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INTERACTION ENERGIES IN SOLUTIONS OF AZOBENZENE COMPOUNDS

BY

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Abstract. The interaction energies between the components of dipolar solutions can be estimated on the bases of solvatochromic correlations which allow separating different types of interactions by their supply at the spectral shifts of the electronic absorption bands, spectral shifts induced by the modifications of the solvent nature. In the theory of the simple liquids, the dependence of the spectral shifts on the macroscopic parameters of the solvents allows to estimate some microscopic parameters of the spectrally active molecules.

Keywords: azobenzene compounds; interaction energies; theory of simple liquids; macroscopic/microscopic parameters.

1. Introduction

As a consequence of π -delocalization, aryl azo compounds have vivid colors, especially red, orange and yellow. Therefore, they are used as dyes, and are commonly known as azo dyes. Azo compounds are extensively utilized in chemical industries as dyes and pigments because of their extraordinary

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coloring (Khanmohammadi *et al.*, 2013; Kinali-Demirci, 2013). Moreover, in biological systems, some of these compounds could be used as inhibitors for tumor-growth (Ross and Warwick, 1955). Some important food colorants (*e.g.* sunset yellow and allura red) also belong to the class of azo dyes. Azo dyes contain the azo functionality, $-N=N-$, with attached aryl groups.

Solvents play an important role in physical and chemical processes. Additionally, solvent effect on absorption spectra can be used to provide information about solute–solvent interactions (Reichardt, 2005). Solute–solvent interactions are determined by the electronic and nuclear solvent polarization and they can be described by functions of the refractive index n and the electric permittivity ε :

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

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

When the excited state of an azo dye is more polar than its ground state, the dye exhibits positive solvatochromism with a bathochromic (red) shift in the UV–Vis spectrum reflecting stabilization of the excited state in the polar solvent environment. Hypsochromic or blue shifts reflect stabilization of more non-polar excited states in more non-polar surroundings (Karukstis *et al.*, 2010).

Azobenzene compounds usually exhibit a low intensity $n-\pi^*$ absorption band in the visible range of the spectrum and a high intensity $\pi-\pi^*$ band in the UV spectra due to the conjugation between azobenzene and aromatic ring system (Airinei *et al.*, 2001).

2. Experimental Part

The azoderivatives (AZ1, AZ2) obtained in our laboratory was used upon purification by recrystallization. The solvents used were of spectrophotometric grade and supply by Aldrich or Fluka.

HyperChem 8.0.6 (www.hyper.com) is a molecular modelling program frequently utilized to determine some physical and structural parameters of different kinds of substances. To obtain a configuration characterized by a minimum free energy the molecules were geometrically optimized using the Polak Ribiere algorithm with maximum gradient set at $0.001 \text{ kcal}/(\text{mol} \cdot \text{Å})$, after that through a single point calculation a number of physical and structural properties have been obtained. The Parametric Method number 3 is a semi-empirical method for the quantum calculation of molecular structure. PM3 (Stewart, 1989) uses the Hamiltonian and it is parameterized to reproduce a large number of molecular properties.

The electronic absorption spectra were recorded at a Specord UV Vis Carl Zeiss Jena Spectrophotometer with data acquisition system.

3. Results and Discussions

The optimized structures of some azo derivatives using the HyperChem 8.0.6. program are represented in Fig. 1 a) 4-aminoazobenzene (AZ1) and b) 4-acetamidoazobenzene (AZ2).

The studied molecules belong to the CS class symmetry: the molecules of this group are planar and they have only one element of symmetry, the plane of the molecules.

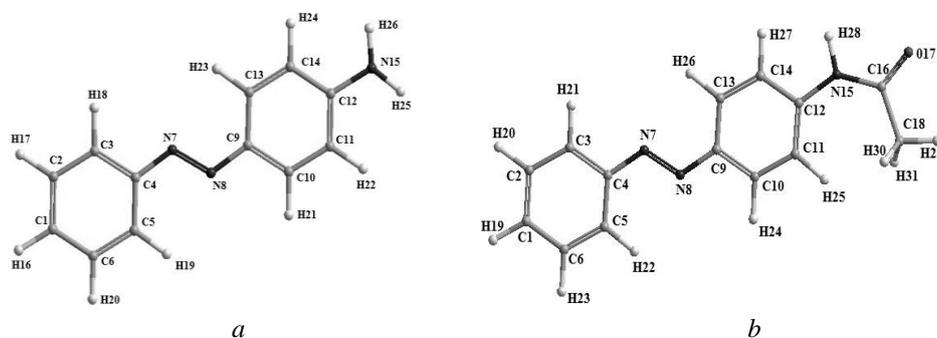
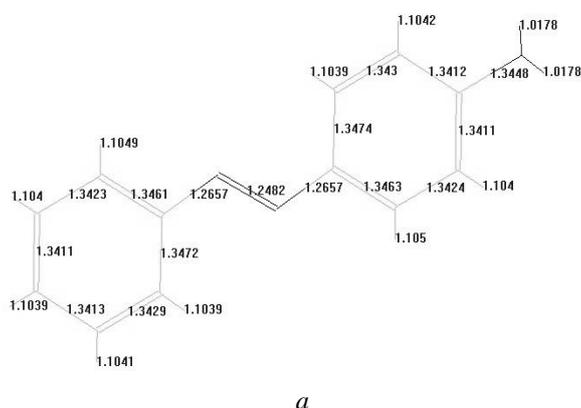
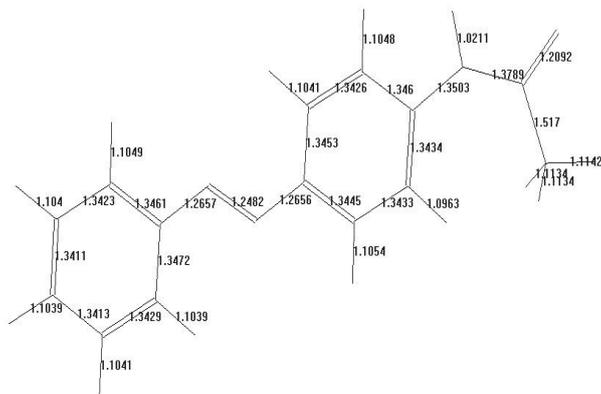


Fig. 1 – The optimized structures of AZ1 and AZ2 and the denomination of the atoms: a) AZ1; b) AZ2.

The bond lengths in [\AA] were computed for a) AZ1 and b) AZ2 are listed in Fig. 2.

The positions of the atoms are those from Fig. 1. The single bond C(12)-N(15) are longer than the single bonds C(4)-N(7) and C(9)-N(8) and also than the double bond N(7)-N(8), as it results from Fig. 2 a) AZ1.



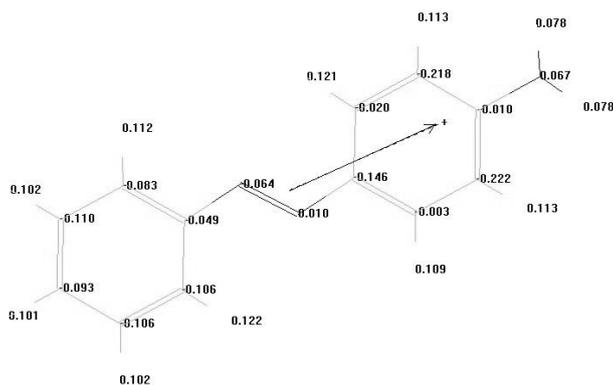


b

Fig. 2 – *a*) The computed bond lengths of AZ1 in [Å]; *b*) The computed bond lengths of AZ2 in [Å].

It is seen from Fig. 2 *b*) AZ2 that the single bonds N(15)-C(12) and N(15)-C(16) are smaller than the single bond C(16)-C(18) and also the double bonds N(7)-N(8) and C(16)-O(17) are smaller than the single bonds N(7)-C(4) and N(8)-C(9). In both Figs. *a*) and *b*) in benzene cycle the values of bond lengths are higher than 1.3 [Å].

The electronic charges on located near the molecular atoms in percents of electron elemental charge [$e = 1.6021662 \times 10^{-19}$ C] are given in Fig. 3 *a*) AZ1 and *b*) AZ2.



a

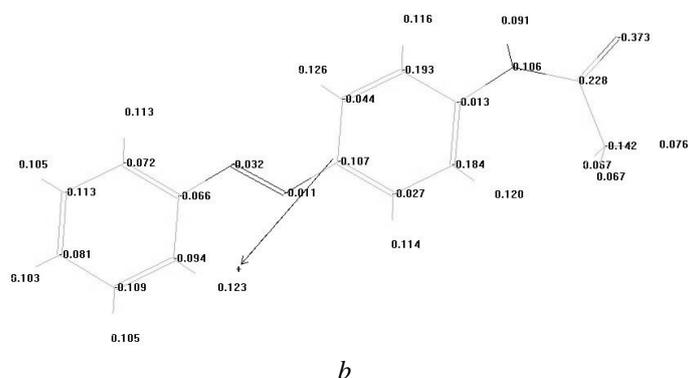


Fig. 3 – *a*) The atomic charges and the dipole moment orientation of AZ1 computed by HyperChem; *b*) The atomic charges and the dipole moment orientation of AZ2.

As one can see from Fig. 3 *a*) AZ1 that the negative charges are located near C, N atoms (the negative values are between -0.003 in C(10) atom and -0.032 in C(9) atom), and the positive charges are located near H atoms and also located near N(8) atom.

The negative charges are located near C, N and O atoms (the negative values are between -0.011 in N(8) atom and -0.372 in O(17) atom), and the positive charges are located near H atoms and also located near N(15) and C(16) atoms, as it results from Fig. 3 *b*) AZ2.

The Frontier Molecular Orbitals determine the molecular chemical stability, chemical reactivity and chemical hardness–softness of molecules, and playing an important role in the optical and electric properties (Fleming, 1976). It is also used to determine the interaction of the molecules with the other species. The energy levels of the molecular orbitals border HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) for azo derivatives give information on the possible electronic transition.

They are highlighted in Fig. 4 AZ1 and Fig. 5 AZ2 (color: gray is positive value and black is negative value).

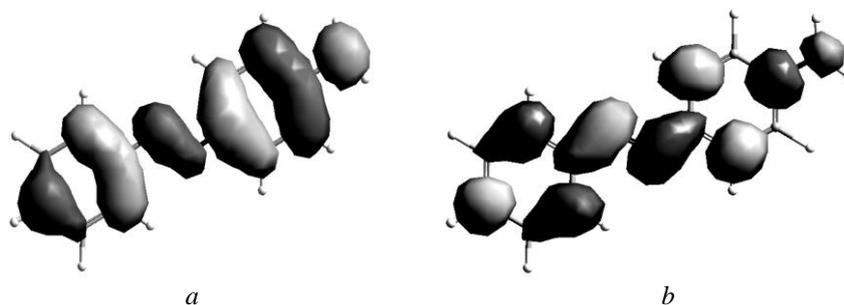


Fig. 4 – The frontier orbitals of 4-aminoazobenzene:
a) HOMO; *b*) LUMO.

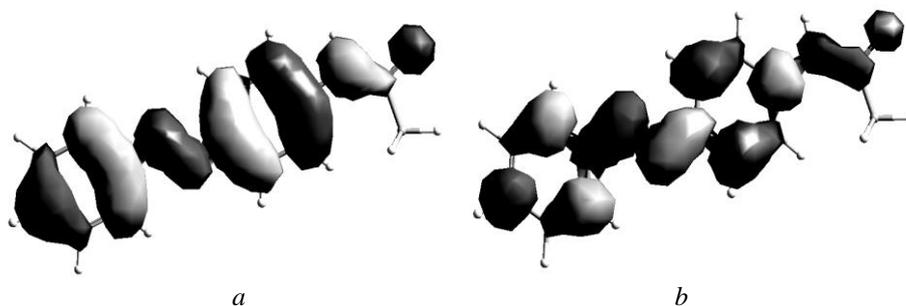


Fig. 5 – The frontier orbitals of 4-acetamidoazobenzene:
a) HOMO; b) LUMO.

The electrophilic attack occurs most likely to the atomic site with a high density of orbital HOMO while nucleophilic attack site is correlated with atomic high-density of orbital LUMO.

Table 1

The Energies Values in the Ground State for the Studied Molecules

Propertiers	AZ1	AZ2
Total energy, [kcal/mol]	-47788.527	-60742.463
Heat of formation, [kcal/mol]	175.626	132.851
Binding energy, [kcal/mol]	-2787.176	-2787.176
Electronic energy, [kcal/mol]	-292280.676	-389698.942
Nuclear energy, [kcal/mol]	244492.149	328956.478
E_{HOMO} , [eV]	-7.977	-8.492
E_{LUMO} , [eV]	-1.029	-1.458
$\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}} $, [eV]	-6.948	-7.035

The AZ2 is more stable than the AZ1 due the higher negative value of the total energy (Table 1).

The difference $\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}}$, known as HOMO/LUMO gap, represents the lowest energy electronic excitation that is possible in a molecule. For AZ1 this value is smaller than for molecule AZ2 and this demonstrate that molecule AZ2 is more available to interact with other species.

The ionization potential (I) and electron affinity (A) can be estimated from the HOMO and LUMO energy values by applying Koopmans theorem (Koopmans, 1934):

$$I = -E_{\text{HOMO}} \quad (3)$$

$$A = -E_{\text{LUMO}} \quad (4)$$

The density of the total electronic charge (Fig. 6), indicate areas with high or low electronegativity which determine the orientation of molecules.

Three regions with density of negative charge corresponding preferential coupling cation sites were highlighted for the studied molecules.

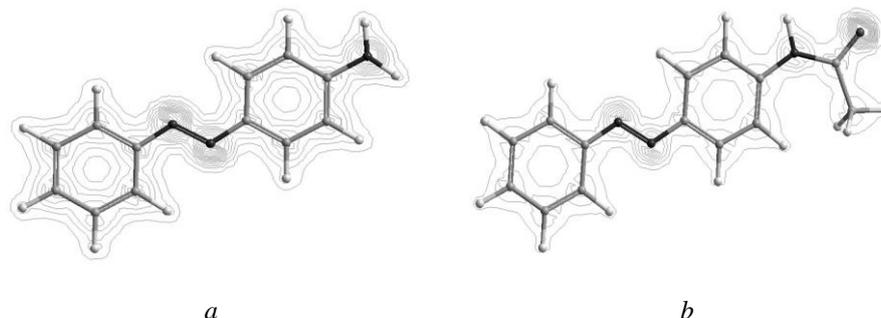


Fig. 6 – The density of the total electronic charge of the studied molecules:
a) AZ1; b) AZ2.

The dipole moment, the polarizability, the refractivity and logP were calculated using the QSAR method. Quantitative Structure - Activity Relationships (QSAR) correlate the molecular structure or properties derived from molecular structure with a particular chemical or biochemical activity (Gallegos, 2004).

Table 2
QSAR Parameters Calculated by HyperChem

Parameters	AZ1	AZ2
Surface area, [Å^2]	401.43	457.97
Volume, [Å^3]	625.46	731.90
Mass, [u.a.m]	197.24	239.28
Hydration energy, [kcal/mol]	-12.94	-9.87
Log P	0.25	0.08
Refractivity, [Å^2]	75.55	82.99
Dipole moment, [D]	3.27	2.22
Polarizability, [Å^3]	23.50	27.26

The hydration energy is defined as the energy absorbed when the substance is dissolved in water. The AZ1 have a higher values of the hydration energy than the AZ2. LogP represents the octanol/water partition coefficient, the positive values of logP shows that the studied compounds is lipophilic. The lipophilicity is a major determining factor in a compound's absorption and distribution in the body (Parthasarathi *et al.*, 2012). A more lipophilic compound will have low aqueous solubility, compromising bioavailability.

The Kamlet - Taft solvent parameters (Taft *et al.*, 1985) and Reichardt's parameters (Reichardt, 2005) used in LSER, the wavenumbers of electronic

absorption spectra, the polarizability function $f(n)$ and the polarity function $f(\varepsilon)$ are given in Table 3.

Table 3
UV-Vis Absorption Maxima and the Solvent Parameters for AZ1 and AZ2

No.	Solvent	$f(\varepsilon)$	$f(n)$	α	β	$\nu_{\text{exp.}} [\text{cm}^{-1}]$	
						AZ1	AZ2
1	n-Hexane	0.229	0.229	0	0	27660	28990
2	Cyclohexane	0.254	0.257	0	0	27510	28900
3	CCl4	0.292	0.273	0	0	27210	28610
4	Toluene	0.315	0.292	0	0.11	26670	28330
5	Chloroform	0.212	0.267	0.2	0.1	26880	28610
6	DCM	0.729	0.258	0.13	0.1	26700	28600
7	DCE	0.758	0.266	0	0	26600	28450
8	1-Pentanol	0.825	0.248	0.7	0.92	25910	28450
9	1-Butanol	0.849	0.237	0.84	0.84	25770	28560
10	2-Butanone	0.854	0.230	0.06	0.48	25640	28170
11	Acetone	0.870	0.220	0.08	0.48	25810	28250
12	Ethanol	0.890	0.221	0.86	0.75	25840	28570
13	Methanol	0.914	0.203	0.98	0.66	25910	28860
14	DMF	0.925	0.259	0	0.69	25030	27860
15	DM Acetamide	0.924	0.263	0	0.76	24720	27890
16	DMSO	0.939	0.282	0	0.76	24750	27780

Solvatochromic studies offer information about the strenght of the dispersive interactions by the spectral shifts measured in non-polar solutions.

The electronic absorption band of 4-aminoazobenzene (AZ1) and 4-acetamidoazobenzene (AZ2) in solvents having different physicochemical parameters has been recorded and the wavenumber in its maximum is listed in Table 3.

The equation which give the wavenumbers in the maximum of the band is:

$$\nu_{\text{calc.}} = \nu_0 + C_1 f(\varepsilon) + C_2 f(n) + C_3 \beta + C_4 \alpha \quad (5)$$

A multilinear dependence of the type Eq. (5) was used to describe the spectral shifts of two azobenzene derivatives measured in the solvents from Table 4.

Table 4
Characteristics of Eq. for Binary Solutions of Two Azobenzene Derivatives

Molecule	$\tilde{\nu}_0, [\text{cm}^{-1}]$	C_1	C_2	C_3	C_4	R
AZ1	29054.677	-1468.633	-5371.207	803.794	-1805.136	0.9233
AZ2	30160.118	-512.885	-5041.258	671.349	-682.334	0.9081

A good correlation was obtained as one can see in Table 4.

The calculated wavenumber in the maximum of the UV-Vis of 4-aminoazobenzene and 4-acetamidoazobenzene using equation mentioned above are plotted versus the corresponding experimental values in Fig. 9 a) AZ1 and b) AZ2.

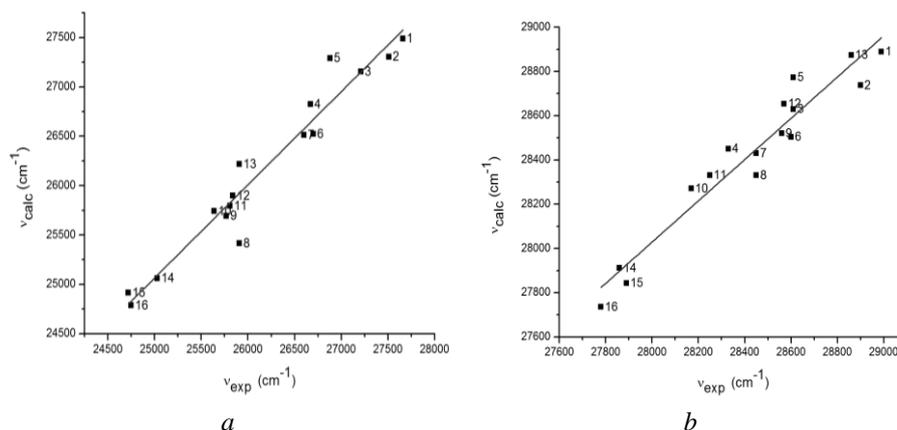


Fig. 9 – $\nu_{calc.}$ [cm^{-1}] versus $\nu_{exp.}$ [cm^{-1}]: a) AZ1; b) AZ2.

There is a good linear correlation between the calculated and experimental values of the wavenumbers in the maximum of the visible band of 4-aminoazobenzene Fig. 9a ($R = 0.94$, $SD = 218.13$) and for 4-acetamidoazobenzene Fig. 9b ($R = 0.93$, $SD = 94.70$).

4. Conclusions

Different solvents with different electric permittivities, refractive indices and Kamlet–Taft and Reichardt constants were used in this study, for to characterize the intermolecular interactions in binary solutions of two azobenzene derivatives.

The separation of the supply of the universal and specific interactions was made based on the correlation coefficients from the equations describing the solvatochromic effect (Rusu *et al.*, 2008).

Dispersive forces are predominant in non-polar solvents containing spectrally active molecules (Gheorghies *et al.*, 2008).

A series of azobenzene derivatives in the ground electronic state were analyzed from quantum-mechanical point of view and their electro-optical parameters were computed, and it demonstrate that the study compounds are lipophilic.

The results of this study could be used when azo-benzene derivatives are precursors in various chemical reactions.

REFERENCES

- Airinei A., Rusu E., Dorohoi D.O., *Solvent Influence on the Electronic Absorption Spectra of Some Azoaromatic Compounds*, Spectrosc. Lett., **34**, 1, 65-74 (2001).
- Gallegos S.A., *Molecular Quantum Similarities in QSAR: Applications in Computer – Aided Molecular Design*, Ph.D. Thesis, University of Girona, 2004.
- Gheorghieș C., Gheorghieș L., Dorohoi D.O., *Solvent Influence on Some Complexes Realized by Hydrogen Bond*, Journal of Molecular Structure, **887**, 122-127 (2008).
- Fleming I., *Frontier Orbitals and Organic Chemical Reactions*, John Wiley and Sons, New York, 1976.
- Karukstis K.K., Litz J.P., Garber M.B., Angell L.M., Korir K.G., *A Spectral Approach to Determine Location and Orientation of Azo Dyes within Surfactant Aggregates*, Spectrochimica Acta Part A, **75**, 1354-1361 (2010).
- Khanmohammadi H., Rezaeian Kh., Amini M.M., Weng Ng.S., *Azo-Azomethine Dyes with N, O, S Donor Set of Atoms and their Ni(II) Complexes: Synthesis, Characterization and Spectral Properties*, Dyes Pigments, **98**, 3, 557 (2013).
- Kinali-Demirci S., Demirci S., Kurt M., *Synthesis, Structure Characterization and Antimicrobial Evaluation of 4-(Substituted Phenylazo)-3,5-Diacetamido-1H-Pyrazoles*, Spectrochim. Acta Part A, **106**, 12 (2013).
- Koopmans T., *Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den Einzelnen Elektronen Eines Atoms*, Physica (Elsevier), **1**, 1-6, 104-113 (1934).
- Parthasarathi R., Subramanian V., Roy D.R., Chattaraj P.K., *Bioorganic & Medicinal Chemistry*, In *Advanced Methods and Applications in Chemoinformatics: Research Progress and New Applications*, E.A. Castro, A.K. Haghi (Eds.) 2012.
- Reichardt C., *Solvents and Solvent Effects in Organic Chemistry*, VCH, New York, 2005.
- Ross W.C.J., Warwick G.P., *Reduction of Cytotoxic Azo Compounds by Hydrazine and by the Xanthine Oxidase–Xanthine System*, Nature, **176**, 298 (1955).
- Rusu E., Dorohoi D.O., Airinei A., *Solvatochromic Effects in Absorption Spectra of Some Azobenzene Compounds*, J. Mol. Struct., **887**, 1, 1-3, 216-219 (2008).
- Stewart J.J.P., *Optimization of Parameters for Semi-Empirical Methods I-Method*, Computational Chemistry, **10**, 2, 209 (1989).
- Taft R.W., Abboud J.L.M., Kamlet M.J., Abraham M.H., *Linear Solvation Energy Relations*, Journal of Solution Chemistry, **14**, 3, 153-186 (1985).
- www.hyper.com (HyperChem, Molecular Visualisation and Simulation Program Package, Hypercube, Gainesville, Fl, 32601).

ENERGII DE INTERACȚIUNE ÎN SOLUȚII A UNOR
COMPUȘI DE AZOBENZEN

(Rezumat)

Energiile de interacțiune dintre componentele dipolare ale unei soluții pot fi estimate în cadrul studiilor solvatocromice care permit separarea diverselor tipuri de interacțiuni prin aportul acestora la deplasările unor benzi electronice de absorbție, deplasări cauzate de modificarea naturii solvenților folosiți. În baza teoriei lichidelor simple, dependența deplasărilor spectrale de anumiți parametri macroscopici ai solvenților permit estimarea unor parametri microscopici din starea excitată a moleculelor spectral active.

