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Supply to the spectral shifts of each type of intermolecular interactions in binary solutions

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The supply to the total spectral shift of each type of interactions from the binary solutions of some benzo-[f]-quinolinium cycloaducts and benzo-[f]-quinolinium-ylids was estimated by using the Bakhshiev model describing the intermolecular interactions influence on the electronic spectrum when the spectrally active molecules pass from their gaseous phase to binary solutions.

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1. Introductory notions

The spectrally active molecules in liquid solutions can measure the strength of the intermolecular interactions by the modifications of their electronic spectra [1,2]. In the theories regarding the solvent influence on the electronic spectra, the spectral shifts, $\Delta\overline{\nu}$ (expressed in cm^{-1}), recorded in a given solvent $\overline{\nu}_{\mathrm{solv.}}$ related to the gaseous phase $\overline{\nu}_{\mathrm{vap.}}$ of the spectrally active molecule:

$$\Delta\overline{\nu} = \overline{\nu}_{\mathrm{solv.}} - \overline{\nu}_{\mathrm{vap.}} \tag{1}$$

are correlated with physical parameters of the both solvent and spectrally active molecules. The total spectral shift in simple liquids is due to the orientation-induction ($\Delta\overline{\nu}_{\mathrm{oriet-ind}}$), polarization ($\Delta\overline{\nu}_{\mathrm{polar}}$) and/or to the dispersion ($\Delta\overline{\nu}_{\mathrm{disp}}$) interactions.

$$\Delta\overline{\nu} = \Delta\overline{\nu}_{\mathrm{orient.-ind.}} + \Delta\overline{\nu}_{\mathrm{polar.}} + \Delta\overline{\nu}_{\mathrm{disp.}} \tag{2}$$

Bakhshiev [3] obtained the following expressions for each type of interactions:

$$\Delta\overline{\nu}_{\mathrm{orient.-ind.}} = \frac{2n^2+1}{n^2+2}\left[\frac{2\mu_g\left(\mu_g - \mu_e\cos\varphi\right)}{r^3}\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right) + \frac{\mu_g^2-\mu_g^2}{r^3}\frac{n^2-1}{n^2+2}\right] \tag{3}$$

$$\Delta\overline{\nu}_{\mathrm{polar.}} = \frac{he^2f}{8\pi m\nu_{00}r^3}\frac{n^2-1}{2n^2+1} \tag{4}$$

$$\Delta\overline{\nu}_{\mathrm{disp.}} = \left(\alpha_g - \alpha_e\right)\left(\frac{3}{2r^3}\frac{II'}{I+I'}\right)\frac{n^2-1}{n^2+2} \tag{5}$$

In relations (3)-(5), n and ε are the solvent refractive index and electric permittivity, μ and α denominate the electric dipole moment and the polarizability in the ground (g) and in the excited (e) states of the spectrally active molecules, e and m are the charge and the mass of the electron, h is Planck constant, I and I' are the ionization potentials of the solvent and spectrally active molecules, f is the oscillator strength for the studied electronic transitions, ν_{00} is the wave number of the pure electronic transition and r is the mean radius of a spectrally active molecule.

Usually, for a great number of solvents, the ratio $\frac{2n^2+1}{n^2+2}$ is a number in the range 1.3-1.6. By considering this ratio as being a constant, independent on the solvent nature, the sum (2) of the terms (3), (4) and (5) can be re-written as separate terms representing orientation and inductive-polarization-dispersive interactions [4,5], especially when dipolar molecules are included in the liquid solutions.

Let be $f(\varepsilon) = \frac{\varepsilon-1}{\varepsilon+2}$ and $f(n) = \frac{n^2-1}{n^2+2}$ the ratios dependent on the solvent nature in relations (3)-(5). The wave numbers in the maxim of the electronic absorption band can be computed by using relation (6) in which a supplementary term was added in order to account the contribution of the specific interactions to the total spectral shift $\Delta\overline{\nu}$.

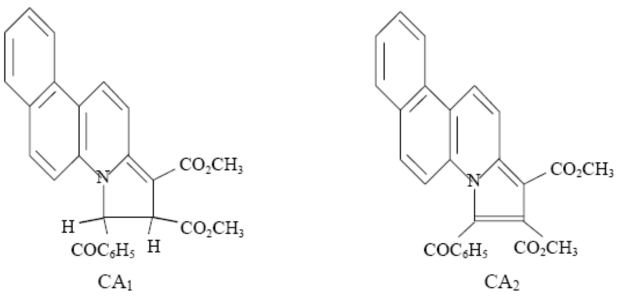
$$\nu_{calc.} = \nu_{vap.} + C_1 f(\varepsilon) + C_2 f(n) + \Delta\nu_{sp.inter.} \qquad (6)$$

The term $\nu_{vap.}$ has the significance of the wave number in the maximum of the electronic band in the vaporous state of the spectrally active molecule. The coefficients $\nu_{vap.}, C_1, C_2$ and $\Delta\nu_{sp.inter.}$ can be obtained by a method of multi-parameter linear regression [6] applied to the experimental data referring to the wave numbers, refractive index and electric permittivity measured in each solvent. The second term, $C_1 f(\varepsilon)$ in relation (6) gives the contribution of the orientation forces to the total spectral shift, and the third one, $C_2 f(n)$, gives the supply of the inductive-polarization-dispersive forces to the total spectral shift. The separation of the inductive, polarization and dispersive interaction supply from the total spectral shift is a difficult problem, because the theories express these interactions by the same function of the refractive index.

When the experimental values of the wave numbers in different solvents are plotted versus the calculated by formula (2) wave numbers, the deviations of the obtained points related to the first bisectrice give the spectral shifts due to the specific interactions $\Delta\nu_{sp.inter.}$. This type of interactions is neglected in the theory about the influence of the universal interactions on the electronic spectra.

The term $\Delta\nu_{sp.inter.}$ was empirically introduced [7,8] for the solutions in which charge transfer interactions, such as hydrogen bonds, could take place. The term $\Delta\nu_{sp.inter.}$ becomes null when in the solution do not act specific forces; when differs from zero, it gives the contribution of the specific interactions to the total spectral shifts.

This study deals with the separation of the contribution of each type of intermolecular interactions to the total spectral shifts measured in the electronic spectra of some benzo-[f]-quinolinium derivatives.



CA_1 CA_2

Fig. 1. Chemical structures of the studied benzo-[f]-quinolinium cycloaducts

2. Experimental

The chemical structure of the studied benzo-[f]-quinolinium cycloaducts is given in Fig. 1. The studied cycloaducts differ by the chemical structure of the molecular five-member cycle.

The chemical structure of the studied benzo-[f]-quinolinium ylids is given in Fig. 2. The studied ylids differ by the chemical structure of the carbanion substituents.

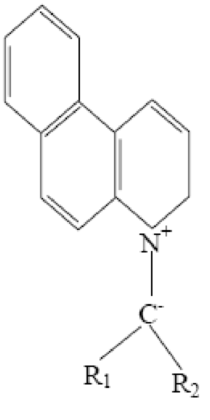
The studied cycloaducts have a visible vibronic band with three vibration components [9,10] and benzo-[f]-quinolinium ylids have a visible band with charge transfer from the carbanion to the heterocycle [13-15].

The wavenumbers of the electronic absorption spectra of the studied compounds were correlated with the solvent parameters. The refractive index and the electric permittivity of each solvent were measured as it is shown in [9,10]

3. Results and discussion

If the general theory of universal interactions is used, a relation of the type (6) permits to obtain by a multi-parameter regression, the values of the coefficients $\nu_{vap.}$, C_1 and C_2 on the basis of the experimental data. The results obtained in this study are given in relations (7)-(8) for the studied cycloaducts and (9)-(10) for the studied benzo-[f]-quinolinium ylids.

The dependences of the type (6), obtained by separating the protic (p) and aprotic (a) solvents, are listed in relations (7_{1a}) - (7_{3p}) for CA_1. In these relations the numerical indices refer to the vibration component of the visible vibronic band of the studied cycloaduct. The contribution of the specific interactions between the protic solvent and the cycloaduct molecules was obtained in this case by the average value of the distance measured



Y_1: R_1 = -H; R_2 = $-COC_6H_4NO_2(p)$
Y_2: R_1 = $-COC_6H_5$; R_2 = $COC_6H_2(NO_2)_3$

Fig. 2. Chemical structures of the studied benzo-[f]-quinolinium ylids.

between the first bisectrice and the points corresponding to the protic solvents in the plane $(\nu_{calc.}, \nu_{exp.})$

The coefficient C_2 is null for CA_1, showing the small influence of the polarization-dispersive-inductive interactions and a great importance of the orientation forces in solutions of this cycloaduct.

$$\nu_{calc.} = 18230 + 855f(\varepsilon) \qquad (7_{1a})$$

$$\nu_{calc.} = 18400 + 1037f(\varepsilon) + 500 \qquad (7_{1p})$$

$$\nu_{calc.} = 19720 + 625f(\varepsilon) \qquad (7_{2a})$$

$$\nu_{calc.} = 19790 + 1177f(\varepsilon) + 600 \qquad (7_{2p})$$

$$\nu_{calc.} = 22025 + 1068f(\varepsilon) \qquad (7_{3a})$$

$$\nu_{calc.} = 22278 + 1368f(\varepsilon) + 600 \qquad (7_{3p})$$

From equations (7_{1a}), (7_{2a}), and (7_{3a}) it results that, in the aprotic (a) solvents, the vibration components of the visible vibronic band of the CA_1 cycloaduct shift in the same direction. In the protic (p) solvents, from the total spectral shift of these components approximately 65% is due to the orientation forces and 35% to the specific interactions. In the aprotic solvents only the orientation interactions determine the spectral shift (C_2 and $\Delta\nu_{sp.inter.}$ coefficients are null in this case).

Different coefficients for the protic and non-protic solvents were obtained by the multi-parameter Linear Regression Method. The different values of C_1 in the protic and non-protic solvents demonstrate that in the protic solvents additionally act specific interactions.

The equations (8_1) – (8_3) were obtained by using all solvents for the multi-parameter linear regression. They show that in the CA_2 cycloaduct solutions, the polarization-inductive-dispersive interactions are prevalent (C_1 coefficient is null in this case). The effect of the specific interactions is negligible in CA_2 solutions ($\Delta\nu_{sp.inter.}$ term is also null).

$$\nu_{calc.} = 26020 + -8413f(n) \qquad (8_1)$$

$$\nu_{calc.} = 29090 + -6319f(n) \qquad (8_2)$$

$$\nu_{calc.} = 29450 + -4336f(n) \qquad (8_3)$$

CA_1 differs from CA_2 by a double bond in the additional five-member cycle. The extensive π-conjugation in the case of CA_2 cycloaduct diminishes the capacity of the molecule to interact by specific forces with the protic solvents.

When the protic solvents (alcohols) were eliminated, the multi-parameter linear regression applied for the Y_1 and Y_2 ylid solutions in the aprotic solvents, gives the results from relations (9_1) and (9_2).

$$\nu_a = 18947 + 2930f(\varepsilon) - 2320f(n) \qquad (9_1)$$

and

$$\nu_a = 18706 + 1614f(\varepsilon) + 1789f(n) \qquad (9_2)$$

Relations (9_1) and (9_2) were obtained by neglecting the specific interactions which could be present in the protic solutions of the benzo-[f]-quinolinium ylids [13]. They are applicable only for aprotic solvents.

When an empirical term of the type $\Delta\nu_{sp.inter.} = C_3 \cdot \delta(ppm)$ is introduced [4,8] in relation (6), the contribution of the specific interactions in the protic solvents can be estimated concomitantly with the contribution of the universal interactions. The supplementary term vanishes for the solutions achieved in the a-protic solvents. The obtained equations in this case are (10_1) and (10_2).

$$\nu_a = 20080 + 2420f(\varepsilon) - 2205f(n) + 419 \cdot \delta(ppm) \qquad (10_1)$$

$$\nu_a = 20680 + 1980f(\varepsilon) - 3150f(n) + 230.6 \cdot \delta(ppm) \qquad (10_2)$$

In relations (10_1) and (10_2) the empirical introduced term takes into consideration the degree of the electron delocalization on the -OH band of the alcohols by the ^{1}HNMR chemical shift δ(ppm) measured for the hydroxyl bond.

Table 2. Supply, in percents, of different type of interactions in the absorption spectrum of the studied benzo-[f]-quinolinium ylids.

Type of interaction	Benzene		Acetone		Ethanol	
	Y_1	Y_2	Y_1	Y_2	Y_1	Y_2
$C_1 f(\varepsilon)$	47.3%	38.9%	81.1%	71.1%	44.4%	48.0%
$C_2 f(n)$	52.7%	61.1%	18.9%	28.9%	10.1%	18.9%
$C_3 \delta(ppm)$	0	0	0	0	45.5%	33.1%

In Table 1 the supply in percents of each type of interactions is given for the studied spectrally active molecules. It results that in a non-polar solvent (benzene) the dispersive-induction-polarization interactions are prevalent, while, in a polar solvent (acetone), the orientation interactions are decisive in the total spectral shift measured in ylid solutions. Benzene and acetone are non-protic; in them the specific interactions of the type proton change between the solvent and ylid molecules are absent.

In a protic solvent, such as ethanol, the specific interactions of the type proton donor-acceptor are predominant in ylid solutions. The orientation interactions have a great importance for the total shift, while the dispersive-inductive-polarization interactions have a small contribution to the total shift in ethanol solutions of the studied ylids [4,14].

In the ground state of ylid molecules are predominant orientation and dispersive interactions in non-protic solvents, while in the protic ones are predominant orientation and specific interactions.

3. Conclusions

The existent theories regarding the solvent influence on the electronic absorption spectra of organic compounds neglect the specific interactions, consequently in the case of the spectrally active molecules with proton acceptor character, a supplemental term must be introduced for the protic solutions, in which the specific interactions have an important role. For these cases a term proportional with the proton degree of freedom in OH bond must be added to the terms describing the supply of the universal interactions in solutions of the proton acceptors spectrally active molecules.

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