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Solvent Effects on Absorption Spectra of Substituted Azobenzenes

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Synopsis. McRae's formula including the quadratic term was applied to an analysis of absorption spectra of substituted azobenzenes in various solvents. It has been suggested that the interaction between the solvent dipole and the solvent-induced solute dipole plays an important role.

Recently, we have reported¹⁾ that the absorption maximum of *trans*-4-dimethylamino-4′-nitroazobenzene (NDAAB) and the rate of its thermal cis-to-trans isomerization are quite sensitive to solvent polarities. Influences of dipole interactions on absorption frequencies were investigated theoretically by Ooshika²⁾ and McRae.³⁾ Irick, Jr. and Pacifici⁴⁾ and Misono *et al.*⁵⁾ applied McRae's formula to absorption spectra of substituted azobenzenes. However, they neglected the quadratic Stark term which represents the contribution of the interaction between the permanent dipole of solvent molecules and the solute dipole thereby induced. Indeed, in the case of less polar solutes such as azulene, the term was reported⁶⁾ as negligibly small. McRae³⁾ suggested, however, that if both solute and solvent are highly polar, the Stark term would make an important contribution.

We reported¹⁾ that solute-solvent interactions such as the dipole-induced dipole one might be operative in very polar solvents for thermal isomerization reactions of NDAAB and 4,4′-bis(diethylamino)azobenzene (BDEAAB). Thereupon, we have examined the Stark term in the McRae equation by using NDAAB and BDEAAB.

Experimental

The reagent grade solvents were used as supplied. The preparation of azobenzenes was described elsewhere.¹⁾

The absorption spectra were measured with a Hitachi 228 spectrophotometer. For BDEAAB, the separation of absorption spectra was made according to an attached program.

Results and Discussion

The frequencies at the absorption maxima of *trans*-NDAAB and *trans*-BDEAAB in various solvents are given in Table 1. In the case of *trans*-BDEAAB, the absorption spectra consist of three bands which are considered to arise from a normal vibrational structure, and the separation of the spectra was successful by taking their fourth-order derivative (Fig. 1). In Table 1, the lowest-frequencies (0-0 band) in various solvents are listed. As shown in Table 1, ν_{obsd} of BDEAAB is also sensitive to solvent polarity as with NDAAB. It is noteworthy that bis-BDEAAB exhibits more remarkable solvent effects on the absorption spectra than 4-dimethylaminoazo-

Table 1. Observed and calculated absorption frequencies of NDAAB and BDEAAB in various solvents and ν_{gas}, $(AL+B)$, C, and F values

		NDAAB		BDEAAB	
		$\nu_{\mathrm{obsd}}/\mathrm{cm}^{-1}$	$\nu_{\mathrm{calcd}}/\mathrm{cm}^{-1}$	$\nu_{\mathrm{obsd}}/\mathrm{cm}^{-1}$	$\nu_{\mathrm{calcd}}/\mathrm{cm}^{-1}$
1	Hexane	22624	22793	21882	21996
2	Heptane	22624	22650	21739	21878
3	Cyclohexane	22371	22244	21692	21540
4	Methylcyclohexane	22422	22278	21786	21566
5	CCl_4	22026	21871	21322	21245
6	Toluene	21459	21515	20964	20953
7	Benzene	21413	21508	20747	20930
8	Diethyl ether	22026	22341	21368	21854
9	Chlorobenzene	20747	20614	20576	20411
10	4-Methyl-2-pentanone	21097	21035	20833	20869
11	Cyclohexanone	20576	20373	20790	20323
12	Ethyl benzoate	20747	20719	20534	20513
13	Propionitrile	20833	20917	20534	20792
14	Acetonitrile	20877	21008	20661	20872
15	DMSO	19920	19820	20080	19876
	$\nu_{\mathrm{gas}}/\mathrm{cm}^{-1}$	28544		26789	
	$-(AL+B)/\mathrm{cm}^{-1}$	30877		25729	
	$-C/\mathrm{cm}^{-1}$	1712		485	
	$-F/\mathrm{cm}^{-1}$	1809		2115	
	S.D.[a]$/\mathrm{cm}^{-1}$	71		136	

a) Standard deviation of the difference between the calculated and observed values in various solvents.

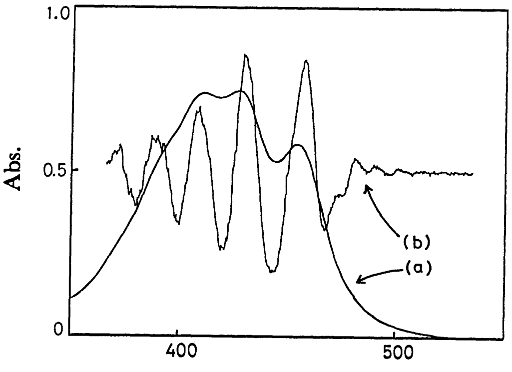

Fig. 1. Absorption spectrum of BDEAAB in hexane (a) and its fourth-order derivative (b).

benzene (DAAB).[1]

McRae[3] proposed a general expression for frequency shifts which arise from dipole interactions:

$$\Delta\nu = (AL+B)\left(\frac{n^2-1}{2n^2+1}\right) + C\left(\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right) + F\left(\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right)^2, \tag{1}$$

where $\Delta\nu$ is the difference between absorption frequencies in solution and in gas phase ($\nu_{\text{obsd}}-\nu_{\text{gas}}$). Other notations are the same as McRae's.

If the contribution of the F-term which comes from solvent dipole–solute induced dipole interaction is sufficiently small to be neglected for polar solvents, as Irick, Jr. and Pacifici[4] reported, a linear relation between $\{\Delta\nu-(AL+B)[(n^2-1)/(2n^2+1)]\}$ and $\{[(D-1)/(D+2)]-[(n^2-1)/(n^2+2)]\}$ is expected. However, as shown in Fig. 2, the upward curvature is obtained when the points for very polar solvents are included. Therefore, we have treated our data by the quadratic regression equation, and the estimated C- and F-values are given in Table 1.

It is noted that the absolute C-value of BDEAAB is considerably small compared with that of NDAAB. This can naturally be understood since the dipole moment of 4,4′-disubstituted *trans*-azobenzenes such as BDEAAB in ground state must be nearly zero. Both of the absolute F-values are considerably large compared with those reported by Robertson *et al.*[6] (*e.g.*, $|F|=12\ \text{cm}^{-1}$ for ${}^1L_b$ of naphthalene and $|F|=200\ \text{cm}^{-1}$ for ${}^1B_b$ of naphthacene). This is considered as a good indication of the change in the solute dipole moment induced by solvents. Very recently, solvent-induced changes in electronic structures of molecules having conjugation systems have been investigated with the help of ^{1}H NMR absorption spectra.[7] Moreover, Betrel *et al.*[8] have made a theoretical investigation using the CNDO/SCI method including solvation on the problem of electronic structure. They suggested a significant increase in the solute dipole moment with increasing solvent polarity. This is in accordance with the above results.

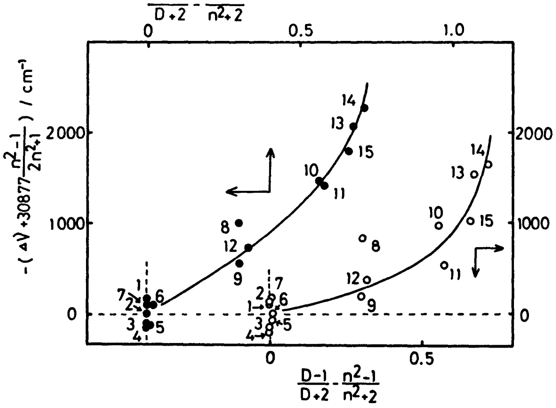

Fig. 2. Relation between $\{\Delta\nu\text{-}(AL+B)[(n^2\text{-}1)/(2n^2+1)]\}$ and $\{[(D-1)/(D+2)]\text{-}[(n^2-1)/(n^2+2)]\}$; ●: NDAAB, ○: BDEAAB. Key is shown in Table 1.

In Table 1, the ν-values calculated by using the estimated constants are also given. The standard deviation for the linear plot of ν_{calcd} against ν_{obsd} is much improved compared with the reported one (S. D. 203 cm^{-1}).[4]

Recently, we have shown that rate constants for the isomerization of NDAAB derivatives were well correlated with the absorption maxima of their *trans*-isomers, and suggested that specific solute-solvent interactions might give rise to a polarization of solute molecules enhanced by surrounding polar solvent molecules upon activation. It has been shown that the quadratic term in Eq. 1 plays an important role for the spectral shifts of the push-pull and push-push azobenzenes by polar solvents. Therefore, the present work supports our previous view just mentioned above.

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