Excited State Polarizability of Some Polycyclic Polyenes

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The electronic absorption spectra of five polycyclic polyenes were recorded in non-polar solvents in order to determine their polarizability in excited states from the strength of the dispersive interactions in their diluted solutions. The bathochromic shifts of π-π vibronic bands prove the increase of the molecular polarizabilty in the photon absorption process. Some molecular parameters of the analyzed polyenes in their ground state were computed by using the programs from Spartan'14.*

Keywords: polycyclic polyenes, electronic absorption bands, excited state polarizability

Non-substituted polycyclic polyenes are non-polar, but polarizable molecules with a very intense vibronic π-π* band [1]. Small spectral shifts were reported for these bands in literature [2-6]. The position of π-π* band of polyenes measured in conditions of the solvent high purity, offers information about the strength of dispersive interactions in non-polar solutions.

The dispersive interactions are due to the cumulative effects of interactions between the instantaneous dipole moments of non-polar molecules. They are the weakest attractive universal interactions which can be evidenced only in the absence of orientation, polarization and induction forces, mainly in solutions with non-polar components [7, 8].

The dispersive interactions modify the potential energy of the solute molecules both in their ground and excited states. The difference of the solvation energies in the electronic states involved in the absorption process determines the position of the electronic band in the wavelength scale. The spectral shifts of the electronic absorption bands due to the dispersion interactions depend both on the structural features of the solute molecules and on the solvent nature [9 - 11].

The theories describing the solvent influence on the electronic band positions, express the wavenumber in their maximum as function of the solvent parameters (refractive index n, polarizability α, electric permittivity ε, ionization potential *I*) and also on the microscopic parameters (ionization potential *I(u)*, polarizability α*(u)*, dipole moment μ*(u)*, dimensions and so one) of the solute molecule.

In the theory developed by Bakhshiev [5], the wavenumber $\bar{\nu}$ (cm^{-1}) in the maximum of the electronic absorption band of a non-polar (spectrally active) solute molecule solved in non-polar solvent is expressed as function of the solvent polarity function *f(n)*;

$$f(n) = \frac{n^2 - 1}{n^2 + 2} \quad (1)$$

as it follows:

$$\bar{\upsilon}_s = \bar{\upsilon}_0 + m \cdot f(n) \quad (2)$$

In relation (2) indices *s* and *0* reffer to the solution, respectively to the gaseous phase of the solute molecule. The slope m from (2) depends on the microscopic parameters of the spectrally active molecule and on the solvent ionization potential [7, 12].

$$m = \frac{3}{2} \cdot \frac{I}{r^3(u)} \cdot \left[\frac{I_g(u) \cdot \alpha_g(u)}{I + I_g(u)} - \frac{(I_g(u) - hc\bar{\upsilon}_s) \cdot \alpha_e(u)}{I + I_g(u) - hc\bar{\upsilon}_s} \right] \quad (3)$$

Indices *g* and *e* in relation (3) refer to the ground and excited states of the solute molecule and *r(u)* is the molecular radius of the solute. The letter *u* refers to the solute molecules. When relations on the type (2) can be established in a class of non-polar, diluted solutions, the slope *m* can be used in estimating the excited state polarizability $\alpha_e(u)$ of the spectrally active molecules.

The purpose of this study is to estimate, in the limits in which Bakhshiev theory has been developed, the excited state polarizability of five polycyclic polyenes (benzene, naphthalene, anthracene, tetracene and phenanthrene), by using the dispersive interactions in non-polar solutions.

Experimental part

The diluted solutions (10^{-4} mol/L) were achieved in non-polar solvents. The polyenes purchased from Merck Company were spectrally grade.

The non-polar solvents, spectrally grade, were obtained from Merck Company and used without supplemental purification.

The wavenumbers in the maximum of the π-π* absorption band were obtained by averaging five consecutive measurements in each solvent, having in view the very small shifts obtained by changing the solvent nature. The refractive index of the solvents was measured, at λ=589.3 nm, with an Abbe refractmeter.

Table 1
SOLVENT PARAMETERS

No.	Solvent	I (eV)	n	ε	f(n)
1	Dodecane	9.60	1.421	2.01	0.254
2	Cyclohexane	9.80	1.427	2.02	0.257
3	n-Octane	9.82	1.398	1.95	0.241
4	Heptane	10.10	1.387	1.92	0.235
5	Hexane	10.13	1.375	1.89	0.229
6	Decane	10.20	1.411	1.99	0.248
7	Pentane	10.53	1.358	1.84	0.220
8	Cyclopentane	10.56	1.407	1.97	0.246

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The statistical analysis of obtained data was performed using Origin Pro8 program.

The solvent parameters: ionization potential of solvent molecules I (eV), refractive index n and electric permittivity ε are listed in table 1. The values of the electric permittivity attest the non-polar nature of the chosen solvents.

Computational details

Molecular modeling is used in many fields such as chemistry, physics, biology, medicine, pharmacy and allows graphical representation of a molecule configuration and calculation of physico-chemical its parameters.

The optimized structures of the studied compounds by Spartan'14 software [13] are given in figure 1. These are also calculations of the polyene molecular parameters in HyperChem 8.0.6 [14].

From formula (3) it results expression (4) for the excited state polarizability.

$$\alpha_e(u) = \frac{I + I_g(u) - hc\upsilon_s}{I_g(u) - hc\upsilon_s} \cdot \left[\frac{I_g(u) \cdot \alpha_g(u)}{I_g(u) + I} - \frac{2m \cdot r^3(u)}{3 \cdot I} \right] \quad (4)$$

Relation (4) shows that the excited state polarizability of the spectrally active non-polar molecules can be calculated when the ionization potentials, molecular radius and the ground state polarizability are known (computed or measured by other methods) and the wavenumber in the maximum of the absorption band is experimentally determined in non-polar solvents.

The ionization potentials are usually known [16] or can be estimated by using quantum-mechanical programs. The ionization potential is the energy of High Occupied Molecular Orbital (HOMO) with changed sign [17]. The ground state polarizability of the spectrally active molecules

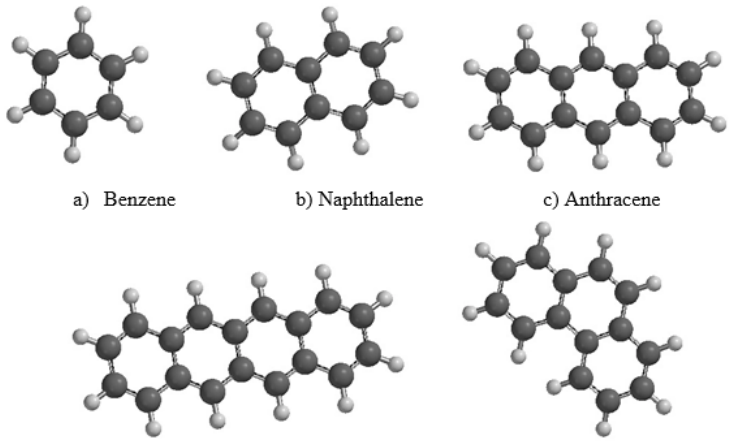

Fig. 1. Optimized structures of studied polyenes

No.	Solute	I_g (u)	α_g (u) A³	V (A³)	S (A²)	r(u) (A)
1	Benzene	9.75	47.03	99.15	115.07	2.585
2	Naphthalene	8.84	51.58	150.35	161.90	2.786
3	Anthracene	8.25	56.01	201.57	208.68	2.898
4	Tethracene	7.87	60.34	252.78	255.44	2.969
5	Phenanthrene	8.74	55.74	200.92	205.81	2.929

Table 2
MOLECULAR PARAMETERS OF POLYENES OBTAINED

The polyene parameters of interest for this study are listed in table 2.

The molecular parameters in the ground state of the studied polyenes was performed using the semi-empirical method PM3 (Parametric Method number 3) by the molecular modeling program Spartan'14 [15].

Results and discussions

Using the data from tables 1 and 2 and the measured values of the wavenumbers in the maximum of π-π* band for the studied polyenes, the slopes *m* and the cut at origin ν_0 (cm^{-1}) of line (2) were estimated. The cut at origin of lines (2), ν_0 (cm^{-1}) signifies the wavenumber in the maxim of the analyzed electronic band for the vapours phase of the spectrally active substance.

can be also computed and the slope of line (2) can be graphically or statistically estimated.

The spectral shifts of π-π* bands $\Delta\nu=\nu_\sigma-\nu_o$ (cm^{-1}) related to gaseous phase of polycyclic polyenes are listed in table 4.

The dependence between the spectral shifts Δν (cm^{-1}) measured in each solvent and the polarity function f(n) are illustrated in figure 2.

In table 4 are listed the values obtained for the excited state polarizability of the studied compounds and the difference between the excited and ground states polarizabilities $\Delta\alpha(u)=\alpha_e(u)-\alpha_g(u)$.

From table 4 it results an increase of the polyene polarizability by excitation. The increase of the molecular

No.	Solvent	$\Delta\upsilon = \upsilon_s - \upsilon_0$ (cm^{-1})				
		Benzene	Naphthalene	Anthracene	Tetracene	Phenanthrene
1	Dodecane	-162	-162	-875	-1131	-3410
2	Cyclohexane	-167	-168	-867	-1123	-3408
3	n-octane	-152	-157	-820	-1041	-3180
4	Heptane	-150	-153	-805	-1020	-3180
5	Hexane	-142	-148	-783	-1015	-3045
6	Decane	-157	-162	-838	-1087	-3350
7	Pentane	-136	-142	-743	-969	-2935
8	Cyclopentane	-162	-157	-833	-1079	-3280

Table 3
SPECTRAL SHIFTS OF BAND OF POLYENES

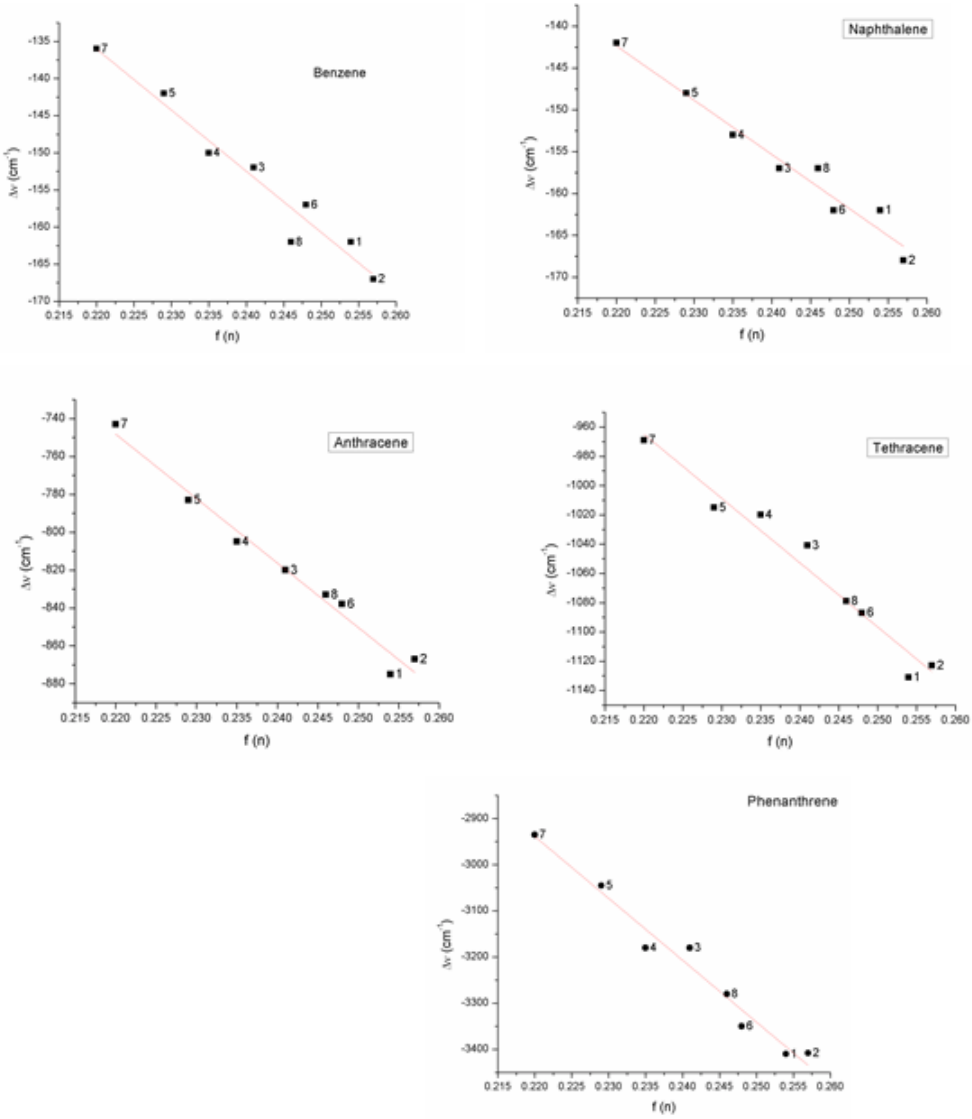

Fig. 2. Difference Δν vs. polarity function *f(n)*

No.	Solute	m (cm⁻¹)	ν_0 (cm⁻¹)	α_e (u) A³	Δα	R	SD
1	Benzene	-822±73	39422	70.80	23.78	0.95	2.45
2	Naphtalene	-647±51	32322	83.27	31.69	0.96	1.72
3	Anthracene	-3402±210	27463	78.33	22.32	0.97	7.01
4	Tethracene	-4386±346	22351	79.90	19.59	0.96	11.59
5	Phenanthrene	-13404±925	37460	97.62	36.54	0.97	30.96

Table 4
EXCITED STATE POLARIZABILITY OF POLYENES

polarizability of anthacene was established by applying Abe [18,19] theory to the spectral data obtained in solvent with various nature [20] and appropriate values were obtained.

The main error in appreciating the excited state polarizability in the present study is caused by the fact that the spectral shifts are determined for the ground state parameters computed for isolated molecules, while in the formula of spectral shifts these parameters modified by the solvent action on the solute molecule must be considered.

The hypotheses in which the theory of liquids is developed can also influence the values of the solute excited state polarizability. For instance realtion (2) was obtained in the hypothesis that orientation, polarization and induction interactions have not influence on the wavenumber in the maximum of the analysed bands.

Even these incovenients, the obtained data are very useful for scientists working in quantum-mechanical chemistry, for comparisons or also for using the data in order to simplify the computational way.

Conclusions

The wavenumber in the maximum of π-π* bands of polycyclic polyenes increases with the number of the component benzenic cycles.

The excited state polarizability is higher than the ground state polarizability for all polycyclic polyenes under the study.

The wavenumber in the maximum of the absorption band of polycyclic polyenes decreases when the solvent polarity function increases.

The cut at origin of the linear dependence between the wavenumber in the maximum of the electronic absorption band of polyenes and the solvent polarity function can be considered as approximating the value of the wavenumber of each polyene in its gaseous phase.

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