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INTERACTION OF FORMAMIDE WITH STILBAZOLIUM BETAINES: STERIC EFFECTS IN AMIDES

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The visible spectrum of di-*tert*-butylstilbazolium betaine (DTBSB) was recorded in eight simple amides. The appearance of a 'coarse' structure in the main absorption band is due to the shielding effect of the *tert*-butyl groups, which hinder the approach of the solvent. Since this structure disappears in formamide, it is concluded that this solvent associates through its NH to the carbonyl group of DTBSB. For the other amides, there is a clear relationship between the steric effect, for both the N- and C-substituents, of the solvent–solute hydrogen bond association and the structure of the visible band.

INTRODUCTION

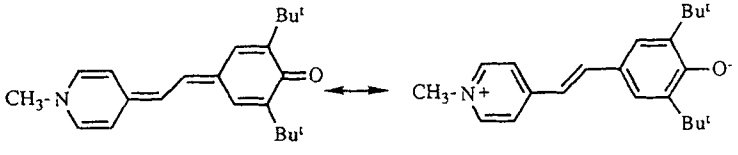
The amide group is an important structural feature in organic and biological chemistry and has been studied extensively both computationally and experimentally (for recent references, see Refs 1–3). In a recent paper,[4] we established that the visible band of stilbazolium betaine dyes shows structure only when the solvent does not interact with its carbonyl group. That this was so was proved by studying di-*tert*-butylstilbazolium betaine (DTBSB) in a set of 28 solvents including protic, aprotic and amphiprotic types.[4]

In this dye, in which the carbonyl group is shielded by the two *tert*-butyl groups, the visible band presents a 'coarse' structure in most solvents. However, in formamide, the chromophore yields a structureless band. Only in water is the spectrum similar; in this case, the explanation[4] lies in the small dimensions of the water molecule, which allow it to approach the carbonyl group in spite of the *tert*-butyl groups.

In order to study the nature of the interaction between formamide and DTBSB, the UV–visible spectra of this dye in a series of liquid amides related to formamide were studied at various temperatures above room temperature. The amides were formamide itself (F), *N*-methylformamide (NMF), *N*-methylacetamide (NMA), *N*-ethylformamide (NEF), *N*-ethylacetamide (NEA), *N-tert*-butylformamide (NTBF), *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMA); acetamide (A) and *N-tert*-butylacetamide (NTBA) are solids (m.p. *ca* 100 °C).

EXPERIMENTAL

The preparation of DTBSB has been described previously.[4] The absorption spectra were measured by using a Shimadzu UV-2100 spectrophotometer and a matched pair of quartz cells of 1 cm thickness. When



DTBSB

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possible, the sample temperature was maintained at 25·0, 35·0, 45·0 and 55·0 ± 0·1 °C by means of a Heto thermostat. Since DTBSB is extremely sensitive to acids, a very small amount of sodium methoxide (less than 10^{-6} M) was added when necessary.

RESULTS AND DISCUSSION

The spectra of DTBSB in the eight amides at 35 °C are shown in Figure 1. From the simple examination of these spectra it follows that the interaction between the amide NH and DTBSB is as in the case of water, a hydrogen-bond donor (HBD)–hydrogen-bond acceptor (HBA) interaction, since the 'coarse' structure is better observed in DMF and DMA.

However, the disappearance of the structure is gradual; in the case of amides with at least one NH, this order is (1) NTBF, (2) NEA, (3) NMA, (4) NEF, (5) NMF and (6) F. Hence the acetamides always have more structure than the corresponding formamides. In consequence, the modification of the visible band does not reflect the autoassociation of amides since the acetamides are less autoassociated than the formamides, i.e. there are more monomers in the former than in the latter.

To explore whether the difference in behaviour is due to steric effects in the DTBSB=O···H(R)N—COR′ association, the steric effects of amides should be assessed. According to Jones[5] and Graham and Chang,[6] the autoassociation of amides is essentially governed by steric effects, these effects being due in approximately the same amounts to the N- and C-substituents. Consider, for instance, the concentration ratio, $\rho = (C_{\text{associated}}/C_{\text{monomeric}})$, as defined by Jones[5] for carbon tetrachloride solutions: NMA, 0·57; *N*-methylpropionamide, 0·36; *N*-methylpivalamide, 0·18; NEA, 0·43; *N*-ethylpropionamide, 0·32; *N*-ethylpivalamide, 0·14; *N*-tert-butylacetamide, 0·23; *N*-ethylpivalamide, 0·14; *N-tert*-butylpivalamide, almost 0. Assuming the hypothesis that these values result additively from the contributions of the N- and the C-substituents, then it is possible to calculate, by multiregression ($r^2 = 0{\cdot}97$), the contributions of these substituents with respect to NMA: constant: 0.525; *N*- and *C*-methyl, 0·00; *C*-ethyl, −0·137; *C-tert*-butyl, −0·328; *N*-ethyl, −0.073, *N-tert*-butyl, −0.272. These contributions, in turn, are approximately linear with steric effects, both Taft's E_s and Chartons's ν:[7] $\rho(\text{C—R}) = -0{\cdot}062 + 0{\cdot}175E_s$, $r^2 = 0{\cdot}85$, for C—H, $\rho = 0{\cdot}156$; $\rho(\text{C—R}) = 0{\cdot}136 - 0{\cdot}379\nu$, $r^2 = 0{\cdot}86$, for C—H, $\rho = 0{\cdot}136$ [averaged value, $\rho(\text{C—H}) = 0{\cdot}146$]; $\rho(\text{N—R}) = -0{\cdot}029 + 0{\cdot}158E_s$, $r^2 = 0{\cdot}96$, for N—H, $\rho = 0{\cdot}167$, $\rho(\text{N—R}) = 0{\cdot}149 - 0{\cdot}339\nu$, $r^2 = 0{\cdot}96$, for N—H, $\rho = 0{\cdot}149$ [averaged value, $\rho(\text{N—H}) = 0{\cdot}158$]. We can now predict the value of ρ for the sixteen cases in Table 1; some of them can be compared with Jones's values[5] and six of them (in italics) correspond to the solvents we actually studied.

Since the spectra in Figure 1 can only be ordered, comparison with the ρ values in Table 1 has to be essentially qualitative. Nevertheless, the order, from 1 to 6, and the ρ values are clearly related. Thus, the data in Table 1 for the six solvents used are in good agreement with the sequential loss of structure of the bands represented in Figure 1. For instance, the bands associated with acetamides show more structure than those of the corresponding formamides (a 0·15 increase in ρ is observed in Table 1); when the alkyl size increases either on the carbonyl group or on the nitrogen, the band is more structured; finally, if acetamide ($\rho = 0{\cdot}69$) were a liquid at the temperatures used in these experiments, a spectrum similar to that of NMF ($\rho = 0{\cdot}68$) would be expected.

The effect of the temperature in the range 25–45 °C is shown in Figure 2(a) (formamide) and 2(b) (*N-tert*-butylformamide). In the first compound, when the temperature increases, there is only a very small bathochromic shift. For NTBF, owing to steric effects, an increase in temperature results *in a more structured* band, i.e. a dissociation of the solute–solvent hydrogen-bonded complex.

The steric effects on the autoassociation of amides (the NH and the C=O being essentially *trans*[1-6,8-11] are due to the fact that monomers are aligned in the dimer in such a way as to bring the substituent on the carbonyl group of one molecule and the NR substituent of the second molecule into close proximity. This explains why both substituents have similar steric requirements.

Assuming that amides of *trans* configuration bind to DTBSB carbonyl group by the NH, the similarity of the solvent effects in Figure 1 and the autoassociation effects in Table 1 indicates that the steric effects are also similar. An examination of the molecular models for the association R′CON(R)H···O=C–DTBSB, shows that both R and R′ are close to one of the *tert*-butyl groups when the amide is free to rotate about the hydrogen bond.

Table 1. Autoassociation of amides (ρ scale)

	C-substituents			
N substituents	H	Me	Et	*t*-Bu
H	*0·84* F	0·69 (A)	0·55	0·36
Me	*0·68* NMF	*0·53* NMA	0·39	0·20
Et	*0·60* NEF	*0·45* NEA	0·31	0·12
t-Bu	*0·40* NTBF	0·25	0·12	0·00

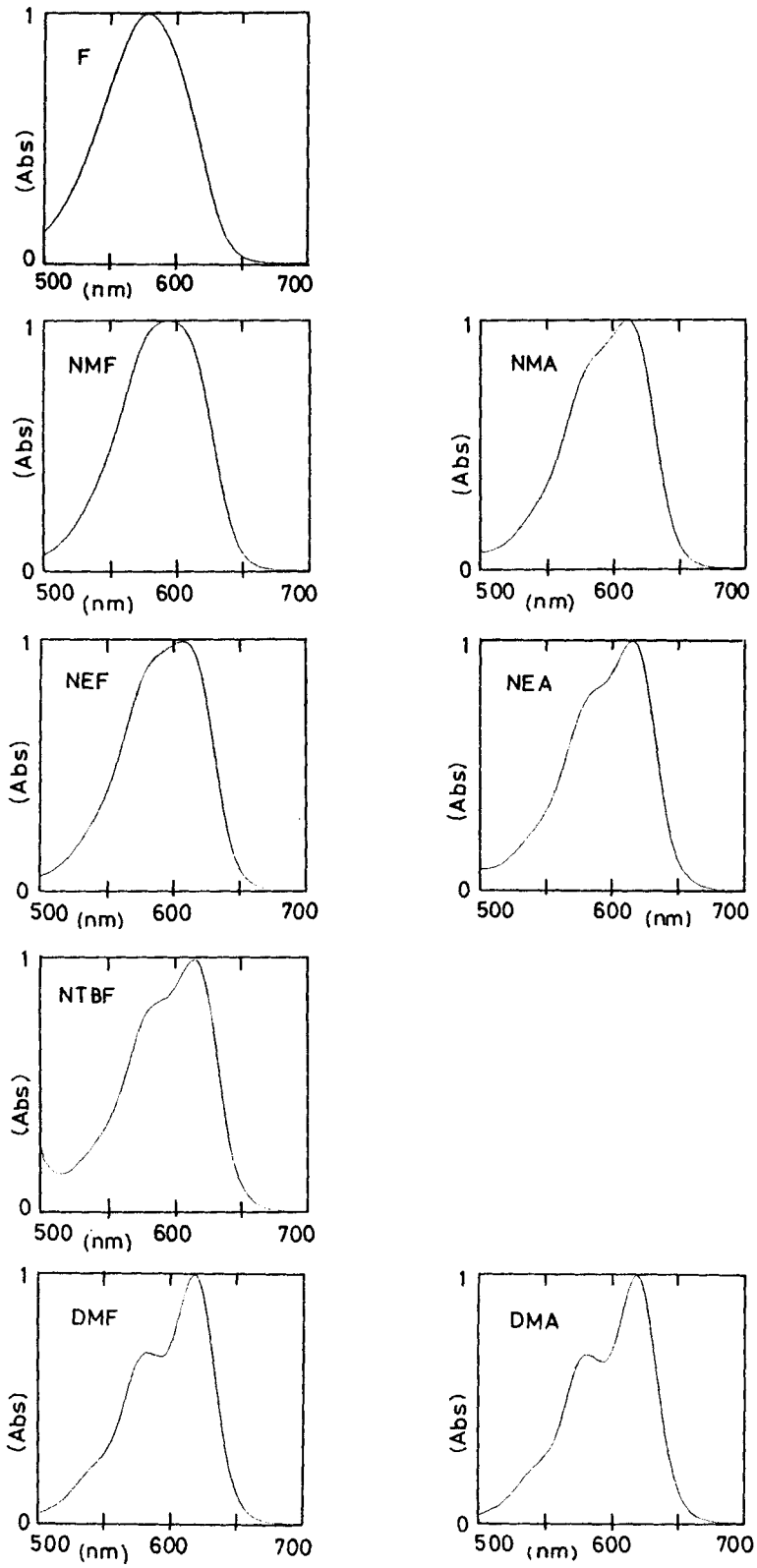

Figure 1. Main absorption band (λ_{max}, nm) of DTBSB in F (579), NMF (595), NEF (607), NTBF (616), DMF (619), NMA (612), NEA (616) and DMA (620)

In conclusion, formamide, like water, is able to reach the carbonyl group of DTBSB through the *tert*-butyl groups. This possibility diminishes as the CH and NH are substituted by alkyl groups of increasing size. The possibility for the hydrogen adjacent to the C=O group in formamides to form hydrogen bonds,[12] and, in general, the differences between formamides and acetamides are worthy of future investigation.[13]

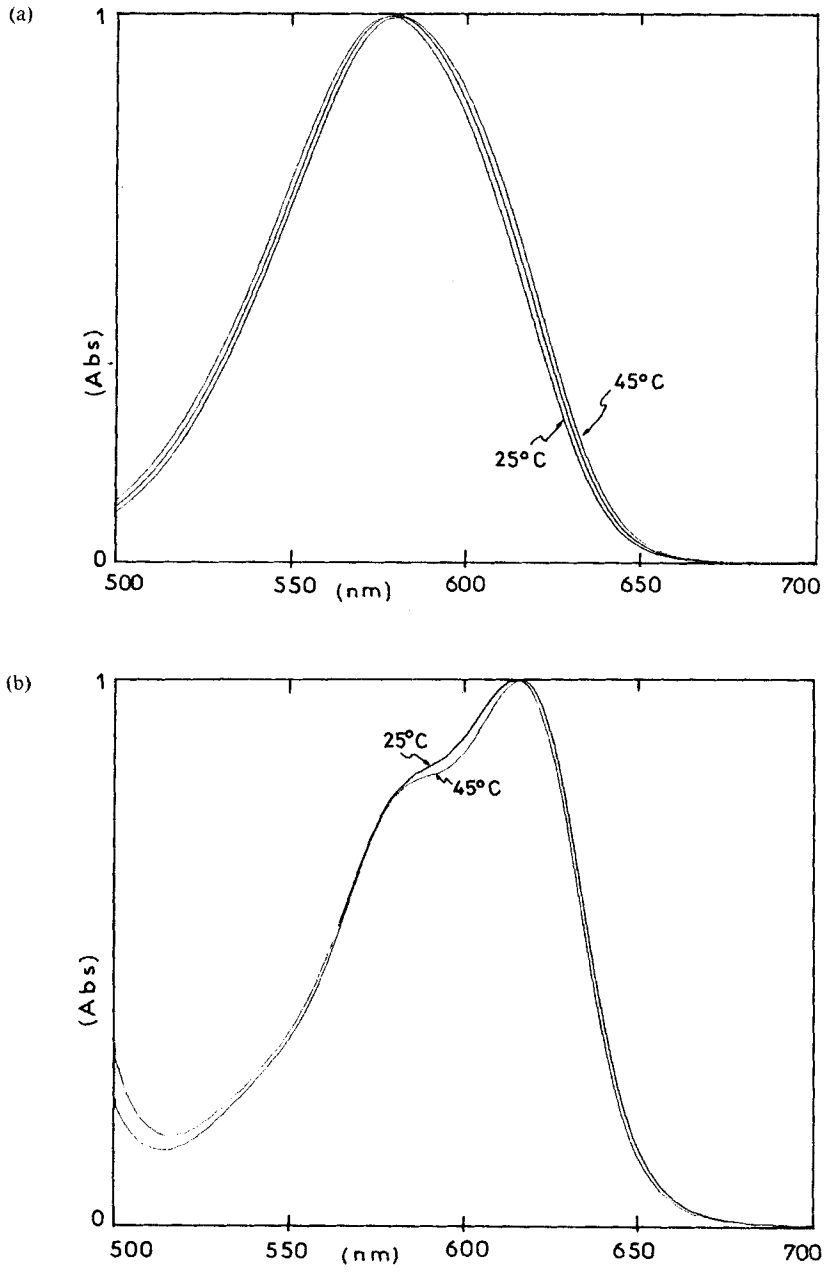

Figure 2. Effects of temperature on the main absorption band of DTBSB: (a) formamide; (b) *N-tert*-butylformamide

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