Solvatochromism of Sterically Hindered Stilbazolium Betaines and Its Relationship to Reichardt's $E_T(30)$ Scale: The Problem of the Measurement of the Polarity vs the Acidity of Alcohols

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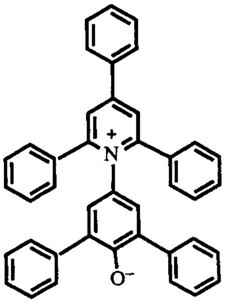
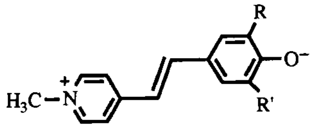
The hydrogen bond acidity of twenty primary, secondary, and tertiary alkanols has been measured by the solvatochromic method by using three stilbazolium betaines: stilbazolium betaine itself (SB), *o-tert*-butyl-substituted (TBSB), and *o,o'*-di-*tert*-butyl-substituted SB (DTBSB). The spectral differences between two of these betaines and in particular the Δ' values which correspond to SB and DTBSB, have been compared with Reichardt's E_T(**30**) values. Excluding sterically hindered alcohols, both scales are linearly related. For normal alkanols, the Δ' values have been compared with the absorbance of the stretching of the OH band both free and associated with *N,N*-dimethylacetamide (DMA). There is a linear relationship between Δ' and ln $[(A_{\nu(\mathrm{OH})\mathrm{associated}})/(A_{\nu(\mathrm{OH})\mathrm{free}})]$ which proves that Δ' is a measure of the hydrogen-bond donor (HBD) acidity of alcohols. Contrary to some expectations, the effect of alkyl substituents shows a slow attenuation with increasing number of carbon atoms in the chain.

The most exhaustively studied and most widely used empirical scale of solvent polarity is Reichardt's E_T(**30**) scale[1–3]. This scale is based on the negative solvatochromism of pyridinium *N*-phenoxide betaine dye **I**, and it has been used as a measure of solvent polarity by Reichardt[1–4] and others[5]. However, Laurence, Reichardt et al.[6] have examined the sensitivity of **I** to acidity in the case of acidic alcohols like CF_3CH_2OH and to steric effects in the case of bulky alcohols like $(CH_3)_3COH$. Nevertheless, it is assumed that E_T(**30**) measures essentially the solvent polarity.



I



II, SB, R = R' = H
III, TBSB, R = H, R' = C(CH3)3
IV, DTBSB, R = R' = C(CH3)3

In a previous paper[7] we have shown that the extremely strong negative solvatochromism of the stilbazolium betaine dye SB **II** (≈6500 cm^{-1}) is not due to the dipolarity-polarizability effect of the solvent but to its acidity (hydrogen-bond donor acidity, HBD acidity). This has been proven by studying the solvatochromic effects of the same solvent on betaine DTBSB **IV** where the basic center, the oxygen atom, is protected against the approach of the solvent by the introduction of two bulky *tert*-butyl groups into the *ortho* position. When this specific solvent effect is prevented, stilbazolium betaines show only a very weak solvatochromism but their electronic spectra exhibit a coarse structure (see below for a definition of this term); vice versa, the appearance of a resolved maximum indicates steric hindrance to the approach of an HBD-acidic solvent. Betaine **I** is not so well protected against specific solvation effects by the two *o*-phenyl rings since they can rotate, i.e. the steric effect of a phenyl ring depends on conformation.

We have synthesized the new betaine TBSB **III** bearing only one *tert*-butyl group in *ortho* position with respect to the basic center, in order to determine more precisely the HBD acidity of the solvents. Since the carbonyl group of stilbazolium betaines has two oxygen lone pairs that lie in the plane of the quinonoid ring, it is possible to have two (SB), one (TBSB), or no channel (DTBSB) for the approach of the acidic solvent depending on the number of *o-tert*-butyl groups. We have found that a comparative study of the electronic spectra of the three betaines in a series of twenty alcohols provides a measure of the acidity of alcohols in the condensed phase, with the only limitation that they must be liquids at room temperature, or near to it.

The results are collected in Table 1 in which Δ corresponds to the wavenumber difference between SB and TBSB, Δ' to the wavenumber difference between SB and DTBSB, and Δ" to the wavenumber difference between TBSB and DTBSB. Thus, by definition, equation $\Delta' = \Delta + \Delta''$ holds. According to the proposed model for the *tert*-butyl gate effect, the following relationship is expected to exist between these increments: $\Delta \approx \Delta'' \approx 1/2\ \Delta'$.

Table 1. Long-wavelength solvatochromic absorption maxima of betaine dyes **II**–**IV** ($\tilde{\nu}$ in cm^{-1}) in twenty hydrogen-bond donor (HBD) solvents and the corresponding E_T(**30**) values of Reichardt

Solvent	SB	TBSB	DTBSB	Δ^{a}	Δ'^{b}	Δ''^{c}	E_T(**30**) [kcal mol^{-1}]	E_T(**30**) [cm^{-1}]^{d}
1 Methanol	20605	18657	(16357)^{e}	1948	(4248)^{e}	(2300)^{e}	55.4	19376.7
2 Ethanol	19471	17807	16226	1664	3245	1581	51.9	18152.6
3 1-Propanol	19104	17538	16110	1566	2994	1428	50.7	17732.9
4 1-Butanol	18839	17436	16099	1403	2740	1337	50.2	17558.0
5 1-Pentanol	18569	17250	16018	1319	2551	1232	49.1	17173.2
6 1-Hexanol	18375	17169	15969	1206	2406	1200	48.8	17068.3
7 1-Heptanol	18282	17098	15947	1184	2335	1151	48.5	16963.4
8 1-Octanol	18188	17051	15922	1137	2266	1129	48.3	16893.4
9 1-Nonanol	18014	16932	15903	1082	2111	1029	[47.8]^{j}	[16718.5]
10 1-Decanol	17921	16871	15886	1050	2035	985	47.7	16683.6
11 1-Undecanol	(17892)^{f}	16850	15876	(1042)^{g}	(2023)^{g}	974	[47.5]^{j}	[16613.6]
12 2-Propanol	18251	17207	16069	1044	2182	1138	48.4	16928.4
13 2-Butanol	17838	16909	16001	929	1837	908	47.1	16473.7
14 2-Methyl-1-propanol	18650	17264	16045	1386	2605	1219	48.6	16998.4
15 2-Methyl-2-propanol	17297	16373^{h}	15985	<924	1312	>388	43.3^{i}	15144.6
16 2-Pentanol	17631	16697^{h}	15960	<934	1671	>737	46.5	16263.9
17 2-Methyl-1-butanol	18323	17098	15978	1225	2345	1120	48.0	16788.5
18 3-Methyl-1-butanol	18530	17227	16009	1303	2521	1218	49.0	17138.3
19 3-Methyl-2-butanol	17589	16612^{h}	15962	<977	1627	>650	45.7	15984.1
20 2-Methyl-2-butanol	16870	16139^{h}	15928	<731	942	>211	41.1	14375.2

[a] $\tilde{\nu}$(SB) – $\tilde{\nu}$(TBSB). – [b] $\tilde{\nu}$(SB) – $\tilde{\nu}$(DTBSB). – [c] $\tilde{\nu}$(TBSB) – $\tilde{\nu}$(DTBSB). – [d] From E_T(**30**) [kcal mol^{-1}] = 2.8591 · 10^{-3} $\tilde{\nu}$ [cm^{-1}][2] it follows that $\tilde{\nu}$ [cm^{-1}] = 349.76 E_T(**30**) [kcal mol^{-1}]. – [e] Estimated value (see text), no 0→0 transition observed. – [f] Estimated; upper limit = 17982. – [g] Estimated from the following linear relationships in *n*-alkanols **2**–**10** (9 compounds): $\Delta'' = 103.71 + 0.8732\,\Delta$ ($r^2 = 0.97$) and $\Delta' = -81.01 + 2.1145\,\Delta''$ ($r^2 = 0.992$). – [h] Coarse structure (the reported value corresponds to the 0→0 transition). – [i] Determined at 30°C[2c]. – [j] From 9 normal alkanols (including the estimated Δ′ value of methanol): E_T(**30**) = $40.27 + 0.00355\,\Delta'$, $r^2 = 0.996$.

In some cases (footnote h), the first absorption band in the visible part of the UV/Vis spectrum of TBSB exhibits a coarse structure (we have used this term[7] to describe an ill-resolved vibrational structure, different from the fine structure due to rotational transitions, and we have shown[7] that this structure indicates a steric hindrance to the approach of the solvent to the carbonyl group), and the reported value corresponds to the 0→0 transition. In these cases, the values of Δ and Δ″ cannot be determined, so that only lower and upper values are given in Table 1. In the case of methanol, the change in color of the DTBSB solution as compared with other alcohols indicates that the solvent molecule is small enough to approach the basic oxygen center. The wavenumber of absorption in methanol (16357 cm^{-1}, note e) has been estimated from the deconvolution of the experimental spectra into a sum of four Gaussians (G = 16285 cm^{-1}), followed by an empirical correction (DTBSB = 723 + 0.96 G, three alkanols) to have comparable values. Even so, the 16357 cm^{-1} value is, at best, only an estimate that must be thoroughly checked. The error in Δ (Δ, Δ′, and Δ″) can be estimated to be less than 10 cm^{-1}.

Another interesting observation is the appearance of an additional maximum near 476 nm (21000 cm^{-1}) in the case of SB when the solvent is decanol or undecanol (its intensity increases in this sequence). It can also be found as a shoulder in heptanol and octanol as solvents. From the fact that this absorption is only observed for SB it may be assumed that if SB contains two alcohol molecules anchored to the carbonyl group by two H bonds, these two molecules could be the origin of a short-distance order in the solvent forming, for instance, a micellar structure.

In Table 1 are also collected values of E_T(**30**) in kcal mol^{-1} and in cm^{-1} for the 20 alcohols as reported by Reichardt[1–3]. Only those of 1-nonanol (**9**) and 1-undecanol (**11**) are not known. Since there is a perfect linear relationship between E_T(**30**) and Δ′

$$E_T(\mathbf{30}) = 40.27 + 0.00355\,\Delta',\ n = 9,\ r^2 = 0.996,\ S_d = 0.17 \qquad (1)$$

we have calculated the E_T(**30**) values for **9** and **11**. Clearly, both E_T(**30**) and Δ′ are extraordinarily sensitive to the number of carbons of the normal alkanol since even 1-decanol and 1-undecanol (ten bonds distant from the OH) show different values. Nevertheless, there is a clear attenuation of the solvatochromic effect with increasing chain length. The simplest model for an attenuation is a hyperbolic equation with asymptotes parallel to the coordinate axis of the form ln E_T(**30**) or $\ln \Delta' = a + b \ln n$ (*n* being the number of carbon atoms of the normal alkanol chain). For the eleven linear alkanols the following equations have been established:

$$\ln E_T(\mathbf{30}) = 4.0009 - 0.0612 \ln n \qquad (n = 11,\ r^2 = 0.97,\ S_d = 0.0075) \qquad (2)$$

$$\ln \Delta' = 8.3333 - 0.3034 \ln n\ (n = 11,\ r^2 = 0.99,\ S_d = 0.018) \qquad (3)$$

Methanol (**1**) slightly deviates from both equations. Even if the whole collection of data (20 points) is considered, the following linear relationship still holds:

$$E_T(\mathbf{30}) = 38.935 + 0.004\,\Delta'\ (n = 20,\ r^2 = 0.95,\ S_d = 0.64) \qquad (4)$$

An examination of the graph clearly shows that both tertiary alcohols **15** and **20** deviate from the regression line, having $E_T(\mathbf{30})$ values lower than expected. If these two points are excluded, the new equation is:

$$E_T(\mathbf{30}) = 40.3503 + 0.0035\,\Delta'\ (n = 18, r^2 = 0.98, S_d = 0.33) \quad (5)$$

This equation predicts $E_T(\mathbf{30})$ values for **15** and **20** to be 44.94 and 43.64 instead of 43.3 and 41.1 kcal mol^{-1}, that is a difference of 574 and 888 cm^{-1} in energy, respectively.

Since we have established that Δ' and $E_T(\mathbf{30})$ are linearly related, eq. (5), save for bulky tertiary alcohols (which probably corresponds to conformational changes of the phenyl groups in *ortho* position with respect to the basic center in compound **I**), the question whether the solvent property which these betaine dyes measure is the polarity or the acidity of the solvent remains to be discussed.

The first remarkable fact of the values of Table 1 is that Δ and Δ'' are approximately the same (see note g of Table 1). This is attributed to the fact that the TBSB maximum is almost equidistant from those of SB and DTBSB, or in other words, the effect of the *tert*-butyl groups is nearly additive:

$$\nu_{TBSB} = -2344 + 0.567\,(\nu_{SB} + \nu_{DTBSB})\ (n = 19, r^2 = 0.97) \quad (6)$$

In this correlation are included values for compounds **11** (Table 1, note f) as well as for **15**, **16**, **19**, and **20** (Table 1, note h) but not those of methanol; the estimated value of DTBSB in methanol is 16456 cm^{-1}. This is almost exactly in accord with the hypothesis that *tert*-butyl groups act like gates, closing the channels used by the alcohol to reach the oxygen lone pairs. Thus, Δ and Δ'' correspond to the closing of one channel, and Δ' corresponds to the closing of both channels. It is remarkable that Δ and Δ'' are very similar, suggesting that both channels of SB are used.

In order to determine if our Δ' values are a measure of the HBD acidity, we have selected an acceptor, *N*,*N*-dimethylacetamide, DMA, and measured the ν(OH) bands of alkanols, from methanol to 1-nonanol, in dilute CCl_4[8]. Two bands are clearly observed, a narrow one at 3630 cm^{-1} corresponding to the free OH and a broad one near 3460 cm^{-1} corresponding to the OH bound to DMA. The second band is too large to determine its wavenumber with precision. On the other hand, the relative intensities of the two bands change smoothly with the alkanol. Assuming that the ratio of absorbances is proportional to the ratio of concentrations, then there should be a linear relationship between Δ' and ln (*Ratio*) (*Ratio* = $A_{ROH:DMA}/A_{ROH}$).

The measured values of ln (*Ratio*) are: methanol (−0.064), ethanol (−0.263), 1-propanol (−0.326), 1-butanol (−0.330), 1-pentanol (−0.393), 1-hexanol (−0.389), 1-heptanol (−0.450), 1-octanol (−0.507), and 1-nonanol (−0.484). These values can be adjusted to a linear equation:

$$\Delta' = 4434.1 + 4721.9 \ln (Ratio) \quad (n = 9, r^2 = 0.961, S_d = 360\ \mathrm{cm}^{-1}) \quad (7)$$

This equation proves that Δ' values are a measure of the HBD acidity of alcohols.

Even if the precedent discussion could have been made with any Δ magnitude, we have selected the parameter Δ' because it is the most sensitive one to the interaction induced by hydrogen bond since it corresponds to $\nu_{SB} - \nu_{DTBSB}$. On the other hand, Δ and Δ'' contain information from the TBSB probe, and for this reason they should be sensitive to steric effects of the solvent. As we have already commented, this phenomenon is reflected in the visible spectrum of TBSB as a coarse structure of the main band. Of all the alkanols studied only in two cases, 2-methyl-2-propanol (**15**) and 2-methyl-2-butanol (**20**), the TBSB betaine spectrum exhibits a clearly resolved band, and in the other two cases, 3-methyl-2-butanol (**19**) and 2-pentanol (**16**), the band is large and asymmetric. A possible way to quantify the steric effect is to use the difference $(\Delta'/2) - \Delta''$, a difference that for the above four compounds amounts to 268, 260, 163, and 98 cm^{-1}, respectively.

General Conclusions

We have developed a model of hydrogen bond donor acidity based on the UV/Vis absorption spectra of three related dyes, the stilbazolium betaines SB, TBSB, and DTBSB. However, instead of directly using the position of the main visible band, the differences Δ' between two betaines have proved more simple to analyze.

This model is sensitive to steric effects which are detected by the appearance of a coarse structure in the visible spectum of the TBSB probe.

From the fact that there exists a linear relationship between $E_T(\mathbf{30})$ and Δ' when steric effects of tertiary alcohols are taken into account, i. e. for primary and secondary alcohols, it cannot be deduced that both parameters measure primarily the HBD acidity of the solvents. This is only true for the alcohols described in this paper. The sensitivity of $E_T(\mathbf{30})$ to the polarity and the acidity of the solvents is a subject to many discussions[5,6,9] which was not the aim of the present publication.

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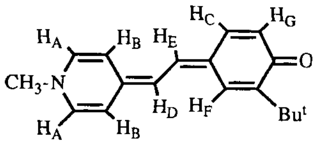
Experimental

Stilbazolium betaine (SB) is commercially available (Aldrich), and the preparation of DTBSB has been described in our previous paper[7]. The mono-*tert*-butyl derivative TBSB has been prepared by starting from 3-*tert*-butyl-4-hydroxybenzaldehyde[11] according to a procedure described in ref.[12] which yields first the protonated betaine which is deprotonated by treatment with 0.2 M KOH (yield of TBSB: 71%).



Spectral data: ^{1}H NMR ([D$_6$]DMSO): δ = 1.4 (s, 9 H, *t*Bu), 4.0 (s, 3 H, CH_3), 6.5 (d, 1 H, H_G), (J_{GF} = 8 Hz), 6.8 (d, 1 H, H_D), (J_{DE} = 16.5 Hz), 7.3 (d, 1 H, H_F), 7.35 (s, 1 H, H_C), 7.78 (2 d, 3 H, H_E + H_B), 8.4 (d, 2 H, H_A), (J_{AB} = 6 Hz). – IR (KBr, cm^{-1}): 2920 (m), 1645 (m), 1610 (m), 1575 (s), 1515 (m), 1475 (s), 1340 (s), 1310 (s), 1180 (s), 1130 (m), 825 (m). – MS (Th[10], %): 268 (51) [MH$^+$], 267 (100) [M$^{+\cdot}$], 253 (72) [MH$^+$ – CH$_3$], 238 (74) [MH$^+$ – 2 CH$_3$], 210 (20) [M$^+$ – *t*Bu].

All the alcohols were of high quality and were carefully dried. Since stilbazolium betaines are extremely sensitive to acids, a very small amount of sodium methoxide (less than 0.01 mg/ml) was added when necessary.

The UV/Vis absorption spectra were measured by using a Shimadzu UV-2100 spectrophotometer and a matched pair of quartz cells of 1 cm thickness. Betaine concentration were less than 10^{-5} M. The sample temperature was maintained at 25.0 ± 0.1°C by means of a Heto thermostat. In the case of *tert*-butyl alcohol (2-methyl-2-propanol), which melts at 25°C, several spectra were recorded at different temperatures and the values extrapolated to 25°C.

The ν(OH) bands were measured with a CARY 5 spectrophotometer using two matched quartz cells of 1 cm of optical path. Tetrachloromethane was of spectroscopic quality (Aldrich), and a new bottle was used inmediately after been opened, DMA was Aldrich HPLC grade, the concentration used in CCl$_4$ were 0.2 M for DMA and $\approx 2 \cdot 10^{-4}$ M for ROH.

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