

SPECTRAL STUDY OF INTERMOLECULAR INTERACTIONS IN WATER- ETHANOL SOLUTIONS OF SOME CARBANION DISUBSTITUTED PYRIDINIUM YLIDS

Mihaela DULCESCU,^{a*} Cristina STAN^b and Dana Ortansa DOROHOI^a

^aFaculty of Physics, Al. I. Cuza University, 11 Carol I Blv., Iași, RO-700506, Roumania

^bFaculty of Applied Sciences, Politehnica University of Bucharest, 313 Spl. Independenței, RO-060042 Bucharest, Roumania

Received December 16, 2009

Some complexes realized by hydrogen bonds between carbanion disubstituted pyridinium ylids and water and/or ethanol were investigated by spectral methods. In water-ethanol mixtures with various molar concentrations, the spectral shifts are due to the global influence of the binary solvent on the hydrogen bonded complexes of the type water-ylid or ethanol-ylid. The modification of the slopes of the linear dependence between the visible absorption band wavenumber in binary solvent and the empirical polarities defined by Kosower proves that the hydrogen bonds are unstable, so concentration and/or thermal motion could determine the substitution of one type of complex such as water-pyridinium ylid by another one, such as ethanol-ylid

INTRODUCTION

In the ground electronic state, ylids¹ are zwitterionic organic compounds with separated opposite charges on atoms or atomic groups. The positive atom of ylids can be Nitrogen, Phosphorous, or Sulfur. Nitrogen ylids²⁻⁷ are reactive species studied not as vastly as Phosphorous or Sulfur ylids, due to their relative instability. When Nitrogen belongs to a heterocycle, N-ylids are named cycloimmonium ylids.⁷⁻¹¹

In pyridinium ylids, Nitrogen atom from heterocycle belongs to a pyridine ring covalently bound to the carbanion, which can be⁷ monosubstituted (Fig.1a) or disubstituted (Fig.1b).

The corresponding compounds are named carbanion mono- and di-substituted pyridinium ylids. They can be generated via decarboxylation process in neutral conditions⁸⁻⁹ and react with electrolytes.

The pyridinium-ylid aromatic nitrogen is near sp^2 hybridization in all circumstances, while for the carbanion, sp^2 (planar pyridinium ylids) and sp^3 (non-planar pyridinium ylids) are the two limits of hybridization.¹²⁻¹⁶ An important difference regarding the chemical behavior of the planar and non-planar pyridinium ylids has been revealed by theoretical and experimental studies.^{17,18}



Fig. 1 – Carbanion cycloimmonium ylids: monosubstituted (a) and disubstituted (b).

* Corresponding author: mihaeladulcescu@yahoo.com

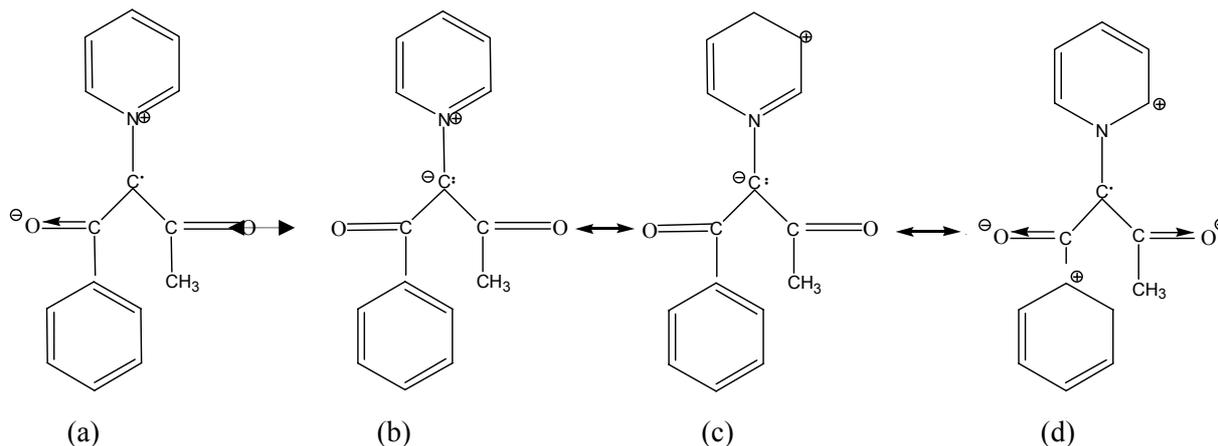


Fig. 2 – Possible stages of the delocalization of positive and negative charges in a pyridinium ylid molecule.

The pyridinium ylids stability is assured by the delocalization of the positive charge on the aromatic ring or of the negative charge on the ylid carbanion (Fig. 2). The coulombian attraction between the opposite separated charges has also a great role in the pyridinium stability. The nature of the substitutes covalently bonded to the ylid carbanion is an essential factor determining the stability of this dipolar structure.¹⁵ The carbanion disubstituted pyridinium ylids are characterized by a high degree of electronic charge delocalization (Fig.2a-d) along the carbanion substitutes, which is a function of the substitutes' electronegativity. The positive charge can be also delocalized on the heterocycle¹⁰ (Figs.2b and 2d). Consequently, the carbanion disubstituted pyridinium ylids, having strong electron acceptor substitutes, are more stable than the monosubstituted ones. The stability of the carbanion disubstituted pyridinium ylids is also determined by the resonance interactions between the molecular parts on which the opposite charges are delocalized.¹²

Pyridinium ylids are dipolar compounds.⁷ The carbanion disubstituted pyridinium ylids are more polar than the monosubstituted ones.¹¹ The electric dipole moment of pyridinium ylids increases when electronegativity of the carbanion substitutes increases.

Pyridinium ylids are nucleophilic reagents.^{7-10,19-21} The carbanion monosubstituted pyridinium ylids have larger nucleophilic character than the carbanion disubstituted ones.⁷ Pyridinium ylids act as 1,3 dipoles in [2+2] or [3+3] cycloaddition reactions with symmetrical or un-symmetrical dipolarophiles giving new heterocycle structures. The cycloaddition are made in situ, so, knowledge about intermolecular interactions in pyridinium ylids are very useful in organic chemistry.

Cycloimmonium ylids can be used in optical-switching and imaging techniques.²² They are of a great importance, due to their potential pharmacological effects.¹⁹⁻²¹ So, pyridazinium ylids can act as cholesterol acyltransferase inhibitors^{23,24} and pyridinium ylids have applications as acid-basic indicators,^{7-9,12} in cycloaddition reactions and in pharmacy as initial substances.

Pyridinium ylids have specific IR,⁷ visible^{7-16, 25-34} or NMR³⁵ spectra. The specificity of the electronic absorption spectra of pyridinium ylids and their changes induced by the solvent action are important in establishing some structural features of these compounds. Consequently, cycloimmonium ylids, particularly pyridinium ylids become exciting subjects from the point of view of spectral analysis applied to estimation of the structural and electro-optical molecular parameters.

The electronic absorption spectra of the dipolar compounds, such as the pyridinium ylids, can be used in estimation the solvent polarity,^{11,16,25} or the solvent electric permittivity,³⁶ due to the hypsochromic shift induced in this kind of spectra by the orientation interactions. In the last time, the pyridinium ylids were used to establish the composition of the first solvation sphere in ternary solutions, due to the great sensitivity to the solvent action of their visible electronic absorption band.³⁶

Having in view the potential pharmacological action of cycloimmonium ylids, it is very important to establish the nature of their interactions with hydrophilic biological solvents (such as water and ethanol).

A spectral study of pyridinium ylids in water, ethanol and in their mixtures of various molar concentrations is made in this paper in order to characterize the complexes formed by hydrogen bonds between the ylid molecules and the hydroxyl solvents.

EXPERIMENTAL

Double distilled water and spectrally grade ethanol were used in order to achieve the binary solvent. The binary solvent was deduced volumetrically and then the molar fraction of ethanol x_e was computed.

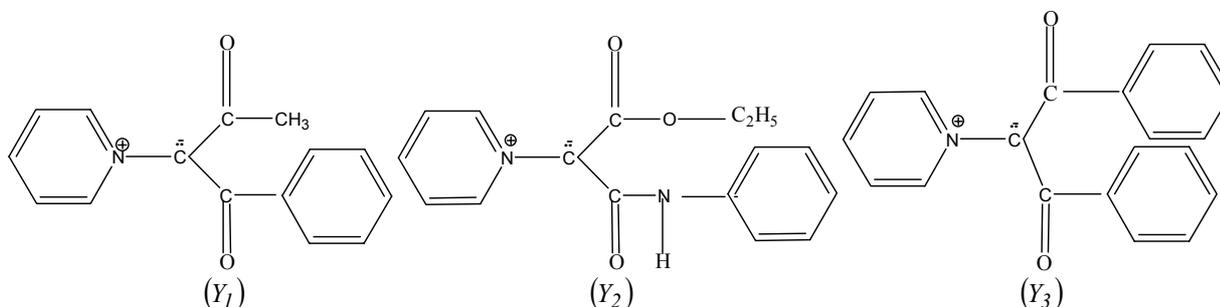


Fig. 3 – Chemical structure of the studied pyridinium ylids.

Pyridinium ylids were prepared after known procedures⁷⁻¹⁰ and their structure was confirmed by NMR and FT-IR spectra.

FT-IR spectroscopy permits to evidence the correlations between the vibrations of different structural groups and the modifications induced by temperature (as a perturbation factor)³⁷ and also to characterize the delocalization degree of the electronic charge on the carbanion substitutes.^{12,31} From the IR spectra of the studied pyridinium ylids it results that the IR band corresponding to the stretching vibrations of the -C=O group attached to the carbanion shifts to the smaller frequencies when the electronegativity of the carbanion substitutes increases, proving a larger delocalization of the negative charge on the ylid carbanion.³¹

The visible spectra of the pyridinium ylids were recorded at a Specord UV VIS Carl Zeiss Jena spectrophotometer with data acquisition system. The wavenumber in the maximum of the electronic charge transfer absorption band (expressed in cm^{-1}) was measured in binary solvent water-ethanol with a variable content in ethanol. The empirical polarities, defined by Kosower¹⁶ as being the energy in the maximum of the visible electronic absorption band (due to electronic charge transfer) of the complex 1-ethyl-4-carbomethoxy pyridinium iodide, are used in this paper. These parameters can be estimated by using the formula (1).

$$E_{\max} (\text{kcal/mol}) = 2.8584 \cdot 10^{-3} \cdot \bar{\nu} (\text{cm}^{-1}) \quad (1)$$

The empirical polarity¹⁶ $Z(\text{kcal/mol})$ and the electric permittivity of the binary solvent water-ethanol were previously measured.^{11,16}

The ylid concentration in the ternary solutions was of about 10^{-4}mol/L . A Mettler MDB-5 balance ($\pm 10^{-5} \text{g}$) was used for mass determination.

RESULTS AND DISCUSSION

The visible radiations determine an intramolecular charge transfer (ICT)⁷⁻¹⁶ from the carbanion to the heterocycle. This process decreases the dipole moment of pyridinium ylid molecules. The mechanism of the intramolecular charge transfer is suggested in Fig. 4.

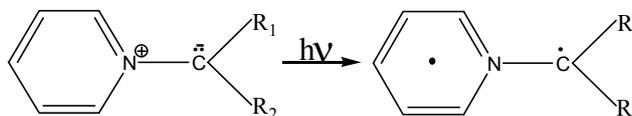


Fig. 4 – Intramolecular charge transfer in pyridinium ylid molecule.

The electronic absorption spectra (Fig.5a) of pyridinium ylids have UV bands due to $\pi \rightarrow \pi^*$ electronic transitions^{7,8,12} and a weak charge transfer band of the type $n \rightarrow \pi^*$ in the visible range. The electronic absorption spectrum of anilido-carboxy-pyridinium ylid (Y₂) in ethanol is given in Fig.5a. In mixtures water-ethanol, the visible ICT band shifts to blue (Fig.5b) when the molar fraction of ethanol diminishes in the binary solvent.

The intramolecular charge transfer is responsible for the visible absorption band appearance in the solutions of pyridinium ylids. This band has low intensity, shifts to blue when the ylid molecule is passed from a nonpolar to a polar solvent and disappears in acid solutions due to the blockage of the electron lone pair of the ylid carbanion.⁷⁻¹⁶

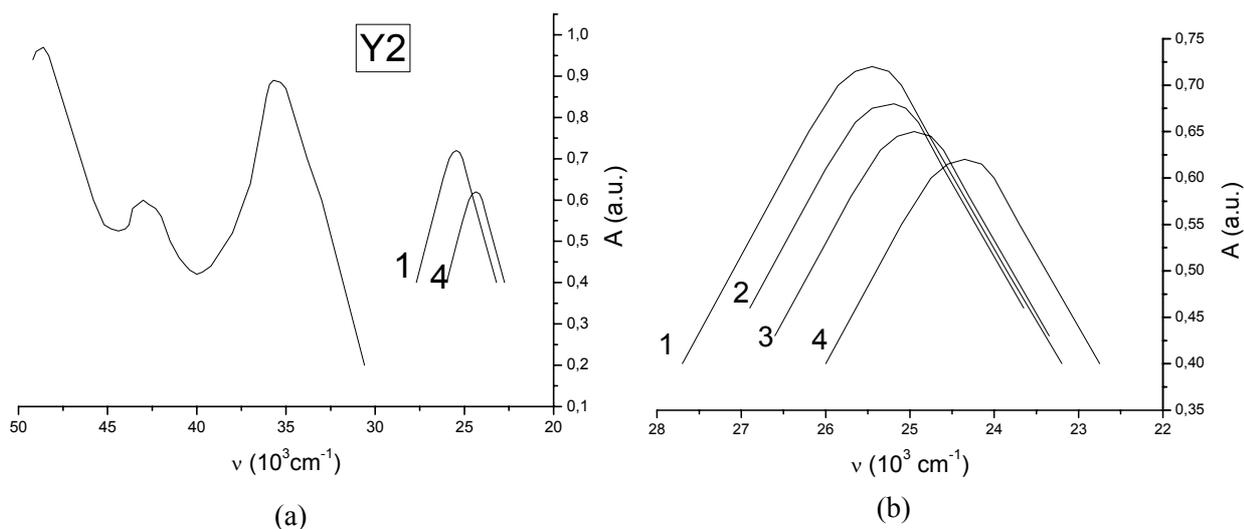


Fig. 5 – (a) Electronic absorption spectrum of anilido-carboxy pyridinium methylid (Y_2) in ethanol; (b) Visible ICT band of anilido-carboxy pyridinium methylid (Y_2) in: 1-water; 2-binary solvent $x_e = 0.32$; 3-binary solvent $x_e = 0.78$; 4-ethanol.

Pyridinium ylids can participate to universal interactions^{35,36} which are predominant in the aprotic solutions. In the protic solutions, pyridinium ylids additionally participate to specific interactions such as hydrogen bonds.^{12,14,26} The strength of the specific interactions in pyridinium ylids solutions is determined by the degree of the delocalization of the electronic charges on the two partners participating to this interaction.^{25,26}

The dependences between the energy in the maximum of ICT visible band, E_{max} (kcal/mol), and the empirical polarities of the binary protic solvent, Z (kcal/mol) are given in Fig.6. These dependences can be linearly fitted using the equation:

$$E_{max}(\text{kcal/mol}) = E_{max}^0 + mZ(\text{kcal/mol}) \quad (2)$$

In equation (2), the slope of the line indicates the sensitivity of the pyridinium ylid to the solvent polarity and E_{max}^0 approximates the energy in the maximum of the visible band registered in gaseous state of the ylid. A change in the slope of the lines (2) is observed in Figs. 6, proving a change in the sensitivity of the spectrally active molecules to the solvent action when the content in ethanol of the binary protic solvent reaches a certain value. As it results from Fig.6, the dependences (2) have different slopes for $Z < 82$ kcal/mol and for $Z > 82$ kcal/mol.

The parameters of the lines (2) are given in Table 1 in which the regression coefficient R , the

standard deviation SD , the number N of the points used in statistics and the precision P are also given.

The modification in the slopes of the lines (2) could be induced by changes in the composition of the solvation spheres, or by the replacement of pyridinium ylid-ethanol complex by pyridinium ylid-water complex, when the concentration of the binary solvent varies. Having in view the aspect of the intramolecular charge transfer visible bands of the studied solutions, one can decide that the changes in the slopes of the lines (2) are induced by the changes in the nature of the complexes formed between the pyridinium ylids and the hydroxyl solvents molecules. In this context, in the solutions with high water concentrations, the pyridinium ylid-water complexes could be predominant, while in the solutions with a small concentration of water molecules, the complexes of the type pyridinium ylid-ethanol are more probable to be formed. The values of the slopes in equation (2) (see Table 1) indicate that the ethanol-pyridinium ylid complexes are more sensitive to the binary solvent action, compared to water-pyridinium ylid ones. The same conclusions were made²⁵ in the case of the spectral study of the ternary solutions carbanion monosubstituted pyridazinium ylids-water-ethanol.

From Table 1 one can observe that the slopes of the lines of the type (2) are smaller for the solutions with a high content in water. This change in the slopes can be an argument that proves the fact that the pyridinium ylid-ethanol complexes are more active in the orientation intermolecular

interaction than the pyridinium-water complexes. This fact was also demonstrated for the carbanion mono-substituted pyridazinium ylids.²⁵ In both classes of N-ylids (pyridinium and pyridazinium

ylids), the visible electronic absorption band becomes an indicator of the intermolecular interactions in which these compounds take part.

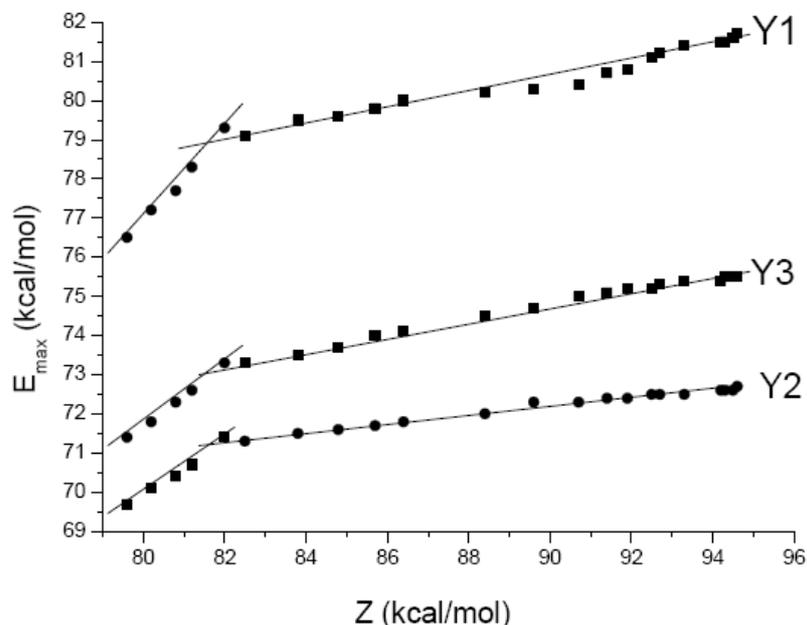


Fig. 6 – E_{\max} (kcal/mol) versus Z (kcal/mol) for the studied pyridinium ylids.

Table 1

Regression coefficients from equation (2) and their deviations, correlation coefficient – R, standard deviation-SD, number of points – N and precision – P.

PY	x_e	$E_{\max}^0 \pm \Delta E_{\max}^0$ (kcal/mol)	$m \pm \Delta m$	R	SD	N	P
Y1	$x_e > 0.78$	15.53 ± 4.37	1.156 ± 0.054	0.997	0.099	5	0.0002
	$x_e < 0.78$	62.61 ± 0.84	0.199 ± 0.009	0.984	0.152	17	0.0001
Y2	$x_e > 0.78$	14.46 ± 3.68	0.693 ± 0.045	0.993	0.084	5	0.0006
	$x_e < 0.78$	62.34 ± 0.32	0.109 ± 0.003	0.992	0.058	17	0.0001
Y3	$x_e > 0.78$	8.09 ± 1.82	0.795 ± 0.022	0.999	0.041	5	0.0001
	$x_e < 0.78$	57.99 ± 0.45	0.186 ± 0.005	0.995	0.081	17	0.0001

Unfortunately, the single study of the ternary solutions of the pyridinium ylids in binary protic solvent could not elucidate the structure and the all types of intermolecular interactions in which these compounds are engaged.

A comparative study of the spectral features in protic and non-protic solvent becomes interesting for these purposes.²⁶ Some theoretical and experimental studies²⁷ emphasized the statistical weights of the universal and specific interactions in the cycloimmonium ylids solutions.

Theoretical estimations of the geometry of the complexes realized by hydrogen bonds between

ylid molecules and the molecules of protic non-toxic solvents water and ethanol are of vital importance in elucidating the intermolecular interaction nature in ternary solutions.

CONCLUSIONS

Our spectral investigations show linear dependences between the energy in the maximum of the visible band of the studied pyridinium ylids in binary solvent water-ethanol and the solvent empirical polarities defined by Kosower. These

modifications prove the common origin of the pyridinium ylid intramolecular charge transfer visible band and of the intermolecular charge transfer absorption band of the standard complex 1-ethyl-4 carbomethoxy - pyridinium iodide.

The slope modification of the linear dependences becomes a signal for the changes in the nature of hydrogen bonded complexes formed between the pyridinium ylids and the protic solvents molecules. The ethanol-pyridinium ylid complexes are more active from the point of view of orientation interactions compared to the water-pyridinium ylid complexes.

REFERENCES

1. A.W. Johnson, "Ylid Chemistry", Academic Press, Inc, New York, 1966.
2. F. Dumitraşcu, E. Georgescu, F. Georgescu, P. Filip, B. Miu and D. G. Dumitrescu, *Rev. Roum. Chim.*, **2008**, *53*, 589-594
3. K.W. Ratts and A.N. Rao, *J. Org. Chem.*, **1968**, *33*, 70-76.
4. A.L. Katritzky, *Tetrahedron*, **1980**, *36*, 679-672.
5. S.S. Lin, J.M. Wang, X. Wang and C.Y. Li, *Chinese Chem. Lett.*, **2003**, *14*, 111 - 114.
6. N.S. Prostakov, A.P. Krapivko, A.T. Soldatenkov, A.A. Savina and I. Romero, *Him. Get. Soed.*, **1979**, *3*, 384 - 389.
7. I. Zugrăvescu and M. Petrovanu, "N-Ylid Chemistry", Pergamon Press, New-York, London, 1976.
8. C.A. Henrick, E. Ritchie and W.C. Taylor, *Austr. J. Chem.*, **1967**, *20*, 2467-2477.
9. W. G. Phillips and K.W. Ratt, *J. Org. Chem.*, **1970**, *35*, 6, 3144-49.
10. D. Dorohoi, M. Cotlet and I. Mangalagiu, *Int. J. Chem. Kinetics*, **2002**, *34*, 613-619.
11. D. Dorohoi, G. Surpăţeanu and C. Mihul, *An. St. Univ. Al. I. Cuza, Iaşi*, **1974**, *XX*, 59-65.
12. D. Dorohoi, *J. Mol. Struct.*, **2004**, *704*, 31-43.
13. G. Surpăţeanu, D. O. Dorohoi and I. Zugrăvescu, *An. St. Univ. Al. I. Cuza, Iaşi*, 1975, *XXI*, 89-96.
14. L.V. Gheorghieş and D.O. Dorohoi, *Rom. J. Phys.*, **2008**, *53*, 71-77.
15. I. Olariu, M. Caprosu, G. Grosu, M. Ungureanu and M. Petrovanu, *Roum. Biotech. Lett.*, **1999**, *4*, 365-368.
16. R.M. Kosower and B.G. Ramsey, *J. Amer. Chem. Soc.*, **1959**, *81*, 856-859.
17. P. Kolar and M. Tisler, *Adv. in Heterocycle Chemistry*, **2000**, *75*, 167-241.
18. Y. Kazarazi and G. Surpăţeanu, *Heterocycles*, **1999**, *51*, 863-925.
19. M.E. Scott, Y. Bethuel and M. Lautens, *J. Am. Chem. Soc.*, **2007**, *129*, 1482- 1484.
20. G.N. Zbancioc, M.D. Caprosu and C.C. Moldoveanu, *Archivoc*, **2005**, *10*, 89-198.
21. V. Melnig, I. Humelnicu and D.O. Dorohoi, *Intern. J. Chem. Kinetics*, **2008**, *40*, 230-239.
22. H. Meier, T. Lifka, P. Seus, A. Oehlhof and S. Hillmann, *Tetrahedron*, **2008**, *64*, 10754-10760.
23. M. P. Giovannoni, V. Dal Piaz and B. M. Kwon, *J. of Medical Chemistry*, **2001**, *44*, 4292-4295.
24. A. Gelain, *J. Heterocyclic Chem.*, **2005**, *42*, 395-400.
25. M. Dulcescu and D.O. Dorohoi, *U.P.B. Sci. Bull. Series A*, **2009**, *71*, 87 - 96.
26. D. Dorohoi, D. Creangă and G. Surpăţeanu, *An. St. Univ. Al. I. Cuza, Iaşi*, **1980**, *XXVII*, 59-63.
27. D. Dorohoi, *J. Mol. Struct.*, **2006**, *86*, 792-794.
28. V. Pop, D. Dorohoi and V. Holban, *Spectrochim. Acta*, **1994**, *50A*, 2281-2289.
29. R. G. Makitra and Y. N. Pirig, *Ukrainskii Khim. Zhurn.*, **1988**, *54*, 747-751.
30. M. Petrovanu, C. Anton, D. Dorohoi, M. Caprosu and I. Fulger, *Rev. Roum. Chim*, **1993**, *38*, 759-764.
31. D. Dorohoi and H. D. Partenie, *J. Mol. Struct.*, **1993**, *293*, 129-133.
32. D. Dorohoi and V. Holban, *J. Mol. Struct.*, **1993**, *293*, 133-136.
33. D. Dorohoi, D. H. Partenie, L. Chiran and C. Anton, *J. Chim. Phys. Chim. Phys. Biol.*, **1994**, *91*, 419-431.
34. S. Dima, R. Creţu and M. M. Dima, *Rev. Chim. (Bucureşti)*, **2007**, *58*, 1016-1018.
35. N. Melniciuc Puica, V. Barboiu, S. Filoti and D.O. Dorohoi, *Spectrosc. Lett.*, **2004**, *37*, 457-467.
36. D. O. Dorohoi, M. Avădanei and M. Postolache, *JOAM-Rapid Comm.*, **2008**, *2*, 511-515.
37. C. Stan, C.P. Cristescu, F. Severcan and D. O. Dorohoi, *Rev. Roum. Chim.*, **2004**, *49*, 777-782.