

Experimental Determination of Dipole Moments of Some Benzamide Derivatives

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The excited state dipole moments of some benzamide derivatives are determined. The method of solvent induced shifts of electronic absorption bands in comparison with their positions in the gas phase is used. Some regular trends revealed in the obtained data are discussed. The present results are compared with those available in the literature.

Key words: Benzamides; Absorption Spectra; Dipole Moments.

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1. Introduction

Benzamide derivatives have attracted the interest of photophysicists, photochemists and photobiologists for a long time [1–7]. These simple molecules, used frequently as “model molecules”, play an important role in photochemical (charge-transfer complexes, photoreactions [8, 9]) and photobiological (proteins, α – helical polypeptide [10]) processes. The main reason is the presence of an electron donor and acceptor moiety bridged by the peptide group –OCN–. In these molecules the fluorescence is often observed from an intramolecular charge transfer state S_1 (CT). In many cases the formation of the charge transfer state is accompanied by an isomerisation reaction in which the donor moiety twists with respect to acceptor, as shown by comparative studies of conformationally restricted derivatives [4–8]. Compounds exhibiting these features are referred to as twisted intramolecular charge transfer (TICT) compounds. The fluorescence spectrum of a TICT compound will generally exhibit strong solvatochromaticity, which is attributed to the existence of two fluorescent isomers of the compound, one being in the so-called locally excited, S_1 (LE), and the second being in the charge transfer, S_1 (CT), configuration. The observed solvatochromaticity is a result of the strong influence of solvent polarizability on the excited state potential energy surface.

The analysis of molecular structures of the compounds under study (see Fig. 1) reveals that the peptide –OCN– group in the molecules denoted as I and II represents a part of the phenyl substituent, whereas in the molecules III and IV it is a bridging linkage of two chromophors. The compounds under study possess very low fluorescence quantum yield in liquid solutions ($\phi_F < 10^{-4}$) [1], therefore the excited state dipole moments, which provide information on electron charge distribution, reactivity etc., can not be determined using standard procedures. For this reason the method of solvent-induced shifts in the UV absorption bands in comparison with the absorption spectrum of the vapour phase has been used. The basis of the method can be found in the theoretical description of solvatochromic effects given by Ooshika [11], Lippert [12], Bilot and Kowski [13], Liptay [14], and Mataga *et al.* [15]. The selected series of molecules under study allows one to find general trends in excited state dipole moment variations due to substitutions and steric hindrance.

2. Theoretical Foundations

Intermolecular interactions in a solution can be roughly classified as dispersion forces (which are electrostatic in nature) and usual electrostatic forces. Taking into account both interactions, McRae obtained the following equation describing the frequency shift from that in the vapour phase, $\bar{\nu}_{\text{abs}}^G$, to the one in a solution, $\bar{\nu}_{\text{abs}}^S$, the shift being caused by solvent effects on the absorption

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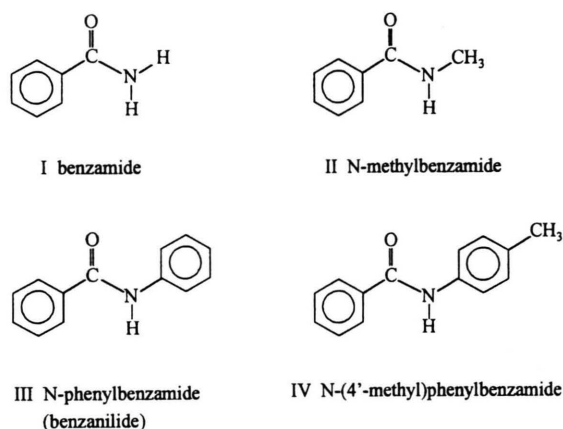


Fig. 1. The chemical structure of the compounds under study.

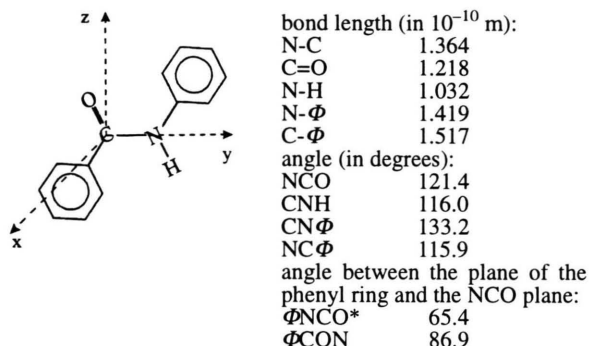
spectra of an isotropic solute molecules [16]:

$$\begin{aligned} \bar{\nu}_{\text{abs}}^{\text{S}} - \bar{\nu}_{\text{abs}}^{\text{G}} = & (A + B)f(n) + \frac{\mu_{\text{g}}^2 - \mu_{\text{ex}}^2}{hca_0^3} f(n) \\ & + \frac{2\mu_{\text{g}}(\mu_{\text{g}} - \mu_{\text{ex}})}{hca_0^3} f(n, \epsilon) \\ & + \frac{6\mu_{\text{g}}^2(\alpha_{\text{g}} - \alpha_{\text{ex}})}{hca_0^6} [f(n, \epsilon)]^2, \quad (1) \end{aligned}$$

where $(A + B)$ represents the contribution of dispersion effects; $f(n) = (n^2 - 1)/(2n^2 + 1)$; $f(n, \epsilon) = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1)$; ϵ and n are the static dielectric constant and the refractive index of the solvent; α_{g} and α_{ex} , μ_{g} and μ_{ex} are the polarisabilities and dipole moments of the solute molecule in the ground and excited state, correspondingly; h , c and a_0 are the Planck constant, the speed of light and the radius of the Onsager cavity, respectively. In the case of the system used (solute dipole – solvent polarizability) the contribution of the dispersion term $(A + B)$ is very small as compared to that from the dipole term (the second term in (1)), therefore it can be ignored. Performing absorption measurements using solvents for which $\epsilon \approx n^2$, we are allowed to neglect the last two terms in (1) (they are equal to zero, because in this case $f(n, \epsilon) \equiv 0$). Therefore for these solvents we obtain

$$\bar{\nu}_{\text{abs}}^{\text{S}} = \bar{\nu}_{\text{abs}}^{\text{G}} + \frac{\mu_{\text{g}}^2 - \mu_{\text{ex}}^2}{hca_0^3} \frac{n^2 - 1}{2n^2 + 1}. \quad (2)$$

Equation (2) can be used to estimate the value of the dipole moment of the excited state, μ_{ex} , when μ_{g} and a_0 are known from:

Fig. 2. Determination of the ellipsoid axes X , Y and Z for N-phenylbenzamide. The main bond lengths and plane angles are taken from [2].

a) the slope of the plot $\bar{\nu}_{\text{abs}}^{\text{S}}$ versus $(n^2 - 1)/(2n^2 + 1)$ or
b) from an absorption measurement determining the $\bar{\nu}_{\text{abs}}^{\text{G}}$ and $\bar{\nu}_{\text{abs}}^{\text{S}}$ values of the gas phase spectrum and of the solution absorption spectrum, respectively.

The Onsager cavity radius, a_0 , can be estimated by approximating the molecular shape to an ellipsoid, as has been shown in [8]. This assumption is applicable to the molecules studied here in view of their planar skeletons (the phenyl rings) and the peptide plane linkage. The bond lengths and bond angles between the phenyl hexagonal skeleton, the peptide linkage and the methyl substituent attached to the ring or the N atom, were taken from [3]. The ellipsoid axes are defined as shown in Figure 2. The lengths of the ellipsoid axes X , Y and Z are determined by taking the sum of various bond length projections along the resulting ellipsoid. The volume of the Onsager cavity is given by

$$V_e = \frac{4}{3} \pi \frac{X}{2} \frac{Y}{2} \frac{Z}{2}. \quad (3)$$

Comparing the effective volume of the ellipsoid (3) with that of an equivalent Onsager sphere $V_e' = \frac{4}{3} \pi a_0^3$, we get

$$a_0 = 0.5 \sqrt[3]{XYZ}. \quad (4)$$

Table 1 presents the estimated values of the Onsager radius, a_0 , for the molecules under study.

3. Experimental

The compounds under study, purchased from Aldrich Chemical Co, are of cp. grade. They were purified by fractional crystallisation from methanol and dried under vacuum in a desiccator over P_2O_5 . The solvents were

Table 1. The absorption band maxima, $\tilde{\nu}_{L_a}$ and $\tilde{\nu}_{L_b}$ (in cm^{-1}), the radius of the spherical Onsager cavity, a_0 (in 10^{-10}m), the permanent dipole moment (in Debye) of the ground, μ_g , and excited, μ_{L_a} and μ_{L_b} , states of the benzamide derivatives. The average values of the dipole moment are given in $\langle \rangle$.

Compound	Solvent					This work		Other authors	
		$\tilde{\nu}_{L_a}$	$\tilde{\nu}_{L_b}$	a_0	μ_g	μ_{L_a}	μ_{L_b}	μ_{L_a}	μ_{L_b}
1	2	3	4	5	6	7	8	9	10
I. Benzamide	vapour	45 750	37 200	1.97	3.42 ^b				
	H	44 692	36 200			6.91	4.41		
	CH	44 800	36 050			6.13	4.23		
	MCH	44 640	36 300			5.95	4.34		
						$\langle 6.33 \rangle$	$\langle 4.33 \rangle$	9.22 ^b	3.91 ^b
II. N-methylbenzamide	vapour	46 080	37 310	2.06	4.37 ^c				
	CH	45 045	36 630			5.26	4.98		
	MCH	44 980	37 190			5.34	4.49		
						$\langle 5.30 \rangle$	$\langle 4.74 \rangle$		
III. N-phenylbenzamide (benzanilide)	vapour	45 660	39 780	2.80	3.66 ^b 3.60 ^a				
	H	44 780	37 450			7.94	6.07		
	CH	44 910	37 523			7.77	5.71		
	MCH	44 770	37 400			8.01	5.42	9.9 ^a	6.7 ^a
						$\langle 7.91 \rangle$	$\langle 5.73 \rangle$	12.7 ^b	6.01 ^b
IV. N-(4'-methyl)phenylbenzamide	vapour	45 645	39 526	2.96	3.80 ^d				
	H	44 500	36 820			9.38	6.75		
	CH	44 480	36 710			9.14	6.56		
	MCH	44 350	36 750			9.23	6.89		
						$\langle 9.25 \rangle$	$\langle 6.73 \rangle$		

^a from [2], ^b from [17], ^c from [8], ^d from [18].

spectroscopic grade and were distilled from a sodium-potassium amalgam in order to get them pure and free of water. The absorption spectra were recorded on a Shimadzu spectrophotometer model UV-200. Suprasil absorption cells, light-pass of 2 or 5 mm, were used for solution absorption measurements. The Suprasil absorption cells for gas phase measurements were 100 mm long; they were filled with dried Ar and some crystals of the compounds under study. A suitable vapour density was obtained by heating the cell with a Philips resistance wire to about 350 K.

4. Results and Discussion

Figure 3 shows the absorption spectra of the molecules investigated in the gas phase and in hexane or cyclohexane solutions at the concentration $c = 2 \cdot 10^{-4}$ M. All the spectra contain two distinct bands, i.e. at ca. 220–235 and 260–280 nm. The long-wave band system of benzamide (I) and N-methylbenzamide (II) is structured in the gas phase and in the hydrocarbon solvents used,

whereas for N-phenylbenzamide (III) and N-(4'-methyl)phenylbenzamide (IV) this band is broad and structureless. Further, the band is very weak for benzamide and N-methylbenzamide, whereas for N-phenyl substituted derivatives of benzamide (III and IV) it is relatively intense, ($\epsilon \cong 12\,500 \text{ M}^{-1}\text{cm}^{-1}$). All the molecules exhibit a relatively intense band in the 220–235 nm region.

In agreement with the Platt notation, the short and long wavelength bands noted above will be called as primary, 1L_a , and secondary, 1L_b , bands. Generally, they are considered as the locally excited benzene bands at 203 nm (${}^1B_{1u} \leftarrow {}^1A_{1g}$) and 254 nm (${}^1B_{2u} \leftarrow {}^1A_{1g}$); shifted to longer wavelengths due to perturbing effects of the substituents. However, in view of the presence of nonbonding pair of p-electrons in the substitution groups of benzene, i.e. $-\text{CONH}_2$; $-\text{CONHCH}_3$; $-\text{CONHC}_6\text{H}_5$ and $-\text{CONHC}_6\text{H}_4\text{CH}_3$, these bands must be considered as charge transfer bands. The determined λ_{max} -values of these bands (converted into wave numbers) for the molecules studied in the gas phase and in the hydrocarbon solvents are collected in Table 1. Also, this table contains the calculated a_0 values, and the μ_g data taken from the

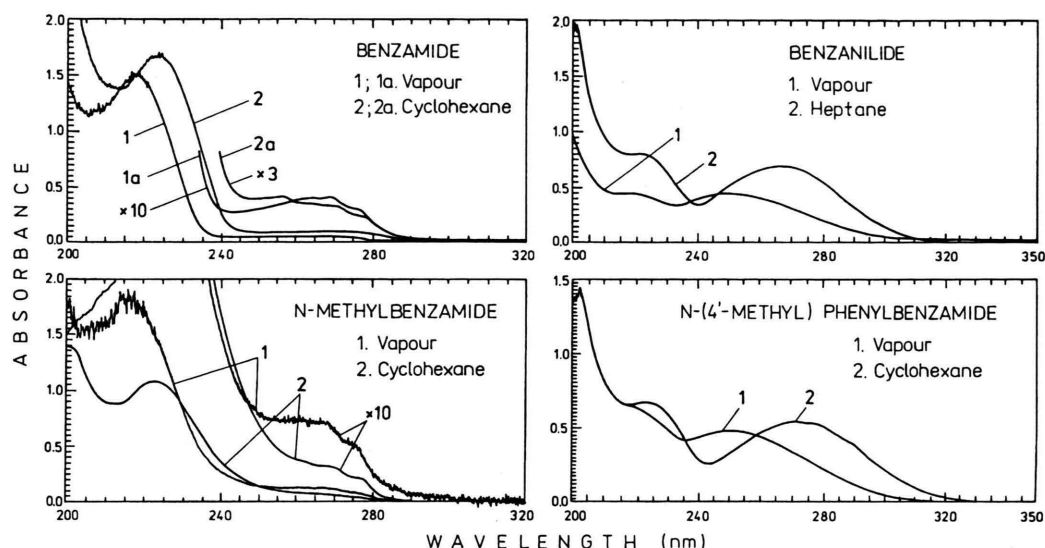


Fig. 3. The absorption spectra of the molecules under study, measured in the vapour-phase 1. and hydrocarbone solvent 2.

literature. The dipole moments of the excited states L_a and L_b are calculated by use of (2) and values of a_0 from Table 1 (column 5), the values of μ_g from the same Table (column 6) and the determined wave numbers $\tilde{\nu}_{L_a}^G$, $\tilde{\nu}_{L_b}^G$, $\tilde{\nu}_{L_a}^S$, $\tilde{\nu}_{L_b}^S$ of the absorption band maxima in the gas phase and hydrocarbon solutions. The obtained μ_{L_a} and μ_{L_b} data are presented in Table 1 (column 7 and 8). The accuracy of the measured $\lambda_{\max}$ -values is ± 0.25 nm, which corresponds to an uncertainty of $\pm(40 - 50)$ cm^{-1} in the $\tilde{\nu}$ values. In view of the uncertainty of the $\tilde{\nu}$'s and a_0 , the μ_{L_a} - and μ_{L_b} -values can be expected to lie within 15% of the values determined. The μ_{L_a} - and μ_{L_b} -data obtained for different hydrocarbon solvents (e.g. hexane, cyclohexane and methylcyclohexane) are within the estimated error limits. Therefore, it is appropriate to give the average value of those results. They are given below in the brackets.

In columns 9 and 10 of Table 1 we cite the experimental and theoretical μ_{L_a} and μ_{L_b} values of benzamide and N-phenylbenzamide obtained by other authors. For the two molecules our μ_{L_a} values differ somewhat from those calculated by Bolotsvetov *et al.* [2] and differ significantly from the experimental data obtained by Prabhumirashi *et al.* [17]. The respective differences between the μ_{L_a} 's are above our error limit of 15%, while for the μ_{L_b} values, and almost satisfactory agreement is noted. It must be stated that Prabhumirashi *et al.* [17] obtained the μ_{L_a} values, using for $\tilde{\nu}_{ab}^G$ the value derived by drawing a linear relationship between $\tilde{\nu}_{ab}^S$ versus $f(n_s)$. They have obtained 55 800 cm^{-1} and 52 200 cm^{-1} as the values

of $\tilde{\nu}_{ab}^G$: for benzamide and N-phenylbenzamide, respectively. The experimentally determined values obtained by us are 45 750 cm^{-1} and 45 660 cm^{-1} , respectively, (see Table 1, column 4); they differ by 10 050 and 6 540 cm^{-1} from those used in [17]. It is obvious that the incorrectly estimated $\tilde{\nu}_{ab}^G$ -values in [17] lead to these discrepancies. Since the dipole moments of the L_a and L_b excited states of benzamide derivatives are here derived using only experimentally determined data, we believe that they are more credible. Also it must be mentioned that the data are obtained for an environment where specific solute-solvent interactions are absent.

The electric dipole moments of the L_a and L_b excited states determined for the molecules under study allow us to find some regular trends:

1. The dipole moments of higher frequency turn out to be larger than those of lower frequency bands, i.e. $\mu_{L_a} > \mu_{L_b}$. This finding is explainable in view of the higher electronic state excitation.
2. A significant increase of the dipole moments is observed for bichromophoric molecules showing a donating electron withdrawing ability. This finding is ascribable to the well-known hyperconjugative effects of the same substitution groups [16, 19]. Such dependence is noted for all TICT-type molecules.

We find that the method of the dipole moment determination using (2) is very practical and applicable to various electronic transitions in the near UV and visible spectral region. The μ data are more reliable if the max-

ima of the band frequencies of the vapour phase are determined experimentally and not taken from the extrapolation procedure: $\bar{\nu}^s$ -versus $f(n)$. In order to confirm the above findings, further experimental and theoretical studies of a longer group of TICT-type molecules (III and IV) are in progress.

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