

# Electric dipole moments in the excited states determined by means of spectral methods

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The electric dipole moments involved in the electronic transitions responsible for the visible band appearance in the absorption and/or emission spectrum of some cycloimmonium ylids are estimated by two methods: -the dipole moments in the ground electronic state were computed by using PM3 procedure; - the dipole moments in the excited state were estimated from the spectral shifts measured in different solvents, related to the gaseous phase of the spectrally active molecule. The Bakhshiev theory was used to express these shifts versus the solution parameters.

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## 1. Introduction

The spectral shifts ( $\Delta\bar{\nu}$ ) of the absorption and/or the fluorescence bands recorded in a given solvent ( $\bar{\nu}_{solv.}$ ) related to the gaseous phase ( $\bar{\nu}_{vap.}$ ) of the spectrally active molecule;

$$\Delta\bar{\nu} = \bar{\nu}_{solv.} - \bar{\nu}_{vap.} \quad (1)$$

are correlated in theories about the liquid solutions with physical parameters of the solvent and spectrally active molecules [1-3].

The spectral shift measures the difference between the solvation energies of the spectrally active molecule in the electronic states involved in the appearance of the corresponding electronic bands. The theories [1,2] regarding solvent influence on the electronic absorption or emission bands express the spectral shifts by relations of the type [3]:

$$\Delta\bar{\nu}^{a,f} = C_1^{a,f} \cdot \left( \frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) + C_2^{a,f} \cdot \frac{n^2 - 1}{n^2 + 2} + \Delta\nu_{sup.pl.}^{a,f} \quad (2)$$

where  $n$  and  $\varepsilon$  are the refractive index and the electric permittivity of the solvent and  $C_1^{a,f}$  and  $C_2^{a,f}$  are coefficients depending on the microscopic parameters (dipole moment, polarizability, ionization potential) of the molecules. The third term in relation (2) expresses the supply of the specific interactions at the total spectral shift. This term is usually neglected in the theories of the liquid solutions. Relation (2) can be used when the solvents have high values of the relaxation time, as compared with the life-time of the excited state of the spectrally active molecule.

The contribution of the orientation forces at the solvatochromic shift is expressed by the first term in (2), while the contribution of the inductive-dispersive and/or

polarization forces is represented by the second term. The third term checks the contribution of the specific interactions to the total spectral shift. It is difficult to separate the contribution induction-polarization and dispersive forces in (2), because they depend on the same function of the refractive index.

The first coefficient, noted with  $a$  and  $f$  for absorption and fluorescence spectra in (2), has the following expressions:

$$C_1^a = \frac{2 \cdot \mu_g \cdot (\mu_g - \mu_e \cdot \cos \varphi)}{r^3} \frac{2n^2 + 1}{n^2 + 2}; \quad (3)$$

$$C_1^f = \frac{2 \cdot \mu_e \cdot (\mu_g \cdot \cos \varphi - \mu_e)}{r^3} \frac{2n^2 + 1}{n^2 + 2}; \quad (4)$$

These coefficients can be used to determine the molecular dipole moments in the electronic states involved in the electronic transition. Measurements both in absorption and emission spectra must be made in order to estimate the values of the dipole moments in the excited electronic state, the dipole moment of the ICT transition and the angles between them when the dipole moment in the ground state of the spectrally active molecule is estimated by other methods.

In order to estimate the dipole moments in the excited states, some carbanion monosubstitutes p-nitrophenacylids having as heterocycle benzo-[f]-quinolinium, p-phenyl-pyridazinium and p-cumyl-pyridazinium were used. They belong to the cycloimmonium ylids [4], substances with amphionic nature, in which a  $sp^2$  hybridized nitrogen atom from a heterocycle is covalently bound to a negative charged carbon. The ylid carbanion has two attached substituents. The bigger the electronegativity of the carbanion substituents, the higher the cycloimmonium ylids stability is [5]. When the hydrogen atom is one of the two substituents, cycloimmonium ylids are called carbanion monosubstituted.

The stability of cycloimmonium p-nitro-phenacylids is due to the  $-\text{NO}_2$  strongly electron withdrawing group, determining a large negative charge delocalization on the carbanion [4].

Cycloimmonium ylids have a visible electronic absorption band with intramolecular charge transfer (ICT) (Fig. 1) from the carbanion to the heterocycle, very sensitive both to the ylid structure and solvent nature [6-9]. The visible fluorescence band of the cycloimmonium ylids has a smaller sensitivity to the solvent action, compared with their electronic absorption band due to the intermolecular charge transfer.

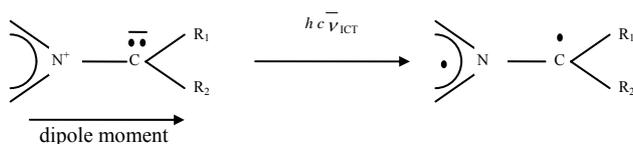


Fig. 1. The intramolecular charge transfer.

Cycloimmonium ylids have applications in chemistry as acido-basic indicators by their specific color, in various heterocycle syntheses of new classes of aza-heterocycle compounds. In pharmacy cycloimmonium ylids are used

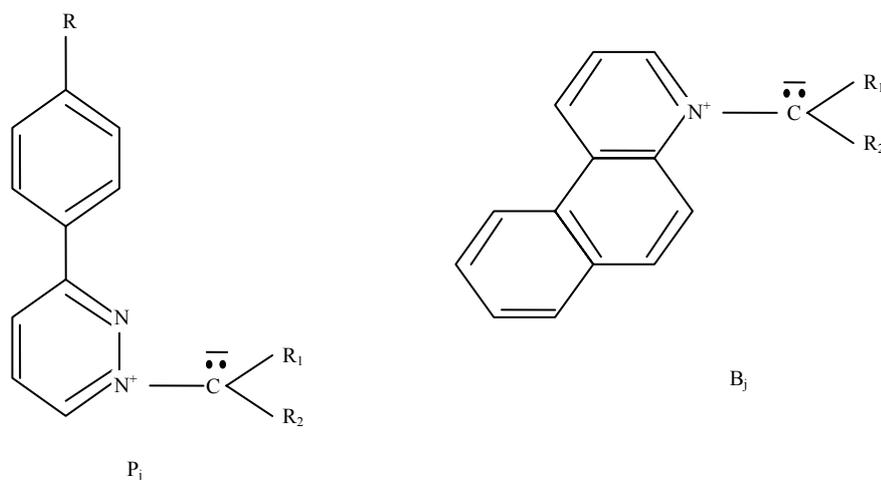


Fig. 2. Cycloimmonium ylids (CY) under the study.

The  $^1\text{H}$  NMR spectra of the protic solvents were recorded with a Tesla BS 487 spectrometer, with a precision of  $\pm 0.01 \text{ ppm}$

The electric permittivity was determined with a DK-meter 600 RL type Oehme, while the refractive index with an Abbe refractometer. The precision in  $\epsilon$  determination was of about 4%, while in the refractive index was 0.001.

as antifungal and anticonsumption substances. Pyridazinium ylids were tested with good results against Cock Bacillus, Escherichia coli and Staphylococcus aureus [10,11].

## 2. Experimental part

The spectrally studied carbanion monosubstituted pyridazinium- and benzo-[f]-quinolinium-methylids (Fig. 2 and Table 1) were prepared as described in [1]. The solvents were spectrally grade or when necessary purified as it is shown in [9].

The wavenumbers in the maximum of the visible ICT absorption and fluorescence bands are listed in Tables 2. The visible electronic absorption spectra were recorded by a Carl Zeiss Jena spectrophotometer Specord UV VIS with data acquisition system, having a precision of  $\pm 20 \text{ cm}^{-1}$ . The fluorescence spectra were recorded at SLM 800 spectrophotometer with a Data Acquisition System, with a precision of  $\pm 1 \text{ nm}$ .

Table 1. Substituents of the analyzed cycloimmonium ylids (See Fig. 2).

Nr.	Ylid	R <sub>1</sub>	R <sub>2</sub>	R
1	P <sub>1</sub> (p-phenyl-pyridazinium-p-nitro-phenacylid)	-H	- COC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	-H
2	P <sub>2</sub> (p-cumyl-pyridazinium-p-nitro-phenacylid)	-H	- COC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	-CH(CH <sub>3</sub> )
3	B <sub>1</sub> (benzo-[f]-quinolinium-p-nitro-phenacylid)	-H	- COC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	-

The dipole moments in the ground state of the studied compounds were determined by DK-metric measurements at infinite dilution [13] of the binary solutions made in

benzene. The weighting of substances was carried out using a Mettler MD B5 digital balance with  $10^{-5}$  precision. The precision in the dipole moment determination was of about 10%, because the determinations were made in benzene a polarizable solvent. Cycloimmonium ylids are less soluble in the non-polar and non-polarizable solvents

### 3. Results and discussion

The data in Table 2 show that visible ICT band is hypsochromically shifted by passing from non-polar to polar solvents. It results that the dipole moment of the studied cycloimmonium ylids decreases in the ICT process, so, in a given solvent, the solvation energy (especially by its orientation component) in the excited state of ICT is smaller than that in the ground state of ylid.

Having a basic character in their ground state, cycloimmonium ylids participates to hydrogen bond in the protic solvents. So, passing from the aprotic to protic solvents, a supplementary shift to blue of the ICT band was evidenced. The third term in (2) which gives the supply of the specific interactions at the spectral shift is expressed as function on the chemical shift of the proton belonging to -OH group of the hydroxyl solvents.

$$\Delta \nu_{\text{sup pl.}}^{a,f} = C_3 \delta_H \quad (5)$$

In order to separate the influence of the different types of interactions from the total spectral shift, relation (2) can be modified, by evidencing the terms in  $\mathcal{E}$  and the term in  $n$ . In this way a part of the orientation interactions supply is separated as function of  $\mathcal{E}$ .

Linear multi-parameters dependences of the visible band wave numbers both for the absorption and the emission spectra were realized using a MULTIREG and HPKA programs [14]. A linear dependence of the type (6), deriving from relations (2) and (5) was evidenced.

$$\bar{\nu} = C_0 + C_1 \frac{\mathcal{E} - 1}{\mathcal{E} + 2} + C_2 \frac{n^2 - 1}{n^2 + 2} + C_3 \delta_H \quad (6)$$

In relation (6)  $C_0^{a,f}$  signifies the values of the wavenumber in the maximum of the ICT band in the vaporous phase of the spectrally active molecule.

The results of the experimental data processing are listed in Tables 3 and 4. These tables contain the values of significant coefficients  $C_j$ , the reliance intervals  $\Delta C_j$ , test parameters  $t_j$ , multiple correlation coefficient  $R$ , standard deviation  $SD$  and the control values per ensemble  $F$  [14].

Table 2. Wavenumbers of visible ICT absorption band of cycloimmonium ylids from Table 1.

Nr.	Solvent	Absorption spectra			Fluorescence spectra		
		P <sub>1</sub>	P <sub>2</sub>	B <sub>1</sub>	P <sub>1</sub>	P <sub>2</sub>	B <sub>1</sub>
1	Dioxan	19.650	19.650	19.210	18.640	18.620	18.350
2	CCl <sub>4</sub>	19.580	19.710	19.140	18.630	18.610	18.320
3	Benzene	19.690	19.690	19.200	18.700	18.560	18.410
4	p-Xilene	19.780	19.790	19.160	18.770	18.650	18.370
5	Toluene	19.820	19.880	19.200	18.670	18.650	18.380
6	Iso-Amyl acetate	19.990	20.000	19.470	18.600	18.630	18.300
7	Chlorobenzene	19.940	19.940	19.430	18.620	18.630	18.350
8	Pyridine	20.190	20.210	19.600	18.560	18.580	18.270
9	n-Benzyl alcohol	21.310	21.300	21.060	18.960	18.900	18.760
10	Cyclohexanol	21.230	21.200	21.010	18.970	18.900	18.700
11	n-Amyl alcohol	21.170	21.180	20.830	18.900	18.860	18.600
12	n-Butyl alcohol	21.240	21.250	20.980	18.950	18.930	18.670
13	iso-Butyl alcohol	21.310	21.360	21.090	18.970	18.930	18.670
14	Iso-Propyl alcohol	21.340	21.390	20.990	18.900	18.810	18.640
15	n-Propyl alcohol	21.240	21.300	21.090	18.960	18.830	18.600
16	Acetone	20.250	20.310	19.750	18.500	18.490	18.210
17	Ethanol	21.270	21.400	21.100	18.910	18.900	18.640
18	Methanol	21.190	21.270	21.150	18.900	18.970	18.540
19	1,3 Propane diol	21.300	21.330	21.300	18.990	18.820	18.720
20	Ethylene glycol	21.370	21.350	21.290	18.900	18.890	18.590
21	Formamide	20.360	20.380	19.900	18.900	18.750	18.650

Table 3. The significant parameters  $C_j^a$ , the reliance intervals  $\Delta C_j^a$ , test parameters  $t_j$ , multiple correlation coefficient  $R$ , standard deviation  $SD$  and ensemble control value  $F$  for the absorption ICT band of the studied cycloimmonium ylids.

Ylid	$C_0^a$	$\Delta C_0^a$	$t_0$	$C_1^a$	$\Delta C_1^a$	$t_1$	$C_2^a$	$\Delta C_2^a$	$t_2$
P <sub>1</sub>	19,348.5	207.6	251.2	929.6	94.9	26.4	332.2	703.7	1.3
P <sub>2</sub>	19,464.4	213.7	244.5	896.9	96.2	25.0	25.3	727.5	0.1
B <sub>1</sub>	19,007.9	245.0	209.4	983.4	110.9	23.9	-463.8	826.9	1.5
Ylid	$C_3^a$	$\Delta C_3^a$	$t_3$	R	SD	CP	F		
P <sub>1</sub>	194.9	7.5	70.0	0.997	50.9	4.0	2670.1		
P <sub>2</sub>	201.9	7.7	70.4	0.994	54.5	4.0	2707.3		
B <sub>1</sub>	246.3	8.8	75.5	0.995	59.4	4.1	3057.0		

The data from Table 3 show that orientation interactions occur ( $C_1^{a,f} \neq 0$ ) in the cycloimmonium ylids solutions with dipolar solvents. The signs of the coefficient  $C_1^{a,f}$  corresponding to the absorption and fluorescence spectra show us that these interactions are bigger in the ground state of the ylids, comparatively with those in excited states. They determine a bathochromic

shift of the visible electronic cycloimmonium ylids bands by passing from nonpolar to polar solvents.

Specific interactions, of the proton donor-acceptor type, supplementary act in protic solvents, inducing a greater bathochromic shift of the ICT band maximum, compared as aprotic ones. These interactions are expressed by the term  $C_3 \cdot \delta_H$  in relation (6).

Table 4. The significant parameters  $C_j^f$ , the reliance intervals  $\Delta C_j^f$ , test parameters  $t_j$ , multiple correlation coefficient  $R$ , standard deviation  $SD$  and ensemble control value  $F$  for the visible fluorescence band of the studied cycloimmonium ylids.

Ylid	$C_0^f$	$\Delta C_0^f$	$t_0$	$C_1^f$	$\Delta C_1^f$	$t_1$	$C_2^f$	$\Delta C_2^f$	$t_2$
P <sub>1</sub>	18,539.3	174.8	312.7	-212.5	96.4	6.5	673.3	576.8	3.4
P <sub>2</sub>	18,615.0	362.6	148.8	-147.1	216.9	2.0	213.9	1152.9	0.5
B <sub>1</sub>	18,106.7	211.9	247.6	-175.9	126.8	4.0	118.4	674.0	4.8
Ylid	$C_3^f$	$\Delta C_3^f$	$t_3$	R	SD	CP	F		
P <sub>1</sub>	79.6	8.8	26.6	0.994	20.9	3.92	383.9		
P <sub>2</sub>	60.6	19.4	9.1	0.946	49.7	4.0	48.2		
B <sub>1</sub>	79.0	11.3	20.2	0.988	29.0	4.1	229.1		

Table 5. The molecular dipole moments involved in the visible electronic transitions for the studied cycloimmonium ylid.

Ylid	$\mu_g$ (D) (PM3)	$\mu_g$ (D) (exp.)	$r$ (Å)	$C_1^a$ (erg)	$C_1^f$ (erg)	$\mu_e$ (D)	$\varphi$ (degree)	$\Delta\mu_{g,e}$ (D)	$\alpha$ (degree)
P <sub>1</sub>	7.3	8.6	8	1,840.6	-420.8	5.0	60	7.4	130
P <sub>2</sub>	8.9	9.9	9	1,755.9	-291.3	6.1	57	8.3	123
B <sub>1</sub>	6.5	7.6	8	1,947.1	-348.3	3.3	80	6.7	152

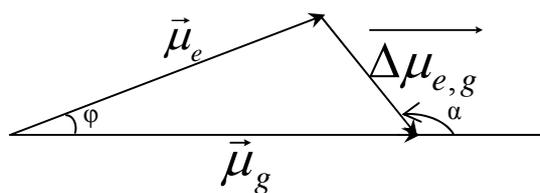


Fig. 3. Triangle of dipole moments.

From Table 4 results that  $C_1^f$  coefficient in (6) is negative for the fluorescence bands. This fact is in concordance with the dynamics of the electronic cloud in the ICT process [6,7]. The ICT is oriented from the carbanion to the heterocycle so, the dipole moment of the cycloimmonium ylids is smaller in the electronic excited state as compared to the ground ground. In ICT process, the dipole moment of cycloimmonium ylids could keep its sense, or change it. The decrease of the dipole moment by

the ICT process determines an important decrease of the orientation interaction energy in the excited state of cycloimmonium ylids [15].

Using the values of the  $C_1^{a,f}$  coefficients from Tables 3 and 4 and the values for the dipole moments in the ground state,  $\mu_g$ , calculated by PM3 method (first column in Table 5) and experimentally verified by the dielectric constant determination at infinite dilution of the ylid solution in a non-polar solvent [12,13] (second column in Table 5), the values of the dipole moments in the excited state  $\mu_e$ , the dipole moments of the ICT transition  $\Delta\mu_{g,e}$ , as well as the angles  $\varphi$  and  $\alpha$  between them (see Fig.3) were determined in the limits of Bakshiev's theory. The results are shown in Table 5. The obtained values are concordant both with the nature of the electronic transition and with the values obtained by the other methods [11,13].

We can affirm that by light absorption, the dipole moment of the cycloimmonium ylids decreases ( $\mu_e < \mu_g$ ). The ICT process also determines a great value of the dipole moment of the electronic transition ( $\Delta\mu_{g,e}$ ). The angles between  $\Delta\mu_{g,e}$  and  $\mu_g$  is bigger than  $90^\circ$ , but the dipole moment in the excited state of the studied ylids has a component in the same sense with the dipole moment in the ground state. It results that, in the ICT process only a partial charge transfer of the negative charge is allowed by the great electron-withdrawing substituents -p-nitro-phenyl.

The substituent p-nitro-benzoyl of the ylid carbanion determines only a partial charge transfer to the heterocycle, nitro group having a great electron withdrawing effect.

#### 4. Conclusions

The obtained values are in good agreement with the charge distribution in the carbanion-monosubstituted cycloimmonium ylids structure and with the previously [4] proposed mechanism for the intramolecular charge transfer.

The accuracy in the calculated values of the dipole moments is limited by the approximations made in theory development. So, using the hypothesis that the solvents have the relaxation time bigger than the life-time of the electronic excited state, relation (2) was obtained.

The solvathochromic theories can be used in electric dipole moments determination, especially in the cases of very sensitive electronic bands to the solvent nature, as in the case of the  $n \rightarrow \pi^*$  electronic bands with charge intramolecular transfer.

#### References

- [1] Mc. Rae, J. Phys. Chem. **61**, 562 (1957).
- [2] H. G. Bakshiev, Spektroskopia Mejmoleculiarnov Vzaimodeistvii, Izd.Nauka, Leningrad, p.162-163 (1972).
- [3] B. S. Neporent, N. G. Bakshiev, Optika I Spectroscopia **8**, 777 (1960); **16**, 351 (1964).
- [4] I. Zugrăvescu, M. Petrovanu, N Ylid Chemistry, Mc Graw Hill, New York, (1976).
- [5] G. Surpăţeanu, Lablache Combier, Heterocycles **22**, 2079 (1984).
- [6] C. A. Henrick, E. Ritchie, W. C. Taylor, Aust. J. Chem. **20**, 2455 (1967); **20**, 2467 (1967).
- [7] E. M. Kosower, B. G. Ramsey, J. Am. Chem. Soc. **81**, 856 (1959).
- [8] D. Dorohoi, V. Holban, J. Mol. Struct. **123**, 1-3, 129 (1993).
- [9] D. Dorohoi, H. Partenie, Do Nhat Van, I. Zugrăvescu, An. Şt.Univ. Iaşi, s. Ib. Fizica, **26**, 51 (1994).
- [10] M. Ungureanu, I. Mangalagiu, M. Roman, Ann. Pharm. Fr. **55**(2), 69 (1997).
- [11] L. Leontie, M. Roman, F. Branza, C. Podaru, G. I. Rusu, Synth. Met. **138**, 57 (2003).
- [12] A. Vogel, Textbook of Practical Organic Chemistry, Fourth edition, Longman, London, 266-268, (1978).
- [13] D. Dorohoi, G. Surpăţeanu, L. Gheorghies, Balkan Phys. Letters, **6**(3), 198 (1998).
- [14] G. Henrion, A. Henrion, R. Henrion, Beispiele zur Datenanalyse mit Basic Programmen VEB D.V.W. Berlin (1988).
- [15] V. Pop, D. Dorohoi, V. Holban, Spectrochimica Acta, **50A**, 14, 2281 (1994).

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