Journal of
NANOSTRUCTURES
JNS NANOSTRUCTURES
JNS.kashanu.ac.ir

Diels–Alder [4+2] Cycloadditions of C_{20} with Some Diene and 1,2-Dioxo Compounds: A Theoretical Study

Zahra Tavangar[a, b]

[a]*Institute of Nano Science and Nano Technology, University of Kashan, Kashan, I.R. Iran.*

[b]*Department of Physical Chemistry, Faculty of Chemistry, University of Kashan, I.R. Iran.*

Article history:
Received 1/11/2011
Accepted 25/1/2012
Published online 1/2/2012

Keywords:
Diels–Alder Cycloaddition
C_{20}
DFT
Diene
1,2-dioxo

**Corresponding author:*
E-mail address:
Z.Tavangar@kashanu.ac.ir
Phone: +98 361 5912366
Fax: +98 361 5912397

Abstract

Diels–Alder [2+4] cycloaddition products of the reaction between C_{20} and $C_4H_4X_2$ or $C_2O_2X_2$ (X = H, F, Cl, CH_3, NH_2, NO_2, and OH) were studied atB3LYP level of theory with 6-31G, 6-31G(d, p) and 6-311G(d, p) basis sets. The HOMO–LUMO gaps of Kohn–Sham orbitals for most of the adducts show evident increase compared with the gap value of C_{20}, suggestive of more stability in the adducts. The thermodynamic calculations indicate that the reaction of diene with C_{20} is exothermic and spontaneous. While, the addition of 1,2-dioxos to C_{20} can be thermodynamically improper when the 1,2-dioxo group consists of electronegative atoms.

2012 JNS All rights reserved

1.Introduction

The C_{20} cage, the smallest and truly unique member of the fullerene family, had been only a theoretical molecule until anion-photoelectron spectroscopy [1] and first-principle calculation [2] showed its existence in vapor phase. Also theoretical studies showed that the C_{20} cage can also form condensed phases in several dimensions and the most stable phase is a simple-cubic-like phase with a metallic property [3].

The C_{20} has been proposed as a possible intermediate to C_{60} or larger fullerenes [4].There has been considerable theoretical and experimental interest in the structure of the C_{20} [5-8].

The geometry of fullerenes obeys the isolated-pentagon rule, which states that the most stable fullerenes are those in which all pentagons located as far as possible from one another and are

www.SID.ir

surrounded by five hexagons [9]. However, it is impossible to satisfy this rule for the smallest possible fullerene, C_{20}, which contains only 12 pentagons. This implies that this fullerene should be highly reactive owing to the fusion of the strained 5-membered rings and somewhat different reaction behavior of the C_{20} cage is expected.

As the C_{20} cage would be one of the candidates for molecular devices, modification of the structural and electronic properties of C_{20} should be a subject of general interest to both experimentalists and theoreticians. Therefore, Functional fullerenes are expected to have potential applications in biology, materials and other fields. Then, an enormous effort has been dedicated to their chemical functionalization. Although a number of synthetic methodologies have been devised, cycloaddition reactions has been found to offer the most versatile routes for the functionalization of the C_{60} fullerene [10-14].

Despite the huge amount of work devoted to the preparation of fullerene cycloadducts, much less is known however about their chemical and thermal stability. The thermal stability of chemically modified fullerenes is a fundamental aspect in order to determine the best candidates to prepare functional fullerene-based materials able to withstand the ambient conditions to maintain their efficiency, thus preventing any further chemical or thermal degradation [15-17].

The adducts of the most stable fullerene C_{20} isomers with C_2H_2 and C_2H_4 have been studied by the B3LYP method [18] .The derivatives $C_{20}(C_2H_2)_n$ and $C_{20}(C_2H_4)_n$ (n = 1-3) exhibit remarkable aromaticity, while $C_{20}(C_2H_2)_3$ and $C_{20}(C_2H_2)_4$ have no spherical aromaticity.

Prior calculations using MP2 methods for smaller systems have shown that for carbon clusters the convergence of perturbation theory is slow, with reliability of the order of 50 kcal/mole [19].

In the present study, a theoretical investigation has been carried out on [2+4] cycloaddition reactions of $C_4H_4X_2$ and $C_2O_2X_2$ (X = H, F, Cl, CH_3, NH_2, NO_2, and OH) to C_{20} molecule.

$$C_{20}(g) + C_4H_4X_2(g) \rightarrow C_{24}H_2X_2(g) + H_2(g) \quad (1)$$

$$C_{20}(g) + C_2O_2X_2\ (g) \rightarrow C_{22}O_2X_2\ (g) \quad (2)$$

Figure 1 displays the ground-state geometries of $C_{24}H_2X_2$ and $C_{22}O_2X_2$ molecules. Relative stability and the reaction activity of the C_{20}toward the addition of a diene or 1,2-dioxo compounds have been studied.

2. Computational details

The computational procedures started with geometry optimization of an isolated molecule using DFT methods with popular hybrid exchange-correlation functional, B3LYP, with 6-31G, 6-31G(d, p) and 6-311G(d, p) basis sets. Also, the vibrational frequencies analysis were carried out at the same level to analyze the relative energies of the compounds and to assure that the final optimized structures give no imaginary frequencies. For all computations, GAUSSIAN 98 software package has been used [20].

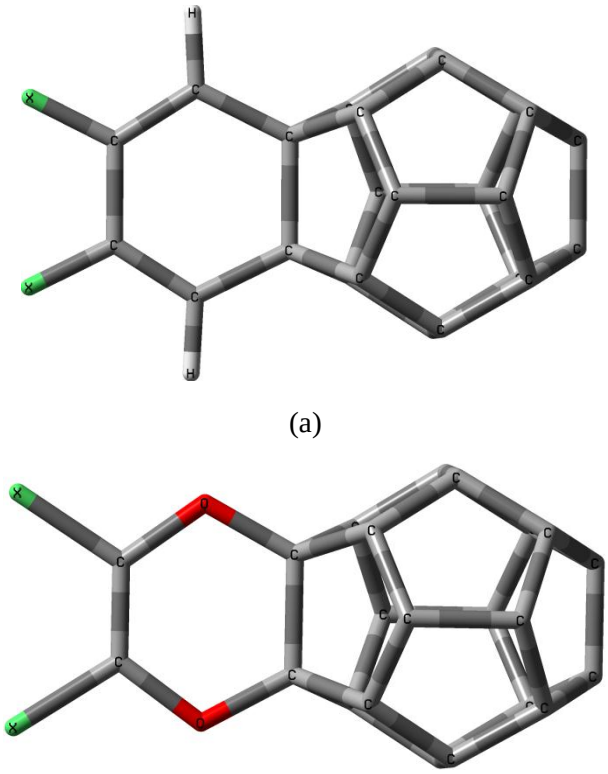
In order to have insight to their reactivity, the relevant frontier molecular orbitals were examined.

3. Results and discussion

All calculations conclude that the ground states of the C_{20} fullerene should have D2h structures. Optimization of the C_{20} fullerene at B3LYP/6-311G(d, p) level of theory shows that the C–C bond length varies from 1.402 to 1.518 Å.

Archive of SID

www.SID.ir



(a)

(b)

Figure 1. The structures of (a) $C_{24}H_2X_2$, (b) $C_{22}O_2X_2$

The electronic characteristics determining the reactivity of the compounds directly are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) maps and energies and their difference, the HOMO-LUMO gap abbreviated as HLG. Total Energy, thermal energy, zero point energy (ZPE), HLG and entropy of $C_{24}H_2X_2$ and $C_{22}O_2X_2$ using of B3LYP method with different Basis sets at 298 K are collected in Table 1.

The adducts of the C_{20} with $C_4H_4X_2$are named A1, A2, A3, A4, A5, A6 and A7 for X = H, CH_3, F, Cl, NH_2, OH and NO_2, respectively. Similarly, the adducts of the C_{20} with $C_2O_2X_2$ are named B1, B2, B3, B4, B5, B6 and B7 for X = H, CH_3, F, Cl, NH_2, OH and NO_2, respectively.

As can be seen from Table 1, addition of polarized basis functions affects all parameters. Furthermore, the following trends with basis set can be deduced for the entropy of each compound.

$$6-31G(\mathrm{d,p}) > 6-311G(\mathrm{d,p}) > 6-31G$$

The HOMO–LUMO gap is traditionally associated with chemical stability against electronic excitation; the larger gap corresponds to greater stability. The HOMO–LUMO gaps of Kohn–Sham orbitals calculated at B3LYP level for the adducts show evident increase compared to the gap value of C_{20}, 1.940 eV (except for B6 with 6-311G(d, p) and 6-31G basis sets and B5 with 6-31G basis set), suggestive of more stability in the adducts. The B6 structure optimized at the B3LYP/6-311G(d, p) level was found to be unstable with three imaginary frequencies. Analysis of the frequency of other compounds shows that they are stable without any imaginary frequency.

The graphical representations of the HOMO and LUMO orbitals of $C_{24}H_2X_2$ and $C_{22}O_2X_2$ at the level of B3LYP/6-311G(d, p) are shown in Figure 2. Figure 2 clearly illustrates the frontier orbital populations of these derivatives.

It is seen that the HOMO and LUMO maps in A-molecules are approximately equivalent and have distribution on the C_{20} cage while the HOMO orbitals of B molecules have different contribution of the C_{20} cage and the additive part. The HOMO orbitals mainly distribute on the additive part of B-molecules and imply that these sites are probably the most reactive sites.

In order to investigate the performance of reactions 1 and 2, the enthalpy and the Gibbs free energy for each reaction was calculated.

Archive of SID

www.SID.ir

Table 1. Total Energy, thermal energy, zero point energy and entropy of $C_{24}H_2X_2$ and $C_{22}O_2X_2$ using of B3LYP method with different Basis sets at 298 K

Mol.	Total Energy (hartree)	$E_{Thermal}$ (Kcal/mol)	ZPE (Kcal/mol)	S (cal/molK)	HLG (eV)	Mol.	Total Energy (hartree)	$E_{Thermal}$ (Kcal/mol)	ZPE (Kcal/mol)	S (cal/molK)	HLG (eV)
			6-31G						**6-31G**		
A1	-916.080	123.243	116.815	98.745	2.463	B1	-989.043	106.828	100.2593	103.697	2.561
A2	-994.698	160.475	152.068	112.725	2.471	B2	-1067.669	143.952	135.3336	115.298	2.514
A3	-1114.497	113.721	106.133	107.877	2.460	B3	-1187.449	97.299	89.7311	108.016	2.517
A4	-1835.220	112.404	104.345	113.077	2.449	B4	-1908.174	95.796	87.7331	113.445	2.512
A5	-1026.759	146.390	138.218	110.686	2.484	B5	-1099.723	129.574	121.1649	112.544	1.769
A6	-1066.455	129.417	121.523	109.213	2.476	B6	-1139.414	112.544	104.2987	112.033	1.924
A7	-1324.890	128.120	118.324	126.429	2.411	B7	-1397.764	110.287	100.5809	123.791	2.427
			6-31G(d,p)						**6-31G(d,p)**		
A1	-916.357	122.684	116.056	99.771	2.664	B1	-989.363	106.341	100.2321	96.352	2.767
A2	-994.999	159.620	151.006	113.817	2.667	B2	-1068.007	141.819	134.4155	105.230	2.449
A3	-1114.814	113.497	105.754	108.632	2.669	B3	-1187.814	97.771	90.1321	108.201	2.721
A4	-1835.538	112.108	103.907	113.709	2.653	B4	-1908.540	96.181	88.06756	113.390	2.713
A5	-1027.078	145.806	137.511	111.298	2.688	B5	-1100.084	129.762	121.4602	111.679	2.191
A6	-1066.796	129.577	121.481	110.298	2.686	B6	-1139.799	113.442	105.1998	111.501	2.161
A7	-1325.334	128.777	118.855	126.966	2.615	B7	-1398.236	111.504	101.8991	122.779	2.542
			6-311G(d,p)						**6-311G(d,p)**		
A1	-916.537	122.343	115.762	99.504	2.640	B1	-989.567	105.962	99.8890	96.159	2.746
A2	-995.193	159.030	150.444	113.720	2.642	B2	-1068.226	143.010	134.324	115.204	2.550
A3	-1115.059	113.180	105.497	108.297	2.642	B3	-1188.079	96.959	89.8178	103.961	2.449
A4	-1835.772	111.806	103.645	113.505	2.629	B4	-1908.797	95.854	87.7769	113.160	2.691
A5	-1027.287	145.395	137.136	111.108	2.661	B5	-1100.318	129.344	121.0713	111.514	2.106
A6	-1067.022	129.255	121.196	110.102	2.659	B6	-1140.042	111.397	104.1991	104.160	1.567
A7	-1325.627	128.389	118.501	126.854	2.596	B7	-1398.547	111.154	101.5991	122.458	2.430

The corresponding heat of reaction ΔH_{298} can be calculated using the following expression:

$$\Delta H_{298}=\Delta E+\Delta(PV)=\Delta E_0+\Delta ZPE+\Delta H_T+\Delta nRT \qquad (3)$$

where ΔE_0 is the change in total energy between the products and the reactants at 0 K, ΔZPE is the difference between the zero-point energies (ZPE) of the products and the reactants, ΔH_T is thermal correction from 0 to 298 K and $\Delta(PV)$ value is the PV work term which equals ΔnRT. $\Delta S_{r,298}$ and $\Delta G_{r,298}$ are entropy and Gibbs free energy difference between products and the reactants at 298 K.

Table 2 shows thermodynamic properties of reactions 1 and 2. The Calculated ΔH_{298} and ΔG_{298} at B3LYP level are negative for A1-A7 compounds which show that all reactions are exothermic and spontaneous. While The Calculated ΔH_{298} for B1-B7 is negative but the decrease of the entropy results a positive ΔG_{298} for some of B-molecules when X is an electron acceptor group. The results of table 2 indicate the important effect of the basis set on the calculation of thermodynamic properties So, ΔG_{298} increases from 6-31G basis set to 6-311G(d, p) basis set.

Archive of SID

www.SID.ir

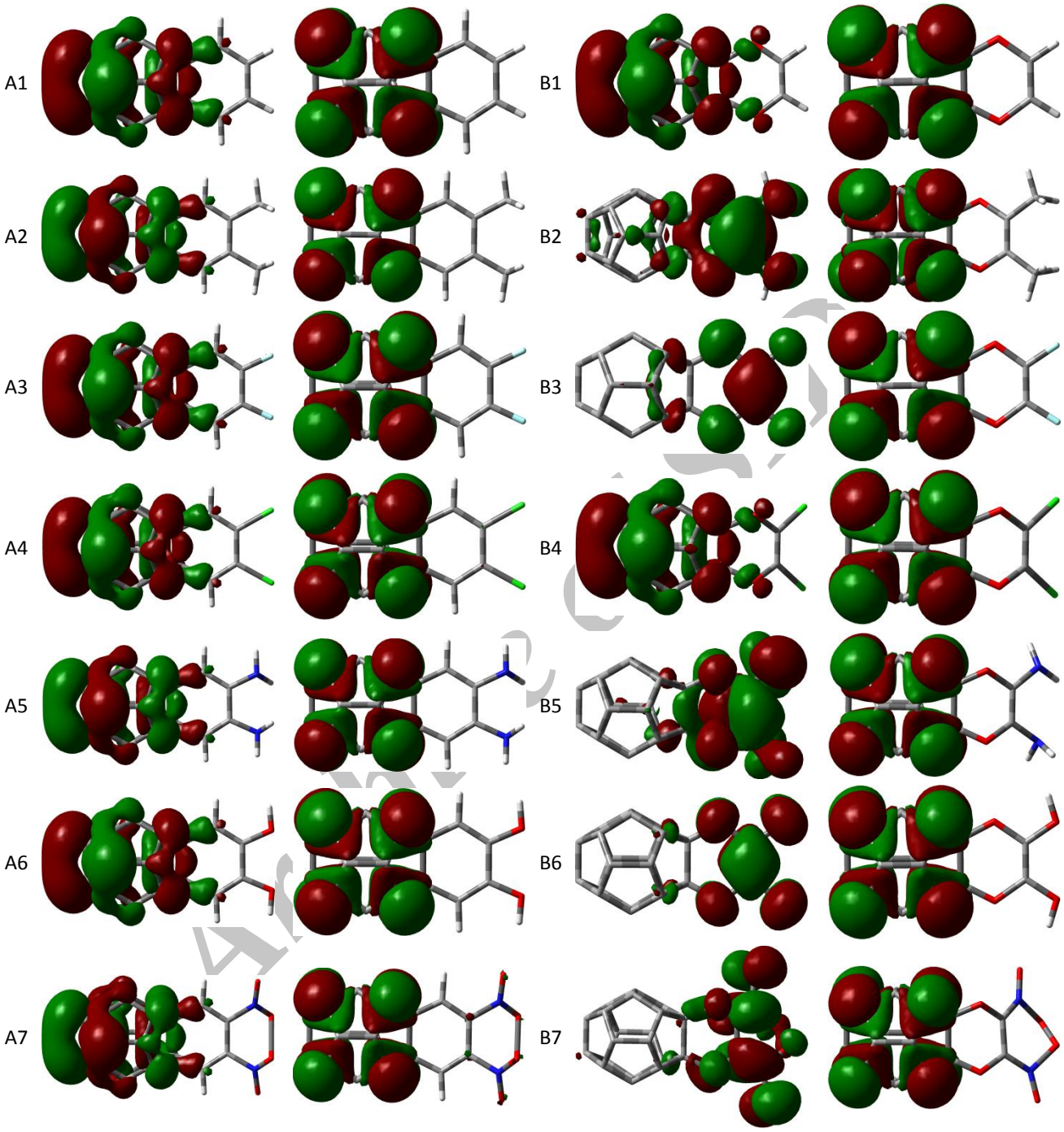


Figure 2. The atomic structures, HOMOs, and LUMOs of $C_{24}H_2X_2$ and $C_{22}O_2X_2$ at the level of B3LYP/6-311G(d, p).

www.SID.ir

Table 2. Thermodynamic parameters of $C_{24}H_2X_2$ and $C_{22}O_2X_2$ using of B3LYP method with different Basis sets at 298 K (in Kcal/mole)

Mol.	ΔE	ΔH	ΔS	ΔG	Mol.	ΔE	ΔH	ΔS	ΔG
		6-31G					**6-31G**		
A1	-62.7779	-62.7779	-0.0250	-55.3158	B1	-52.6476	-53.2400	-0.0497	-38.4163
A2	-67.3619	-67.3619	-0.0228	-60.5796	B2	-44.1161	-44.7085	-0.0519	-29.2241
A3	-57.7661	-57.7661	-0.0250	-50.3160	B3	-24.5878	-25.1802	-0.0552	-8.7250
A4	-59.3074	-59.3074	-0.0253	-51.7609	B4	-31.1837	-31.7761	-0.0559	-15.1214
A5	-67.3619	-67.3619	-0.0228	-60.5796	B5	-7.23074	-7.82314	-0.0503	7.1705
A6	-61.8522	-61.8522	-0.0238	-54.7630	B6	-17.3419	-17.9343	-0.0504	-2.8950
A7	-60.3876	-60.3876	-0.0114	-57.0001	B7	-13.1419	-13.7343	-0.0467	0.1932
		6-31G(d,p)					**6-31G(d,p)**		
A1	-60.4716	-60.4716	-0.0297	-51.6068	B1	-50.6213	-51.2137	-0.0630	-32.4389
A2	-64.7720	-64.7720	-0.0274	-56.5988	B2	-41.3470	-41.9394	-0.0680	-21.6581
A3	-56.9814	-56.9814	-0.0296	-48.1490	B3	-19.0857	-19.6781	-0.0606	-1.6069
A4	-59.1032	-59.1032	-0.0298	-50.2055	B4	-29.9226	-30.5150	-0.0613	-12.2307
A5	-65.5024	-65.5024	-0.0264	-57.6352	B5	-7.56584	-8.15824	-0.0587	9.3306
A6	-60.4584	-60.4584	-0.0285	-51.9506	B6	-11.5323	-12.1247	-0.0564	4.7020
A7	-61.0491	-61.0491	-0.0163	-56.1795	B7	3.1215	2.5291	-0.0533	18.4298
		6-311G(d,p)					**6-311G(d,p)**		
A1	-57.8945	-57.8945	-0.0274	-49.7362	B1	-45.4302	-46.0226	-0.0606	-27.9657
A2	-62.1234	-62.1234	-0.0250	-54.6651	B2	-42.4547	-43.0471	-0.0555	-26.4891
A3	-54.0162	-54.0162	-0.0273	-45.8913	B3	-11.6872	-12.2796	-0.0622	6.2543
A4	-56.1897	-56.1897	-0.0274	-48.0097	B4	-23.9053	-24.4977	-0.0591	-6.8898
A5	-62.2312	-62.2312	-0.0241	-55.0604	B5	-1.9566	-2.5490	-0.0560	14.1552
A6	-57.3786	-57.3786	-0.0260	-49.6282	B6	-4.4108	-5.0032	-0.0611	13.2194
A7	-58.3663	-58.3663	-0.0139	-54.2148	B7	14.1886	13.5962	-0.0513	28.8889

4. Conclusion

The structures and stabilities of fullerenes C_{20} and some of its derivatives have been studied by DFT calculations. The calculations show that the fullerene C_{20} has a high activity toward addition of diene or 1,2-dioxo and the adducts have high stabilities relative to C_{20} except for $C_{22}O_2(OH)_2$. The thermodynamic calculations indicate that the reaction of the addition of diene to C_{20} is exothermic and spontaneous. While, the addition of 1,2-dioxos to C_{20} can be thermodynamically improper when the 1,2-dioxo group consists of electronegative atoms.

References

[1] H. Prinzbach, A. Weiler, P. Landenberger, F. Wahl, J.Worth, L.T. Scott, M. Gelmont, D. Olevano, B. v. Issendorff, Nature 407 (2000) 60-63.

[2] M. Saito, Y. Miyamoto, Phys. Rev. Lett. 87 (2001) 035503-4.

[3] Y. Miyamoto, M. Saito, Phys. Rev. B. 63 (2001) 161401-161405.

[4] H. W. Kroto, K. Mckay, Nature 331 (1988) 328-331.

[5] S. Grimme C. Muck-Lichtenfeld, Chem. Phys. Chem. 3 (2002) 207-209.

Archive of SID

www.SID.ir

[6] B. Paulus, Phys. Chem. Chem. Phys. 5 (2003) 3364-3367.

[7] H. Handschuh, G. Ganteför, B. Kessler, P. S. Bechthold, W. Eberhardt, Phys. Rev. Lett. 74 (1995) 1095-1098.

[8] W. An, Y. Gao, S. Bulusu, X. C. Zenga, J. Chem. Phys. 122, (2005) 204109-8.

[9] T. Z. Schmalz, W. A.Seitz, D. J. Klein, D. G.Hite, J. Am. Chem.Soc. 110 (1998) 1113-1127.

[10] O.V. Boltalina, A.D. Darwish, J.M. Street, R. Taylor, X.W. Wei, J. Chem. Soc., Perkin Trans. 2 (2002) 251-256.

[11] W. Qian, Y. Rubin, J. Am. Chem. Soc. 122 (2000) 9564-9565

[12] L. Tu¨rker, J. Mol. Struct. Theochem 588 (2002) 165–174

[13] V. Nair, D. Sethumsdhavan, K. C. Sheela, S. M. Nair, G. K. Eigendorf, Tetrahedron 58 (2002) 3009-3013

[14] J. L. Segura, N. Martin, Chem. Rev. 99 (1999) 3199-3246.

[15] S. Lee, Y. Suh, Y. G. Hwang, K. H. Lee, Bull. Korean Chem. Soc. 32 (2011) 3372-3376.

[16] C. H. Choi, H.-I. Lee, Chem. Phys. Lett. 359 (2002) 446–452.

[17] Y. Liang, Z. Shang, G. Wang, Z. Cai,Y. Pan, X. Zhao, J. Mol. Struct. Theochem 677 (2004) 15–19.

[18] C. Zhang, W. Sun, Z. Cao, J. Chem. Phys. 126 (2007) 144306-7.

[19] V. Parasuk, J. AImliif, Chem. Phys. Lett. 184 (1991) 187-190.

[20] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. MontgomeryJr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam,A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi,V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C.Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala,Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck,K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz,A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz,I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith,M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez,M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W.Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S.Replogle, J.A. Pople, GAUSSIAN 98, Gaussian, Pittsburgh, PA,USA, 1998.

Archive of SID

www.SID.ir