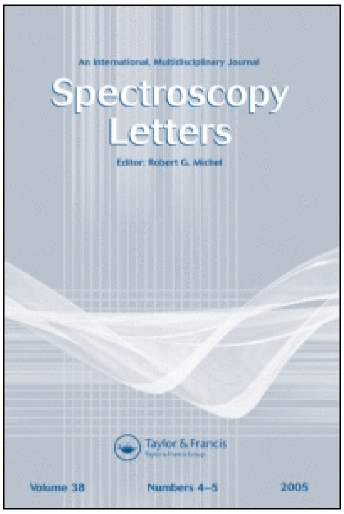

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Reactivity of Some 1(*N*)-[(*para*-R_2)-Phenacyl]-4(*N*)-[(*para*-R_1)-phenyl]-1,2,4-triazolium-methylides by UV-VIS, IR, and NMR Spectra and Molecular Modeling

Nicoleta Melniciuc-Puică[a]; Virgil Bărboiu[b]; Şerban Filoti[c]; Dana-Ortansa Dorohoi[c]
[a] Faculty of Theology, "Al. I. Cuza" University, Iaşi, Romania [b] "P. Poni" Institute of Macromolecular Chemistry, Iaşi, Romania [c] Faculty of Physics, "Al. I. Cuza" University, Iaşi, Romania

To cite this Article Melniciuc-Puică, Nicoleta , Bărboiu, Virgil , Filoti, Şerban and Dorohoi, Dana-Ortansa(2004) 'Reactivity of Some 1(*N*)-[(*para*-R_2)-Phenacyl]-4(*N*)-[(*para*-R_1)-phenyl]-1,2,4-triazolium-methylides by UV-VIS, IR, and NMR Spectra and Molecular Modeling', Spectroscopy Letters, 37: 5, 457 — 467

To link to this Article: DOI: 10.1081/SL-120039702

URL: http://dx.doi.org/10.1081/SL-120039702

SPECTROSCOPY LETTERS
Vol. 37, No. 5, pp. 457–467, 2004

Reactivity of Some 1(*N*)-[(*para*-R_2)-Phenacyl]–4(*N*)-[(*para*-R_1)-phenyl]-1,2,4-triazolium-methylides by UV-VIS, IR, and NMR Spectra and Molecular Modeling

Nicoleta Melniciuc-Puică,[1] Virgil Bărboiu,[3]
Şerban Filoti,[2] and Dana-Ortansa Dorohoi[2],*

[1]Faculty of Theology and [2]Faculty of Physics,
"Al. I. Cuza" University, Iaşi, Romania
[3]"P. Poni" Institute of Macromolecular Chemistry, Iaşi, Romania

ABSTRACT

The results obtained in molecular modeling achieved for some carbanion mono-substituted and di-substituted 1(*N*)-[(*para*-R_2)-phenacyl]–4(*N*)-[(*para*-R_1)-phenyl]-1,2,4-triazolium-methylides and the information from the NMR, IR, and UV-VIS spectra were used to do a qualitative estimation of the stability and the reactivity of these compounds. The molecular electric dipole moments were theoretically and experimentally estimated.

Key Words: 1,2,4-Triazolium methylides; UV-VIS; IR and ^{1}H NMR; Molecular modeling by AM1; Dipole moments.

---

*Correspondence: Dana-Ortansa Dorohoi, Faculty of Physics, "Al. I. Cuza" University, 11 Carol I Bd., 700506 Iaşi, Romania; E-mail: ddorohoi@uaic.ro.

DOI: 10.1081/SL-120039702
0038-7010 (Print); 1532-2289 (Online)

www.dekker.com

INTRODUCTION

The cycloimmonium ylides[1,2] are substances of a great interest from both the theoretical and practical points of view. The 1,2,4-triazolium methylides are stable, colored cycloimmonium ylides[3–9] with specific properties induced by the presence of three nitrogen atoms in the heterocycle.

Some carbanion mono- and di-substituted 1,2,4-triazolium ylides were subjected to a modeling procedure by Surpăţeanu and co-workers,[5,6] establishing the most and the least stable conformers. A comparison between the theoretical results in the 1,2,4-triazolium ylides modeling and the experimental data is of the great interest in this field.

Previous researchers[7–9] showed the possibility of obtaining a series of 1,2,4-triazolium ylides by the "salt method." Some mono-substituted carbanion cycloimmonium ylides were subjected to molecular modeling based on the library of CAChe programs.[10] The optimization of molecular geometries, potential energies, and rotation barriers around the ylide bond $N^+–C^-$ was performed by multiconformational analysis (MM2 with the improved parameters method) and by rotational analysis $N^+–C^-$ (MM2 with the improved parameters method and Austin method 1 AM1). The algorithm of the CAChe program package consists of accomplishing all possible rotations of the hole molecular system around all bonds that allow rotation, simultaneously with the discovery of molecular conformers with a low as possible steric energy (more stable) for every given situation.

For instance, the chemical shifts corresponding to the heterocycle protons, measured by ^{1}H NMR spectra[11] can be indicators of charge density, offering information on the ylide stability and reactivity. The visible intramolecular charge transfer (ICT) band from the electronic absorption spectra is also very sensitive to the structure of the ylides.[12,13]

This paper deals with a comparative study of reactivity, information from UV-VIS, IR, and NMR spectra and the results obtained by molecular modeling of some 1(*N*)-[(*para*-R_2)-phenacyl]–4(*N*)-[(*para*-R_1)-phenyl]-1,2,4-triazolium-methylides.

The molecular electric dipole moments were experimentally estimated by methods proposed in Refs.[14,15] in order to check the accuracy of the molecular modeling by AM1 and PM3.

EXPERIMENTAL

The studied 1,2,4-triazolium ylides, with the structures T_j, $j = 1–9$, from Fig. 1 and the substituents from Table 1, were prepared from the corresponding salts and purified as previously described.[7–9] The purity was

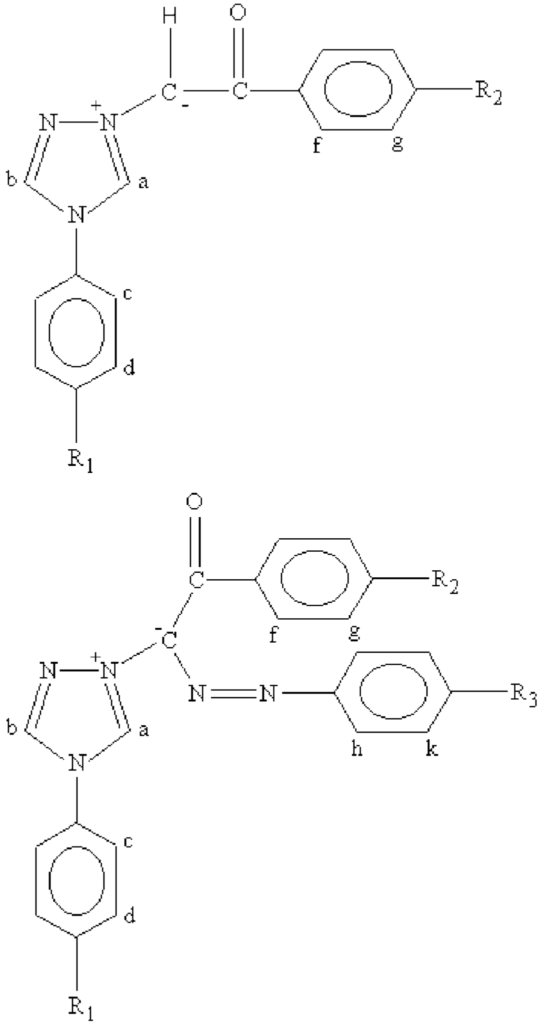

Figure 1. Structure of the studied 1,2,4-triazolium ylides.

checked by elemental analysis (C, H, N) and the structure confirmed by spectroscopic (IR, ^{1}H NMR) studies.

^{1}H NMR spectra, at 400 MHz and 20°C, were recorded with a Bruker spectrometer. A spectrophotometer, Specord UV-VIS, was used to obtain the electronic absorption spectra in benzene solutions. IR spectra were recorded with a Specord NIR 71 Carl Zeiss Jena spectrophotometer in KI

Table 1. Substituents of the 1,2,4-triazolium ylides.

Ylides	T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_8	T_9
R_1	H	H	H	CH_3	CH_3	CH_3	H	H	H
R_2	H	Cl	NO_2	H	Cl	NO_2	H	Cl	NO_2
R_3	—	—	—	—	—	—	SO_3H	SO_3H	SO_3H

pellets. DRS spectra in MgO pellets were recorded with a VSU-2P spectrophotometer and computed as described in Ref.[16].

The solubility of 1,2,4-triazolium ylides in non-polar and non-polarizable solvents is very small. This is the reason that benzene was chosen in order to determine their dipole moments. With this end of view[14,15] the following parameters were measured: (1) the dielectric constant [using a Waine Kerr Autobalance Universal Bridge B-641 (300 MHz) coupled with a Telmes TR-9701 dielectric cell for liquids, thermostated with U-10 Ultra Thermostat 0.2°C precision]; (2) the refractive indices (with a RPL Carl Zeiss immersion refractometer of 10^{-5} precision, thermostated at 25°C with the same thermostat used for ε determination); and (3) the densities of benzene solutions (with a 25 mL picnometer, using Mettler MDB-5 balance 10^{-5} g). Solutions of 1,2,4-triazolium ylides in benzene with concentrations 10^{-3}–10^{-4} M were used. Spectral grade benzene was treated with sodium to eliminate the water traces. The picnometer was initially standardized with distilled water. Precision in the determination of the dielectric constant was estimated to be 4%. Precision in the dipole moment determination by the DK-metric method can be considered to be about 6%, due to the high polarizability of the benzene.

RESULTS

MM2, the most general method for molecular mechanics calculation, mainly developed for organic molecules, was used for molecular geometry optimization, and the self-consistent field (SCF) AM1 for electronic properties.[10] Using the SCF method RMF spin pairing was selected. Hyperchem^{TM} (release 3 for Windows) Molecular Modeling System, Hypercube, Inc. was used.

The geometry of all studied 1,2,4-triazolium ylides has been estimated for the most stable conformers of each molecule, whose electronic energy reached a minimum value in the rotational analysis around the ylidic bond. Figure 2 presents the results regarding the geometry of the most

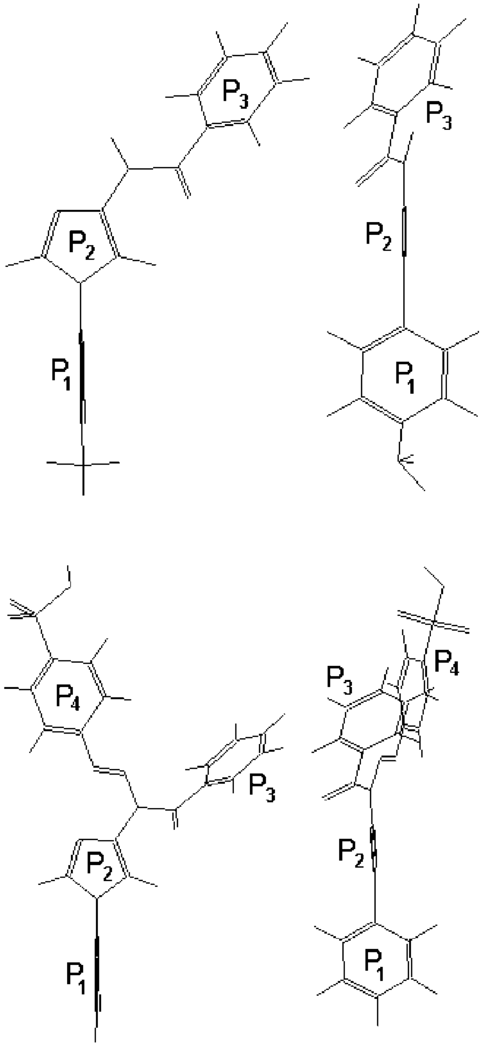

Figure 2. Geometry of T_4 and T_7 1,2,4-triazolium ylides.

stable conformers of T_4 and T_7 1,2,4-triazolium ylides. Figure 2 indicates that the benzene ring directly bonded to the triazolium ring is contained in a plane P_1 perpendicular to the plane P_2 of triazolium ring. The orientation of these planes is the same for all the 1,2,4-triazolium ylides that were studied.

Table 2 lists the charges on the carbon atoms from the positions a, b, f, g for the carbanion mono-substituted 1,2,4-triazolium ylides and a, b, f, g, h, k for the carbanion di-substituted ones, and the chemical shifts of ^{1}H NMR signals δ_i ($i =$ a, b, f, g, h, k) measured in ppm for the adjacent protons of these atoms.

Table 3 contains the total energy of the molecules E_T (kcal mol^{-1}) computed in AM1—the length of the ylidic bond, the wave number $\nu_{C=O}$ at the maximum of the vibrational IR band of the carboxylic group, the wave number ν_{VIS} at the maximum of the visible ICT band, and the wave number ν_{DRS} in the DRS visible band. Finally in this table are also listed the dipolar moments theoretically and experimentally estimated.

Table 4 lists the energies of the frontier orbitals (E_{HOMO} and E_{LUMO}), the charge on the carbanion and the coefficients of the carbanion orbitals from the frontier molecular orbitals.

DISCUSSION

The measured parameters (chemical shifts from ^{1}H NMR spectra, the wave numbers in IR, the electronic absorption spectra and DRS, dipole moments) are in good agreement with the computed values by the AM1 method.[9,10] Therefore, the experimental values determined using the DK-metric method[15] are comparable both with those theoretically obtained for the studied structures T_j, $j = 1-9$, and with those obtained for similar structures. Also, the chemical shifts of the ^{1}H NMR signals are directly dependent on the charges at the adjacent carbons (Table 2). As it results from Table 3 and Fig. 3, in the series of 1,2,4-triazolium ylides with a common heterocycle and one of the carbanion substituent variable, there are linear dependencies between the total molecular energies E_T, computed by AM1 and the dipole moments, and experimentally determined by DK-metric method at infinite dilution.

The interatomic distances and the angles between the bonds obtained by the AM1 method are in good agreement with those obtained by x-ray diffraction for the molecules with a similar structures.[17,18]

Data from Table 4 show that the total charge on the ylidic carbanion of the carbanion mono-substituted triazolium ylides is greater than those of di-substituted triazolium ylides.

The chemical reactivity of 1,2,4-triazolium ylides can be estimated from the values of HOMO and LUMO energies, from the total charges on the atoms, and from the atomic orbital coefficient corresponding to the molecular frontier orbitals (Table 4).

Table 2. Chemical shifts of ^{1}H NMR signals (ppm) and the computed by AM1 charges on the carbon atoms bonded to the corresponding protons.

	a		b		f		g		h		k	
Ylides	δ (ppm)	Q (e)	δ (ppm)	Q (e)	δ (ppm)	Q (e)	δ (ppm)	Q (e)	δ (ppm)	Q (e)	δ (ppm)	Q (e)
T_1	10.85	−0.6952	9.91	−0.2924	7.19	−0.0450	7.50	−0.1297				
T_2	10.90	−0.6742	9.93	−0.2937	8.15	−0.0500	7.65	−0.1250				
T_3	11.12	−0.6714	10.04	−0.2914	8.32	−0.0862	7.97	−0.0347				
T_4	10.92	−0.6782	10.03	−0.3025	7.20	−0.0595	7.58	−0.1229				
T_5	10.87	−0.6774	9.90	−0.3013	7.15	−0.0504	7.53	−0.1257				
T_6	11.46	−0.6755	10.50	−0.2998	7.82	−0.0865	7.91	−0.0353				
T_7	11.14	−0.6287	9.69	−0.2982	7.85	−0.0535	7.29	−0.1244	7.80	−0.1259	7.80	0.0767
T_8	11.27	−0.6311	9.72	−0.2953	8.01	−0.0495	8.16	−0.1217	7.90	−0.1255	7.90	0.0775
T_9	11.67	−0.6285	9.90	−0.2920	8.13	−0.0825	8.26	−0.0363	7.93	−0.1205	7.98	0.0799

Table 3. Total energy computed by AMI; the length of the ylidic bond; the wave numbers measured in IR, the visible electronic absorption and DRS spectra and the computed and experimentally determined dipole moments for the di-substituted ylides.

Ylides	E_T (kcal mol^{-1}) AM1	$N^+–C^-$ (Å)	$\nu_{C=O}$ (cm^{-1})	ν_{VIS} (cm^{-1})	ν_{DRS} (cm^{-1})	μ (D) AM1	μ (D) exp.
T_1	−66180.17	1.4110	1,530	25,460	25,790	7.31	7.00
T_2	−73140.91	1.4126	1,535	25,980	26,160	9.06	8.20
T_3	−83047.73	1.4117	1,536	26,410	26,710	13.78	12.31
T_4	−69397.90	1.4123	1,550	26,460	26,510	10.01	9.62
T_5	−76349.44	1.4121	1,540	26,490	26,800	11.01	10.87
T_6	−86257.47	1.4120	1,560	26,410	27,010	15.52	14.10
T_7	−116033.02	1.4175	1,560	25,120	25,400	14.41	12.10
T_8	−122984.65	1.4171	1,555	25,340	25,700	14.86	12.36
T_9	−132891.32	1.4176	1,550	26,560	26,970	17.71	14.23

The statistical reactivity has been evaluated both from the substrate energies and the wave functions obtained in AM1.[9,19] So, from Table 4 the results are that:

1. All atomic orbital coefficients of carbanion for HOMO orbitals have high absolute values in the case of carbanion mono-substituted

Table 4. Data characterizing the reactivity of the studied 1,2,4-triazolium ylides.

	Energy of the frontier orbitals (kcal mol^{-1})			Total charge on the ylidic carbanion, see Ref.[3]	Coefficients of carbanion orbitals from the frontier molecular orbitals, see Ref.[3]	
Ylides	E_{HOMO}	E_{LUMO}	ΔE		C_{HOMO}	C_{LUMO}
T_1	−8.2800	+2.2199	−10.499	−0.2928	+0.7018	+0.1008
T_2	−8.2095	+2.1904	−10.399	−0.2931	+0.7016	+0.1001
T_3	−8.1943	+2.2064	−10.401	−0.2613	+0.7021	+0.1018
T_4	−8.4423	+1.3894	−9.832	−0.2694	+0.7064	−0.0314
T_5	−8.2794	+2.2235	−10.503	−0.2916	+0.7023	+0.1024
T_6	−8.4534	+1.3701	−9.824	−0.2688	+0.7073	+0.0239
T_7	−8.6536	+2.4723	−11.036	−0.2424	−0.6213	+0.2831
T_8	−8.5537	+2.4633	−11.017	−0.2501	+0.5231	+0.3004
T_9	−8.6253	+2.3110	−10.936	−0.2564	−0.6002	+0.2831

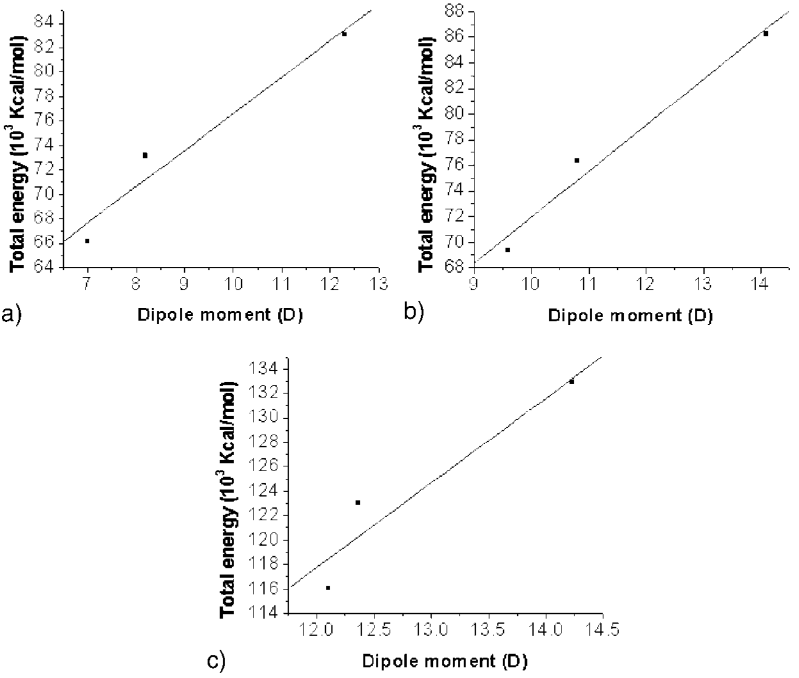

Figure 3. The dependence E_T vs. experimentally determined dipole moments: (a) T_1–T_3; (b) T_4–T_6; and (c) T_7–T_9.

ylides. The corresponding values for the same orbital coefficients in the case of carbanion di-substituted ylides are smaller, some of them being negative.

2. The total charge on the carbanion is negative. The likely result is that the carbanion of all ylides T_1–T_9 must be susceptible to reactions with electrophilic agents. The reactivity of carbanion mono-substituted 1,2,4-triazolium ylides must be higher compared with that of the carbanion di-substituted ones, as $\Delta E = E_{LUMO} - E_{HOMO}$ values demonstrate.
3. The stability increases by substituting the hydrogen atom of the carbanion by an electronegative substituent, which is passing from the carbanion mono-substituted to di-substituted ones.

There are good concordances between theoretical results on the molecular structure estimated by the AM1 method and the experimentally obtained data.

CONCLUSIONS

The data regarding the atomic charges on the carbanion, the atomic coefficient of molecular frontier orbitals and the total molecular energies correlated with the experimentally determined dipole moment values, and offer information about the stability and reactivity of 1,2,4-triazolium ylides. The higher the negative charge delocalization on the carbanion substituents, the higher the dipole moment value and the ylid becomes more stable.

The stability of the carbanion di-substituted 1,2,4-triazolium ylides is higher than those of the carbanion mono-substituted ones.

The high values of the negative charge computed for the carbanion indicate the susceptibility of 1,2,4-triazolium ylides to reaction with the electrophilic agents.

REFERENCES

1. Zugrăvescu, I.; and Petrovanu, M. *N-Ylid Chemistry*; McGraw Hill: London, New York, 1976.
2. Couture, A.; Lablache-Combier, A.; Grandclaudon, P.; Surpăţeanu, G. Study and characterization of tautomeric triazolium ylides. Heterocycles **1990**, *31*, 2111.
3. Surpăţeanu, G.; Yasser Karzazi. Structure and reactivity of cycloimmonium ylides. Heterocycles **1999**, *51* (4), 863.
4. Surpăţeanu, G.; Lablache Combier, A.; Grandclaudon, P.; Couture, A.; Mouchel, B. Synthesis and characterization of tautomeric triazolium ylides. Rev. Roum. Chim. **1993**, *38*, 671.
5. Surpăţeanu, G.; Lungu, N.C.; Avarvarei, N.; Lablache Combier, A.; Grandclaudon, P.; Couture, A. Characterization of tautomeric equilibrium of triazolium ylides by NMR spectroscopy. J. Chim. Phys. **1994**, *91*, 1648.
6. Surpăţeanu, G.G.; Vergoten, G.; Surpăţeanu, G. A comparative study by AMI and PM3 ab initio HF/3-21G methods and the structure and the reactivity of monosubstituted carbanion 1,2,4-triazolium ylides. J. Mol. Struct. **2000**, *526*, 143.
7. Surpăţeanu, G.; Caea, N.; Sufleţel, L.; Grandclaudon, P. Synthesis and characterization of new azatriazolium ylides. Rev. Roum. Chim. **1995**, *40* (6), 133.
8. Melniciuc-Puică, N. Synthesis of Some Polar Structure Auxiliaries Used in Leather Technology; Al.I. Cuza University of Iaşi, 1998; Ph.D. Thesis.

9. Surpăţeanu, G.; Melniciuc-Puică, N.; Lungu, N.C. *Molecular Modelling of Some Monosubstituted Cycloimmonium Ylides*; Analele Univ. “Al.I.Cuza,” Iaşi, s.Chimie; 1999; Vol. T.VII, 293.
10. CAChe User Guide, Version 3.0, Tektronics Company CAChe Scientific Inc., Oxford Molecular Group, 1997.
11. Dorohoi, D.; Caproşu, M.; Mangalagiu, I. Spectral study of some carbanion monosubstituted pyridazinium ylides. J. Soc. Alger. Chim. **1998**, *8* (2), 213.
12. (a) Dorohoi, D.; Holban, V. Intermolecular interactions in solutions of pyridazinium ylids. J. Mol. Struct. **1993**, *293*, 133; (b) Dorohoi, D.; Partenie, H. The spectroscopy of the cycloimmonium ylides. J. Mol. Struct. **1993**, *293*, 129.
13. Pop, V.; Dorohoi, D.; Holban, V. Molecular interactions in binary solutions of 4-amonophthalimide and 3-*p*-cumyl-pyridazinium acetyl-benzoyl-methylid. Spectrochim. Acta 50A **1994**, *14*, 2281.
14. Halvrstadt, I.F.; Kumler, W.D. Solvent polarization error and its elimination in calculating dipole moments. J. Am. Chem. Soc. **1942**, *64*, 2988.
15. Dorohoi, D.; Surpăţeanu, G.; Gheorghies, L. A spectral method to determine some molecular parameters of cycloimmonium ylides. Balkan Phys. Lett. **1998**, *6* (3), 198.
16. Dorohoi, D.; Partenie, H.; Chiran, L.; Anton, C. About the electronic absorption spectra (EAS) and the electronic diffusion spectra (EDS) of some pyridazinium-ylides. J. Chim. Phys., Phys. Chim. et Biol. **1994**, *91*, 419.
17. Abarca, B.; Ballestros, R.; Mojarrad, F.; Metni, M.R.; Garcia Granda, S.; Perez-Carreno, E.; Jones, G. Triazolopyridines Part II, ylides derived from 2-acylmethyl-triazolopyridinium salts. Tetrahedron **1991**, *47*, 5277.
18. Karzazi, Y.; Vergoten, G.; Surpăţeanu, G. Structure of dicyano-pyridinium methylide and amidocyano-pyridinium methylide using ab initio and semi-empirical methods. J. Mol. Struct. **1997**, *435*, 35.
19. Surpăţeanu, G.; Melniciuc-Puică, N.; Lungu, N.C. *Molecular Modelling of Some Disubstituted Cycloimmonium Ylides*; Analele Univ. “Al.I.Cuza”, Iaşi, s.Chimie; 1999; Vol. T.VII, 303.

Received September 12, 2003
Accepted April 19, 2004