Available online at www.scholarsresearchlibrary.com

Scholars Research Library

Archives of Physics Research, 2014, 5 (3):25-30
(http://scholarsresearchlibrary.com/archive.html)

Scholars Research Library
ISSN : 0976-0970
CODEN (USA): APRRC7

Study of azoxy-based liquid crystals (*p*-Azoxyanisole, *p*-Azoxyphenetole, Ethyl-*p*-Azoxybenzoate, ethyl-*p*-Azoxycinnamate and *n*-octyl-*p*-Azoxycinnamate) based on bond properties

Gayasuddin Khan*, Rajendra Prasad Tewari and Alok Shukla

*Department of Physics, Vimla – Vikram P.G. College, Pachperwa, Balrampur, (U.P.) INDIA
Department of Physics, Maharani Lal Kunwari Post Graduate College, Balrampur,(U.P.) INDIA.*

ABSTRACT

The electronic structure of some of azoxybenzene-based liquid crystals belonging to nematicclass: p-azoxyanisole, p-azoxyphenetole, ethyl-p-azoxybenzoate, ethyl-p-azoxycinnamate and n-octyl-pazoxycinnamate have been studied by computational method. The DFT based calculation of bond length, bond order and bond angle were performed with CAChe software. The study shows that replacement of –OCH3 group of RC by –OC2H5, –COOC2H5, –CH=CH–COOC2H5 and –CH=CH–COOC8H17 groups formed p-azoxyphenetole, ethyl-p-azoxybenzoate, ethyl-p-azoxycinnamate and n-octyl-p-azoxycinnamate, respectively and replacement of –OCH3 group of RC by –OC2H5, –COOC2H5, –CH=CH–COOC2H5 and –CH=CH–COOC8H17 groups show bond angles between N1-N2-C9 and C3-N1-N2 mostly remain intact in these compounds and a slight deviation is due to steric effects of substituting groups. Thus, results of computational calculations provide valuable information related to crystographic structure of the compounds.

Keywords: Azoxy-based liquid crystals, Partial atomic charges, Austin model-1, parametric model 3, parametric model 5 and density functional theory.

INTRODUCTION

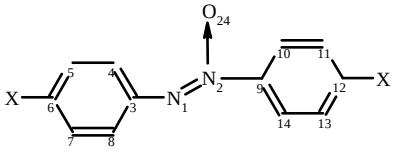
p-Azoxyanisole (PAA) is well known compound and its crystographic structure was established in 1970 [1, 2]. Presently, a number of azoxy based liquid crystals are well known [3, 4]. Some of azoxy-based liquid crystals belonging to nematic class are *p*-azoxyanisole, *p*-azoxyphenetole, ethyl-*p*-azoxybenzoate, ethyl-*p*-azoxycinnamate and *n*-octyl-*p*-azoxycinnamate. Crystographic structure of these compound could not be performed for want of necessary requirements. The computational chemistry [5] and availability of software have made it possible to obtained such informations about a molecule which were earlier possible only by crystographic study. The importance of bond length and bond angle in describing the nature of binding in a compound has recently been emphazized [6, 7]. We in this chapter present a study on bond length and bond angle of above compounds.

MATERIALS AND METHODS

The compounds, which are study material of this chapter, are listed in Table-1. For present study the three dimensional modeling and geometry optimization of all the compounds have been done in DGauss using the DFT B88-PW91 GGA functional with the DZVP basis sets [8, 9]. The application of DFT has given a new concept to

chemical system. This concept focuses on the one electron density function instead of wave function [10]. The DFT based calculation of bond length, bond order and bond angle were performed with CAChe software [11]. The optimized structures of compounds 1 to 5 are shown in figure 1 to 5.

Table 1. List of compounds

Parent Skeleton	X	Compd. No.
	$-OCH_3$	(1)
	$-OC_2H_5$	(2)
	$-COOC_2H_5$	(3)
	$-CH=CH-COOC_2H_5$	(4)
	$-CH=CH-COOC_8H_{17}$	(5)

RESULTS AND DISCUSSION

If *p*-azoxyanisole is treated as reference compound (RC) then the study shows that replacement of $-OCH_3$ group of RC by $-OC_2H_5$, $-COOC_2H_5$, $-CH=CH-COOC_2H_5$ and $-CH=CH-COOC_8H_{17}$ groups formed *p*-azoxyphenetole (fig.2), ethyl-*p*-azoxybenzoate (fig.3), ethyl-*p*-azoxycinnamate (fig.4) and *n*-octyl-*p*-azoxycinnamate (fig.5), respectively. These compounds are listed in Table-1. The first stage of the study is confined to the measurement of various bond length and bond angles of PAA (fig.1) followed by the same measurements of the *p*-azoxyphenetole, ethyl-*p*-azoxybenzoate, ethyl-*p*-azoxycinnamate and *n*-octyl-*p*-azoxycinnamate.

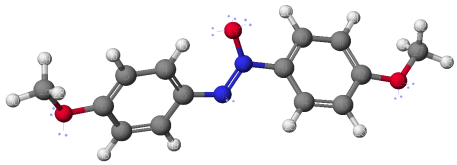


Figure 1: *p*-Azoxyanisole

Table 2. Selected bond distances (Å) and angles (˚) with esd's in parenthes

Bond distances			
N1-N2	1.302(1)	C10-C11	1.401(11)
N1-C3	1.399(2)	C11-C12	1.410(12)
C3-C4	1.422(3)	C12-C13	1.415(13)
C4-C5	1.401(4)	C13-C14	1.394(14)
C5-C6	1.409(5)	C14-C9	1.408(15)
C6-C7	1.415(6)	C6-O17*	1.373(18)
C7-C8	1.389(7)	C12-O22*	1.372(23)
C8-C3	1.427(8)	N2-O24	1.278(25)
N2-C9	1.459(9)	O17-C26*	1.438(27)
C9-C10	1.401(10)	O22-C27*	1.438(28)
Bond angles			
C6-O17-C26	117.4	N1-N2-C9	115.9
C3-N1-N2	124.7	C12-O22-C27	117.8

**indicates the bond length related to $-OCH_3$ group*

3.1. *p*-Azoxyanisole: PAA is an organic compound. In a solid state, it appears as a white powder, but when heated it forms a liquid crystal. As one of the first known and most readily prepared liquid crystals, PAA has been played an important role in the development of liquid crystal displays [12, 13]. A molecule of PAA is composed of thirty three atoms, out of which there are fourteen carbon, fourteen hydrogen, three oxygen and two nitrogen atoms. The computational result of bond length and bond angles of various bonds between N—N, N—C, N—O, C—O and C—C of PAA are included in Table-2, which indicates that the N_1—N_2 bond length is 1.302 Å. N—C bonds have length 1.399 Å and 1.459 Å in N_1—C_3 and N_2—C_9, respectively. The bond N_2—O_{24} has a length of 1.278 Å. C—O bonds have length in the range 1.37 Å in two bonds (C_6—O_{17} and C_{12}—O_{22}) and 1.438 Å in two cases (O_{17}—C_{26} and O_{22}—C_{27}). C—C bonds have length in the range 1.3 Å in two cases, 1.4 Å in five cases, 1.41 Å three cases and 1.42 in two cases. However, three is little differences in length in all the cases. The bond lengths of RC show deviation from the average covalent bond length of common bonds, N−N (1.47 Å); N=N (1.24 Å); N≡N (1.10 Å);

N−C (1.39 Å); N−O (1.36 Å); N=O (1.22 Å); C−C (1.54 Å); C=C (1.34 Å); $C=C_{aromatic}$ (1.34 Å) and C≡C (1.20 Å), due to resonance, electronegativity, hybridization and steric effect. The bond angles in PAA between C6-O17-C26, C3-N1-N2, N1-N2-C9 and C12-O22-C27 are 117.4˚, 124.7˚, 115.9˚ and 117.8˚, respectively. These show deviation from the bond angles as shown by Scridonesi (2005) 109˚47', 109˚47', 120˚ and 109˚47' [14]. This due to repulsion between non-bonded electrons, repulsion between atoms or groups attached to central atom.

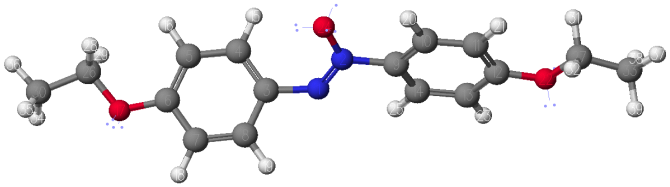


Figure 2: *p*-Azoxyphenetole

Table 3. Selected bond distances (Å) and angles (˚) with esd's in parenthes

Bond distances			
N1-N2	1.301(1)	C11-C12	1.409(12)
N1-C3	1.397(2)	C12-C13	1.415(13)
C3-C4	1.423(3)	C13-C14	1.393(14)
C4-C5	1.402(4)	C14-C9	1.409(15)
C5-C6	1.410(5)	C6-O17*	1.371(18)
C6-C7	1.414(6)	C12-O22*	1.370(23)
C7-C8	1.387(7)	N2-O24	1.278(25)
C8-C3	1.426(8)	O17-C26*	1.447(27)
N2-C9	1.460(9)	O22-C27*	1.447(28)
C9-C10	1.400(10)	C26-C30*	1.523(31)
C10-C11	1.401(11)	C27-C33*	1.523(34)
Bond angles			
C6-O17-C26	117.1	N1-N2-C9	115.9
C3-N1-N2	124.7	C12-O22-C27	117.5

**indicates the bond length related to -OC_2H_5 group*

3.2. *p*-Azoxyphenetole: On substitution of $–OCH_3$ group by $–OC_2H_5$ group, *p*-azoxyanisole is converted into *p*-azoxyphenetole. A molecule of *p*-azoxyphenetole is composed of thirty nine atoms, out of which there are sixteen carbon, eighteen hydrogen, three oxygen and two nitrogen atoms. The computational result of bond length and bond angles of various bonds between N—N, N—C, N—O, C—O and C—C of *p*-azoxyphenetole are included in Table-3, which indicates that the N_1—N_2 bond length is 1.301 Å. N—C bonds have length 1.397 Å and 1.46 Å in N_1—C_3 and N_2—C_9, respectively. The bond N_2—O_{24} has a length of 1.278 Å. C—O bonds have length in the range 1.37 Å in two bonds (C_6—O_{17} and C_{12}—O_{22}) and 1.447 Å in two cases (O_{17}—C_{26} and O_{22}—C_{27}). C—C bonds have length in the range 1.3 Å in two cases, 1.4 Å in five cases, 1.41 Å three cases and 1.5 Å in two cases. However, three is little differences in length in all the cases. The bond angles in *p*-azoxyphenetole between C6-O17-C26, C3-N1-N2, N1-N2-C9 and C12-O22-C27 are 117.4˚, 124.7˚, 115.9˚ and 117.8˚, respectively.

3.3. Ethyl-*p*-azoxybenzoate: On substitution of $–OCH_3$ group by $–COOC_2H_5$ group, *p*-azoxyanisole is converted into ethyl-*p*-azoxybenzoate. A molecule of ethyl-*p*-azoxybenzoate is composed of forty three atoms, out of which there are eighteen carbon, eighteen hydrogen, five oxygen and two nitrogen atoms. The computational result of bond length and bond angles of various bonds between N—N, N—C, N—O, C—O and C—C of ethyl-*p*-azoxybenzoate are included in Table-4, which indicates that the N_1—N_2 bond length is 1.3 Å. N—C bonds have length 1.4 Å and 1.468 Å in N_1—C_3 and N_2—C_9, respectively. The bond N_2—O_{24} has a length of 1.272 Å. C—O bonds have length in the range 1.2 Å in two bonds, 1.3 Å in two bonds and 1.46 Å in two cases. C—C bonds have length in the range 1.39 Å in four cases, 1.4 Å in six cases, 1.423 Å two cases and 1.5 Å in four cases. However, three is little differences in length in all the cases. The bond angles in ethyl-*p*-azoxybenzoate between C6-C17-O26, C3-N1-N2, N1-N2-C9 and C12-C22-O27 are 123.5˚, 124.8˚, 115.7˚ and 123.3˚, respectively.

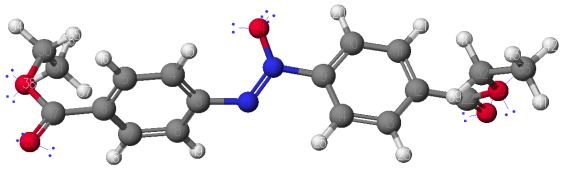


Figure 3: Ethyl-*p*-azoxybenzoate

Table 4. Selected bond distances (Å) and angles (˚) with esd's in parenthes

Bond distances			
N1-N2	1.300(1)	C13-C14	1.399(14)
N1-C3	1.400(2)	C14-C9	1.405(15)
C3-C4	1.423(3)	C6-C17*	1.507(18)
C4-C5	1.399(4)	C12-C22*	1.512(23)
C5-C6	1.409(5)	N2-O24	1.272(25)
C6-C7	1.411(6)	C17-O26*	1.224(27)
C7-C8	1.391(7)	C22-O27*	1.222(28)
C8-C3	1.423(8)	C17-O28*	1.370(29)
N2-C9	1.468(9)	C22-O29*	1.366(30)
C9-C10	1.402(10)	O28-C30*	1.465(31)
C10-C11	1.399(11)	C30-C31*	1.526(32)
C11-C12	1.407(12)	O29-C32*	1.468(33)
C12-C13	1.409(13)	C32-C33*	1.523(34)
Bond angles			
C6-C17-O26	123.5	C3-N1-N2	124.8
N1-N2-C9	115.7	C12-C22-O27	123.3

**indicates the bond length related to –$COOC_2H_5$ group*

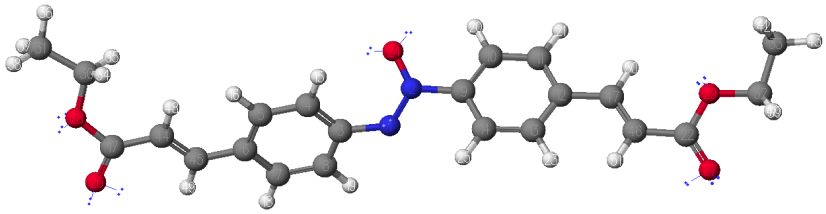


Figure 4: Ethyl-*p*-azoxycinnamate

Table 5. Selected bond distances (Å) and angles (˚) with esd's in parenthes

Bond distances			
N1-N2	1.304(1)	C17-C44*	1.491(18)
N1-C3	1.395(2)	C22-C46*	1.481(23)
C3-C4	1.428(3)	N2-O24	1.272(25)
C4-C5	1.394(4)	C17-O26*	1.228(27)
C5-C6	1.419(5)	C22-O27*	1.232(28)
C6-C7	1.419(6)	C17-O28*	1.377(29)
C7-C8	1.389(7)	C22-O29*	1.371(30)
C8-C3	1.423(8)	O28-C30*	1.457(31)
N2-C9	1.462(9)	C30-C31*	1.524(32)
C9-C10	1.402(10)	O29-C32*	1.464(33)
C10-C11	1.398(11)	C32-C33*	1.524(34)
C11-C12	1.415(12)	C44-C45*	1.359(45)
C12-C13	1.418(13)	C45-C6*	1.463(46)
C13-C14	1.393(14)	C46-C47*	1.357(47)
C14-C9	1.408(15)	C47-C12*	1.467(48)
Bond angles			
C6-C45-C44	122.6	C3-N1-N2	124.9
N1-N2-C9	115.7	C12-C47-C46	122.2

**indicates the bond length related to –CH=CH-$COOC_2H_5$ group*

3.4. Ethyl-*p*-azoxycinnamate: On substitution of –OCH_3 group by –CH=CH–$COOC_2H_5$ group, *p*-azoxyanisole is converted into ethyl-*p*-azoxycinnamate. A molecule of ethyl-*p*-azoxycinnamate is composed of fifty one atoms, out

of which there are twenty two carbon, twenty two hydrogen, five oxygen and two nitrogen atoms. The computational result of bond length and bond angles of various bonds between N—N, N—C, N—O, C—O and C—C of ethyl-*p*-azoxycinnamate are included in Table-5, which indicates that the N_1—N_2 bond length is 1.304 Å. N—C bonds have length 1.395 Å and 1.462 Å in N_1—C_3 and N_2—C_9, respectively. The bond N_2—O_{24} has a length of 1.272 Å. C—O bonds have length in the range 1.2 Å in two bonds, 1.3 Å in two bonds and 1.4 Å in two cases. C—C bonds have length in the range 1.3 Å in six cases, 1.4 Å in twelve cases and 1.5 Å in two cases. However, three is little differences in length in all the cases. The bond angles in ethyl-*p*-azoxycinnamate between C6-C45-C44, C3-N1-N2, N1-N2-C9 and C12-C47-C46 are 122.6˚, 124.9˚, 115.7˚ and 122.2˚, respectively.

3.5. *n*-Octyl-*p*-azoxycinnamate: On substitution of -OCH_3 group by –CH=CH–$COOC_8H_{17}$ group, *p*-azoxyanisole is converted into *n*-octyl-*p*-azoxycinnamate. A molecule of *n*-octyl-*p*-azoxycinnamate is composed of eighty seven atoms, out of which there are thirty four carbon, forty six hydrogen, five oxygen and two nitrogen atoms. The computational result of bond length and bond angles of various bonds between N—N, N—C, N—O, C—O and C—C of *n*-octyl-*p*-azoxycinnamate are included in Table-6, which indicates that the N_1—N_2 bond length is 1.306 Å. N—C bonds have length 1.395 Å and 1.46 Å in N_1—C_3 and N_2—C_9, respectively. The bond N_2—O_{24} has a length of 1.273 Å. C—O bonds have length in the range 1.2 Å in two bonds, 1.3 Å in two bonds and 1.4 Å in two cases. C—C bonds have length in the range 1.3 Å in six cases, 1.4 Å in twelve cases and 1.5 Å in fourteen cases. However, three is little differences in length in all the cases. The bond angles in *n*-octyl-*p*-azoxycinnamate between C6-C45-C14, C3-N1-N2, N1-N2-C9 and C12-C47-C46 are 126.9˚, 119.9˚, 114.8˚ and 126.1˚, respectively.

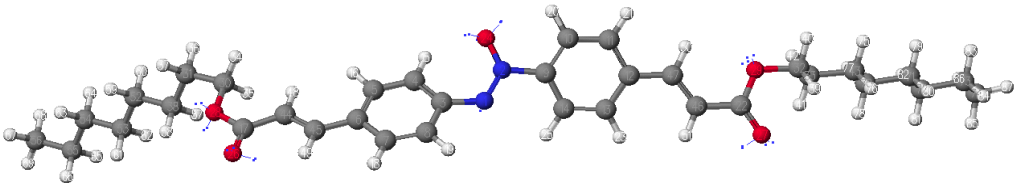


Figure 5: *n*-Octyl-*p*-azoxycinnamate

Table 6. Selected bond distances (Å) and angles (˚) with esd's in parenthes

Bond distances			
N1-N2	1.306(1)	C22-O29*	1.367(30)
N1-C3	1.395(2)	O28-C30*	1.459(31)
C3-C4	1.426(3)	C30-C31*	1.528(32)
C4-C5	1.390(4)	O29-C32*	1.465(33)
C5-C6	1.418(5)	C32-C33*	1.531(34)
C6-C7	1.419(6)	C31-C38*	1.539(39)
C7-C8	1.391(7)	C33-C43*	1.540(44)
C8-C3	1.422(8)	C44-C45*	1.358(45)
N2-C9	1.460(9)	C45-C6*	1.463(46)
C9-C10	1.402(10)	C46-C47*	1.358(47)
C10-C11	1.398(11)	C47-C12*	1.468(48)
C11-C12	1.417(12)	C38-C52*	1.538(53)
C12-C13	1.418(13)	C52-C53*	1.538(54)
C13-C14	1.391(14)	C53-C54*	1.538(55)
C14-C9	1.407(15)	C54-C55*	1.538(56)
C17-C44*	1.486(18)	C55-C56*	1.537(57)
C22-C46*	1.481(23)	C43-C70*	1.540(71)
N2-O24	1.273(25)	C70-C71*	1.539(72)
C17-O26*	1.228(27)	C71-C72*	1.539(73)
C22-O27*	1.233(28)	C72-C73*	1.540(74)
C17-O28*	1.377(29)	C73-C74*	1.538(75)
Bond angles			
C6-C45-C44	126.9	N1-N2-C9	114.8
C3-N1-N2	119.9	C12-C47-C46	126.1

**indicates the bond length related to –CH=CH-$COOC_8H_{17}$ group*

3.6. Effect of Substituting Group:

On replacement of –OCH_3 group of RC by –OC_2H_5, –$COOC_2H_5$, –CH=CH–$COOC_2H_5$ and –CH=CH–$COOC_8H_{17}$ groups formed *p*-azoxyphenetole, ethyl-*p*-azoxybenzoate, ethyl-*p*-azoxycinnamate and *n*-octyl-*p*-azoxycinnamate, respectively. The bond length of various bonds of the parent skeleton, Table-1, mostly remain intact in these

compounds and a slight deviation is due to steric effects of substituting groups. And the bond angles between N1-N2-C9 and C3-N1-N2 mostly remain intact in these compounds (except in compd. no. 5) and a slight deviation is due to steric effects of substituting groups. The comp. no. 5, *n*-octyl-*p*-azoxycinnamate, shows prominent deviation due to steric hindrance of bulky –CH=CH–$COOC_8H_{17}$ groups.

CONCLUSION

We have concluded following points from the above study:

1. The computational results of bond lengths of RC show deviation from the average covalent bond length of common bonds, which is due to resonance, electronegativity, hybridization and steric effect. On replacement of –OCH_3 group of RC by –OC_2H_5, –$COOC_2H_5$, –CH=CH–$COOC_2H_5$ and –CH=CH–$COOC_8H_{17}$ groups formed *p*-azoxyphenetole, ethyl-*p*-azoxybenzoate, ethyl-*p*-azoxycinnamate and *n*-octyl-*p*-azoxycinnamate, respectively. The bond length of various bonds of the parent skeleton, Table-1, mostly remain intact in these compounds and a slight deviation is due to steric effects of substituting groups.

2. The computational results of bond angles between C6-O17-C26 (117.1˚), C3-N1-N2 (124.7˚), N1-N2-C9 (115.9˚) and C12-O22-C27 (117.5 ˚) of RC show deviation from the bond angle as shown by Scridonesi. This due to repulsion between non-bonded electrons, repulsion between atoms or groups attached to central atom. On replacement of –OCH_3 group of RC by –OC_2H_5, –$COOC_2H_5$, –CH=CH–$COOC_2H_5$ and –CH=CH–$COOC_8H_{17}$ groups show bond angles between N1-N2-C9 and C3-N1-N2 mostly remain intact in these compounds (except in compd. no. 5) and a slight deviation is due to steric effects of substituting groups. The comp. no. 5, *n*-octyl-*p*-azoxycinnamate, shows prominent deviation due to steric hindrance of bulky –CH=CH–$COOC_8H_{17}$ groups.

3. Thus, results of computational calculations provide valuable information related to crystographic structure of the compounds.

5. Acknowledgement
This paper is dedicated to beloved brother Mr. Salil Singh “Titu”, Manager, Vimla – Vikram P.G. College, Pachperwa, Balrampur, 271206 (U.P.) INDIA

REFERENCES

[1] Krigbaum, W. R.; Chatani, Y.; Barber, P. G. *Acta Cryst.* **1970**, B26, 97.
[2] Carlisle, C. H.; Smith, C. H. *Acta Cryst.* **1971**, B27, 6.
[3] Konstantinov, I. I. *Journal de Physique* **1979**, 40, C3475.
[4] Gray, G. W., *Molecular Structure and the Properties of Liquid Crystals*, New York, Academic Press, London, **1962**.
[5] David, E.R. *Chem. Rev.* **2000**, 100, 351.
[6] Frenking, G.; Frohlich, N. *Chem. Rev.* **2000**, 100, 117.
[7] Singh, P. P.; Srivastava, V. B. L.; Singh, D. *Inorg. Chem.-An Indian J.* **2006**, 1, 32.
[8] Parr, R. G.; Yang, W. Density Functional Theory of Atoms and Molecules, Oxford University Press, New York, **1989**.
[9] Parr, R. G.; Donnelly, R. A.; Palke, W.E.; Levy, M. *J. Chem. Phys.* **1978**, 69, 3801.
[10] Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, B136, 864.
[11] www.CACheSoftware.com
[12] Shao, Y.; Zerda, T. W. *J. Phys. Chem. B.* **1998**, 102, 3387.
[13] Chandrasekhar, S. *Liquid Crystals* (2nd ed.). Cambridge: Cambridge University Press, **1992**. ISBN 0-521-41747-3.
[14] Scridonesi, V. C. Analele Universiţătii din Bucureşti – Chimie, Anul XIV (serie nouă), vol. I-II, pg. 407-415, **2005**