so the determination of $\bar{\nu}_0$, $s$ and $a$ was carried out by using the reduced eqn. (2).

$$\bar{\nu} = \bar{\nu}_0 + s\pi^* + a\alpha \qquad (2)$$

It must be noticed in the case of NBDOMe that aromatic solvents apparently gave rise to a specific effect. By discarding the data relative to benzene and toluene, the correlation coefficient passes from 0.900 to 0.972. A similar improvement of the fit may be obtained by introducing the $\delta$ polarity correction term, while performing the calculation on the whole set of data. The use of this parameter is not rigorous since the absorption spectra is shifted bathochromically with increasing solvent dipolarity. However, it may find some justification in the fact that increasing the HBD character of the solvent led to a hypsochromic shift (positive coefficient $a$). As for NBDO$^-$ **2**, the treatment of the whole set of data using eqn. (2) did not provide a correct fit of the experimental points. The maximum variation is close to the standard deviation, indicating that the correlation with $\pi^*$ and $\alpha$ is hardly significant. The correlation coefficient, which takes into account both the maximum variation and the standard deviation, is particularly poor ($r$ = 0.833). As a matter of fact, the charge transfer band of NBDO$^-$ appeared at (21.64–21.46) × $10^{-3}$ cm$^{-1}$ (462–466 nm) in every hydrogen-bond donor solvent, whatever the HBD capacity of this solvent on the $\alpha$-scale. According to this observation, the treatment was restricted to non-hydrogen-bond donor solvents (solvents 3–12), using eqn. (3), since in those solvents the $\alpha$-

$$\bar{\nu} = \bar{\nu}_0 + s\pi^* \qquad (3)$$

value is equal to zero. This provided a more satisfactory correlation ($r$ = 0.945) (see Table 2).

## Discussion

The absorption spectra of the five compounds studied are highly characteristic of NBD derivatives where a charge transfer takes place between the substituents in the 4 and 7 positions. As expected, the position of the CT band, given by the $\bar{\nu}_0$ value in Table 2, varies in the order **2** ≈ **5** < **4** < **1** < **3**, indicating that the band is displaced to lower energies upon increasing the electron-donor ability of the group at the 4 position.

Solvatochromic properties have been observed for each of those derivatives, although the correlation with the Taft and Kamlet treatment provided a far better fit in the case of the amino derivatives than for the oxygenated ones. This can be partly attributed to uncertainties due to the weak wavelength shifts observed for the latter compounds. However, it seems that among the five compounds studied the NBDO$^-$ anion exhibited a particular behaviour, according to whether the solvent was protic or not. In aprotic media, the characteristics of the NBDO$^-$ anion seem to be intermediate between those of the amino derivative and those of the hydroxy derivative. The absorption occurred at high wavelength, but the position of the band was poorly affected by a change in polarity/polarizability of the medium, the value of the $s$ parameter resembling that obtained for the phenol derivative. It is in protic solvents that the NBDO$^-$ anion differed more strikingly from the parent compounds. The maximum bathochromic effect was obtained as soon as the medium displayed any protogenic character, so that the $\alpha$-scales were no longer sufficient to take these variations into account. It would be appealing to relate the high sensitivity observed in protic media to the fact that NBDO$^-$ lacks the stabilization due to intramolecular hydrogen bonding which existed in the conjugate phenol[7] (Scheme 1). However, parent compounds such as DEA-NBD **5**, where no intramolecular hydrogen bonding is possible, do not give rise to any particular solvatochromic behaviour in the presence of a protic solvent. At this stage of the discussion, one may wonder if this behaviour of NBDO$^-$ in protic solvents is a characteristic of phenolate anions. In order to establish a comparison with closely related anions, the solvatochromic behaviour of 2,4-nitrophenolate and picrate has been tentatively investigated according to the procedure used for NBDO$^-$. However, for these compounds, the overlap of two closely adjacent absorption bands (which correspond to transitions involving the *para* and *ortho*-quinoid states[8]) obscures the characteristics of both and makes the data difficult to exploit directly, since the shape of the spectrum undergoes considerable variations from one solvent to another. It is obvious anyway that the proton donating character of the solvent did not have a drastic effect upon the solvatochromic shift as was encountered for NBDO$^-$. In fact, an aprotic polar solvent such as dimethylformamide led to a stronger bathochromic shift than equally polar protic solvents (see Fig. 2).

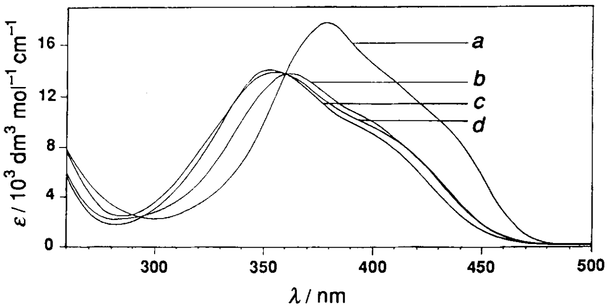
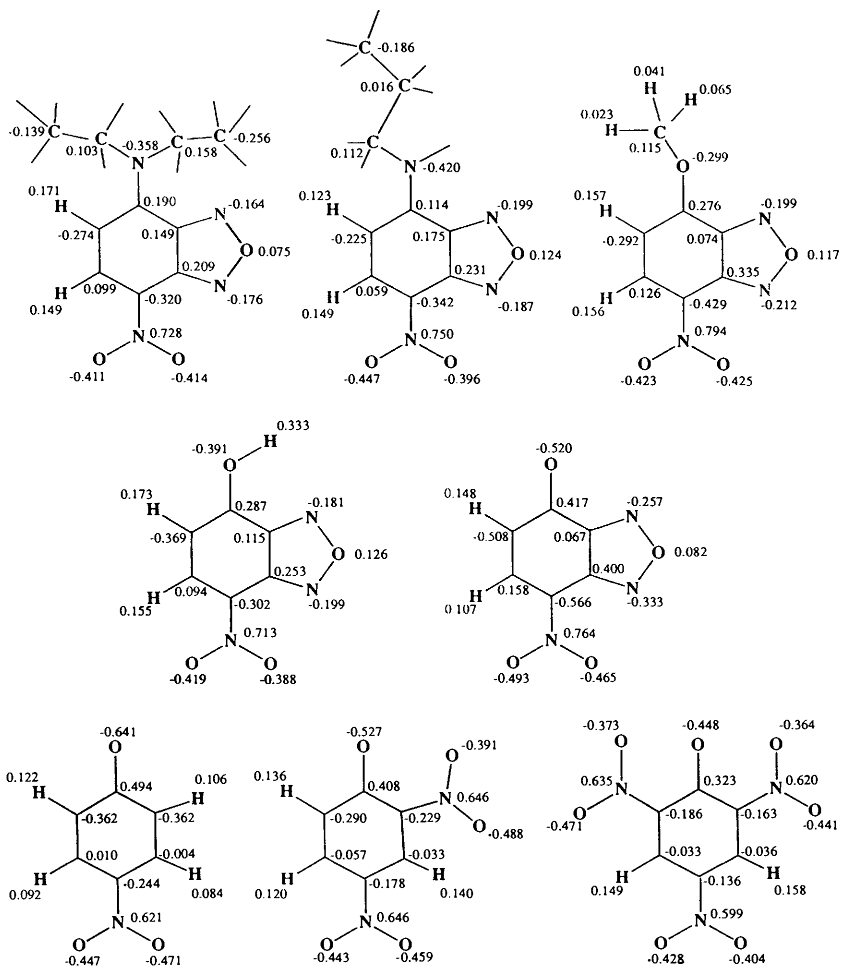


**Fig. 2** Absorption spectra of picrate in (*a*) DMF, (*b*) propan-2-ol, (*c*) methanol and (*d*) water

We have tried to understand why the NBDO$^-$ anion exhibited such a peculiar behaviour towards protonation. Electrostatic potentials have been calculated using the MNDO approach for the NBD derivatives studied above as well as for different nitrophenols: results are displayed in Scheme 3. When considering the NBD compounds, it is obvious that in all cases the nitro group in the 7 position as well as the furazan act as attractors, but the difference in electrostatic potential observed on the heteroatoms remains quite small from one compound to another. In contrast, comparing the structure of NBDO$^-$ with that of the other NBD derivatives shows a drastic decrease in electrostatic potential located on the C(7) and, to a minor extent, on the C(5) atoms of the anion. The charge on the C(7) atom is even higher than that located on the phenoxide oxygen atom. Let us now consider other nitrophenolates. It may be clearly seen that upon going from 4-nitrophenolate to 2,4-dinitrophenolate and then to picrate, the negative charge first located on the phenoxide oxygen atom becomes delocalized onto the whole structure when adding one, then two nitro groups. Therefore, the localization of the charge on a particular carbon atom, as is the case for NBDO$^-$, was not encountered for the other nitrophenolates. This may partly explain the peculiar spectroscopic behaviour of the NBDO$^-$ anion, because the increase in electron density appearing on the C(5) and C(7) atoms could generate a very likely site of electrophilic attack. In protic solvents, it is likely that strong hydrogen bonding is established between the carbon atoms in the 5 or 7 position and solvent molecules.

We now turn our interest towards the dissociation equilibrium of the NBDOH/NBDO$^-$ system, in order to discover to what extent this equilibrium is affected by the stabilization of the anion due to the involvement of hydrogen bonds. It is indeed widely acknowledged that the dissociation of uncharged acids may be split into two phases: ionization to form an ion pair, and then separation of the ions, the former depending on the acid–base properties of the solvent, whereas the solvent relative permittivity is the limiting factor of the latter. However, it must be emphasized that the dissociation equilibrium is also affected by other solvent interactions capable of stabilizing the produced anion[9,10] and which are usually refered to as 'solvation effects'. This term includes hydrogen bonding and van der Waals forces, and among the latter, London dispersion forces are of considerable importance in the equilibrium of dissociation of nitrophenols. The nitrophenolate anion being usually more strongly polarizable than the parent phenol, it can establish with suitable organic solvents very strong London dispersion interactions, whose contribution significantly displaces the equilibrium towards dissociation. By definition, the polarizability of a compound is directly related to electron mobility. Well, it is obvious that the electronic system is more delocalized in NBDO$^-$ than in NBDOH: it may be seen with the naked eye that NBDOH in solution is pale yellow whereas NBDO$^-$ is intensely coloured, which leads to the appearance of absorption bands in the visible spectrum. Moreover, the calculation confirms that, although



**Scheme 3** Electrostatic potentials for DEA-NBD (**5**), nPA-NBD (**4**), NBDOMe (**3**), NBDOH (**1**), NBDO$^-$ (**2**), 4-nitrophenolate, 2,4-dinitrophenolate and picrate (from top to bottom)

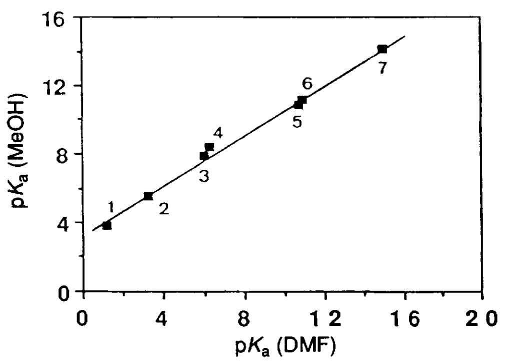


**Fig. 3** Plot of p$K_a$ (MeOH) *vs.* p$K_a$ (DMF) at 20–25 °C for different phenols: (1) picric acid; (3) 2,4-dinitrophenol; (4) 4-nitrothiophenol; (5) thiophenol; (6) 4-nitrophenol; (7) phenol (data from Clare *et al*, ref. 10). (2) 4-Hydroxy-7-nitrobenzofurazan (data from Tsentovskii *et al*, ref. 11).

**Table 3** p$K_a$ of acids at 20–25 °C

| | p$K_a$ | | | |
|---|---|---|---|---|
| | MeOH | DMF | DMSO | $H_2O$ |
| 2,4-Dinitrophenol[a] | 7.9 | 6.0 | 5.2 | 4.1 |
| NBDOH | 5.5[b] | 3.2[b] | 2.6[b] | ≤1.8[c] |
| Picric acid[a] | 3.8 | 1.2 | −1.9 | 0.71 |

[a] Ref. 10 and refs. cited therein. [b] Ref. 11. [c] Ref. 7.

the negative charge concentrates on the C(7) and C(5) atoms, it is widely spread over the NBDO$^-$ structure, as shown by the tautomeric forms in Scheme 1. Thus there is no doubt that NBDO$^-$ is more strongly polarizable than NBDOH. Conductimetrically determined p$K_a$ values of NBDOH (which may be considered as being the most accurate[1]), have been extracted from the literature.[11] Let us consider methanol and DMF, two solvents of similar relative permittivity ($\varepsilon_r$ = 32.66 and 36.71, respectively), but which differ in polarizability, as expressed by the difference between the $\pi^*$ values. It may be seen that the p$K_a$ value is 5.5 in methanol and 3.2 in DMF. This may be interpreted by considering that DMF, whose molecules are good dispersion centres, provides more efficient solvation than methanol does. This observation (which must be tempered by the fact that methanol and DMF have different HBD abilities) agrees well with the involvement of dispersion forces in the dissociation equilibrium.

Let us now compare the acidity of NBDOH with that of other phenols (Table 3). It appears that the p$K_a$ values of NBDOH is intermediate between that of 2,4-nitrophenol and that of picric acid. This observation holds true in solvents as different as water, methanol, DMF and DMSO. This confirms that the three compounds behave similarly, because if it had not been the case, a reversal of acidity sequence could have been found when changing the solvent, as is generally observed when comparing the strength of two acids, one of which gives rise to a large polarizable anion whereas the second dissociates into a smaller anion with localized charge.[9,10,12,13] It can also be verified according to Clare *et al.*,[10] by plotting the p$K_a$ values obtained in methanol *versus* the p$K_a$ values obtained in DMF (Fig. 3), that NBDOH is perfectly on line with the six other phenols considered ($r$ = 0.996). Such a linear relationship maintained when passing from an aprotic solvent to a protic one of identical relative permittivity shows that the effect of hydrogen-bonding upon the dissociation equilibrium is analogous for all these compounds. No particular behaviour in protic solvents was detected for the NBDOH/NBDO$^-$ system with respect to dissociation. This agrees with the conclusion of a previous study,[1] that the dissociation of NBDOH follows a very simple model: NBDOH + $H_2O \rightleftharpoons$ NBDO$^-$ + $H_3O^+$, only involving the water traces of the organic solvent, the latter being protic or not.

Therefore, it seems that the dissociation equilibrium mainly depends on the overall increase of electronic delocalization on the anion, as is the case in the phenol series, the contribution of hydrogen bonding not being perceptible in this respect. On the other hand, the increase of the charge pin-pointed on the C(7) and C(5) atoms might well govern the solvatochromic properties, giving NBDO$^-$ its very unusual behaviour in protic solvents.

## Experimental

4-Hydroxy-7-nitrobenzofurazan was prepared as previously described.[1] The synthesis of 4-propylamino- and 4-diethylamino-7-nitrobenzofurazan has also been given in a previous paper.[3] 4-Methoxy-7-nitrobenzofurazan was prepared as follows, according to a procedure reported in the literature,[14] slightly modified to obtain a product of high spectroscopic purity. Potassium methoxide (175 mg, $2.5 \times 10^{-3}$ mol) dissolved in methanol (10 cm$^3$) was added dropwise to a solution of 4-chloro-7-nitrobenzofurazan (Aldrich, 250 mg, $1.25 \times 10^{-3}$ mol) in anhydrous methanol (50 cm$^3$). After 10 min stirring at room temperature, the solution was acidified (conc. hydrochloric acid) and then evaporated to dryness. The light yellow powder obtained was recrystallized (dichloromethane) and then sublimed under vacuum (yield 80%). IR, NMR, mass spectra and elemental analyses were as expected. Picric acid and 2,4-dinitrophenolate (Aldrich) used for comparative spectra were recrystallized twice (absolute ethanol) and dried *in vacuo* over $P_2O_5$.

Spectroscopic grade solvents (SDS and Merck) were used as received—they may contain up to 0.05% water (0.1% for alcohols). It has been shown elsewhere[1] that water traces induce the dissociation of NBDOH. For this reason, when necessary, perchloric acid (70%; 10 µl; 1µl = 1mm$^3$) was added to the cuvette to obtain the spectrum of the pure acidic form of NBDOH. In such an acidic medium, the total amount of water (that already present in the solvent and that introduced with the acid) remained low enough not to change the properties of the bulk solvent and did not affect the UV spectra. Conversely, an identical volume of triethylamine (redistilled over potassium hydroxide) was used to obtain the spectrum of the pure phenolate.

Absorbance spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer recording the wavelength every 2 nm. The solvatochromic data were analysed on a HP 9000 series 710 workstation running under UNIX. Electrostatic potentials were calculated according to the modified neglect of diatomic overlap (MNDO) method. Calculations were performed on a 4D30 Silicon Graphics computer by using Insight Discover Biosym software (Biosym Technologies, Inc.).

## Acknowledgements

Dr Jean-Claude Micheau is gratefully acknowledged for fruitful discussions and his interest in this work. We also are indebted to Dr Robert Wolf for his comments and bibliographic assistance, and to an unknown referee for helpful suggestions.

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*Paper* 5/03073K
*Received* 15*th May* 1995
*Accepted* 22*nd August* 1995