A quantum-chemical investigation on 3,4'-bi(4H-1,2,4-triazole)

Riza Abbasoglu, Necdet Saltek & A Aykut Ikizler*

Department of Chemistry, Karadeniz Technical University, 61080-Trabzon, Turkey

The conformational analysis of 3,4'-bi(4H-1,2,4-triazole) molecule has been performed using the semiempirical methods MNDO, AM1 and PM3, and the stable conformations, the rotational barriers and geometric parameters have been determined. The total energies, heats of formation, dipole moments, ionization potentials, full atomic charges, energies of frontier molecular orbitals (E_{HOMO} and E_{LUMO}) and electron densities have been calculated and discussed. In order to determine the orientation centers of proton attacks at the 3,4'-bitriazole system, the molecular electrostatic potential (MESP) of the molecule has been also calculated. The conformational analyses of mono- and diprotonated species have also been performed by AM1 aand PM3 routes and their stable conformations determined. The proton affinity for the different nitrogens of the 3,4'-bitriazole molecule has been calculated using AM1 and PM3 methods and more basic centers have been determined. Furthermore, the complex formation ability of the molecule with metal cations is also discussed. The electronic properties of the complexes formed by Mg^{2+} and Fe^{2+} ions have been investigated using PM3 and ZINDO/1 methods, and the stabilities of these complexes are discussed.

The quantum-chemical investigations of 3,3'-bi(1H-1,2,4-triazole) and 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole systems have recently been made by us[1,2]. The results obtained from these studies have prompted us to continue the quantum-chemical invetigations for the other bitriazole systems. The present study deals with the investigation of molecular conformations and electronic properties of 3,4'-bi(4H-1,2,4-triazole) molecule. It is obvious that 3,4'-bi(4H-1,2,4-triazole) (A) and 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole system (B) are tautomers (Scheme 1). According to X-ray results tautomeric form B is preferred by the molecule in crystalline state[3]. In fact, 4H-tautomer of 1,2,4-triazole molecule has been found to be more stable than 1H-tautomeric form according to the investigations involving MNDO, AM1 and PM3 methods[4,5]. But, the relative stabilities of 1H-1,2,4-triazole and 4H-1,2,4-triazole tautomers are not definitely determined yet. Hence, the determination of relative stabilities of A and B tautomers would be interesting. On the other hand, it is possible that 3,4'-bi(4H,1,2,4-triazole) molecule can exist in various conformations as a result of rotation around C_3-$N_{4'}$ single covalent bond. However, the 3,4'-bi(4H-1,2,4-triazole) molecule containing two 4H-1,2,4-triazole rings and having several nitrogen atoms differing from each other in position may
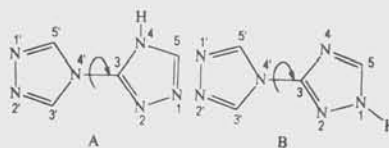
Scheme 1

have basic and also acidic properties[6-8]. Moreover, the difficulty of the experimental determination of the protonation centers of the molecules containing several heteroatoms differing from each other in position has been reported[9,10]. Hence, the conformational investigation and the theoretical calculations of protonation parameters of the 3,4'-bi(4H-1,2,4-triazole) molecule also appeared important. The selectivity of complex formation ability of 3,4'-bi(4H-1,2,4-triazole) molecule having competing coordination centers can be theoretically evaluated and their stabilities predicted. Due to the effects of the interactions between the two 4H-1,2,4-triazole rings on basicity, the theoretical investigation of the bitriazole system is also important. It is known that *ab initio* methods as well as semiempirical methods[4,5,11-32] have been used widely for the conformational analysis and for the calculations of the protonation parameters of heterocycles and biheterocycles. Also, AM1 and PM3 methods are generally

used to calculate the proton affinities of various heterocyclic compounds[20,29]. In the present study, the semiempirical methods such as MNDO[33], AM1[34] and PM3[35] have been used for the detailed investigation of the conformations and electronic properties of 3,4'-bi(4H-1,2,4-triazole) molecule. The proton affinity of the molecule was calculated by AM1 and PM3 methods for different nitrogen atoms. The electronic properties of the Mg^{2+} and Fe^{2+} complexes of the molecule were investigated using PM3 and ZINDO/1[36] routes. All calculations related to the study were performed using *HyperChem* 3.0 program with a IBM PC/AT-486 DX4-100 computer.

Results and Discussion

It is possible that 3,4'-bi(4H-1,2,4-triazole) molecule may exist in different conformations due to the rotation of triazole rings around C_3-$N_{4'}$ single bond. Hence, the conformational analysis of the molecule was performed with full geometry optimization using MNDO, AM1 and PM3 methods. According to MNDO method, a minimum was found at the conformation corresponding to $\varphi = 86°$ (Scheme 1-A). A maximum was reached at the planar conformation corresponding to $\varphi = 0°$ or $\varphi = 180°$. The calculated internal rotation barrier value for the molecule by MNDO method is 4,920 kJ/mol. According to the conformational analysis results obtained by AM1 and PM3 calculations, it seems that the planar conformation of the molecule ($\varphi = 0°$ or 180°) with maximum conjugated two 1,2,4-triazole rings is the most stable conformation. In contrast, it is apparent that the most unstable conformation corresponds to $\varphi = 90°$ with the minimum conjugated triazole rings. The length of C_3-$N_{4'}$ single covalent bond reaches a maximum value in the most unstable conformation (1,396Å, AM1 and 1,425Å, PM3). The internal rotation barriers were found

to be 4,197 kJ/mol and 2,201 kJ/mol by AM1 and PM3 methods, respectively. In general, the calculated internal rotation barriers of the molecule by the semiempirical methods are small. The results obtained for the 3,4'-bi(4H-1,2,4-triazole) system by AM1 and PM3 methods in the present study are in agreement with the results obtained for the conformations of some conjugated molecules by *ab initio* and semiempirical methods[11-14,16,17,32]. The calculated internal rotation barrier of 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole (B) is higher than that of 3,4'-bi(4H-1,2,4-triazole) molecule (A) (Table 1). Total energies (E_{tot}), the heats of formation (ΔH_f^0), internal rotation barriers (ΔE) and internal rotation angles (φ_{min} and φ_{max}) for these molecules are given in Table 1.

The results obtained by PM3 are in conformity with the published X-ray results[3] and indicate that the tautomer B is more stable than the other tautomer in gas phase. However, the MNDO and AM1 results indicate tautomer A to be more stable in gas phase. So, structures A and B are in a tautomeric equilibrium in gas and liquid phases.

In our previous study, the electronic properties of 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole (B) molecule have been investigated[2]. Taking into consideration the fact that calculated internal rotation barrier of the molecule is small, the electronic properties of 3,4'-bi(4H-1,2,4-triazole) (A) molecule were investigated for planar conformation ($\varphi = 0°$) with the aid of the semiempirical methods in the present study. The calculated values for ionisation potentials (IP), dipole moments (μ) and energies of frontier molecular orbitals (E_{HOMO} and E_{LUMO}) are presented in Table 2.

The experimental ionisation potential of 1,2,4-triazole has been reported to be 10.00 eV[8]. In the present study, the ionisation potential of 4H-

Table 1—Total energies (in kcal/mol), heats of formation (in kcal/mol), internal rotation barriers (in kJ/mol) and internal rotation angles (in degree) for 3,4'-bi(4H-1,2,4-triazole) (A) and 3-(4H-1, 2,4-triazol-4-yl)-1H-1,2,4-triazole (B)

Molecule	E_{tot}	$\Delta H_f^°$	ΔE	ϕ_{min}	ϕ_{max}
		MNDO			
A	-41721.792	90.175	4.920	86	0
B	-41721.212	90.755	7.517	0	90
		AM1			
A	-41605.024	167.094	4.197	0	90
B	-41602.816	169.302	13.984	0	90
		PM3			
A	-34732.295	112.297	2.201	0	90
B	-34735.442	109.151	11.602	0	90

1,2,4-triazole calculated using MNDO, AM1 and PM3 methods, was found to be 10.025 eV, 10.033 eV and 10.215 eV, respectively. The ionisation potential of 3,4'-bi(4H-1,2,4-triazole) molecule is thus relatively lower than that of 4H-1,2,4-triazole system.

An analysis of frontier orbitals (HOMO and LUMO) of 3,4'-bi(4H-1,2,4-triazole) molecule reveals that these orbitals are formed by the p_z atomic orbitals of carbon and nitrogen atoms. In the case of HOMO, the electron density (q_i) is higher at C-5, C-3, N-2, N-4, N-1, N-1' and N-2' atoms (Table 3), as shown in Fig. 1. However, N-4, N-4', N-2', N-2, N-1 and N-1' atoms have higher atomic charges (Q_i) in the molecule (Table 3), as also shown in Scheme 2. The values shown in Table 3 were calculated by means of MNDO method.

In order to investigate the basicity and to find out the coordination centers, the determination of the protonation sites of 3,4'-bi(4H-1,2,4-triazole) molecule containing different nitrogens is important. The N-4 atom is predicted to be the main basic center of the bitriazole system in accordance with the negative charge distribution on nitrogen atoms (Scheme 2 and Table 3). However, negative atomic charges are also present on the other nitrogen atoms of the molecule. In order to determine the possible protonation centers of the bitriazole system, the molecular electrostatic potential (MESP) (in kcal/mol) of the molecule was calculated by means of the three semiempirical methods. The electrostatic potential contour maps of the molecule reveal that the electrophilic attacks of proton predominantly occur on N-1' and N-2' atoms. At the same time, the probability of proton attack onto N-1 and N-2 atoms is also high. Figure 2 shows the MESP countour map according to MNDO method.

To determine the exact protonation centers of 3,4'-bi(4H-1,2,4-triazole), the proton affinities for the different nitrogen atoms of the molecule were calculated by means of AM1 and PM3 methods. The stable conformations for the cations formed by the protonation of each nitrogen atom of the molecule were determined, and the heats of formation (ΔH_f^0) were calculated with full geometry optimization by AM1 and PM3 routes (Table 4). The conformational analysis of the mono cations
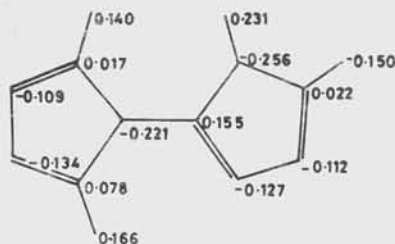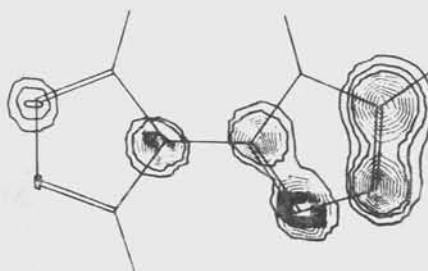

Scheme 2

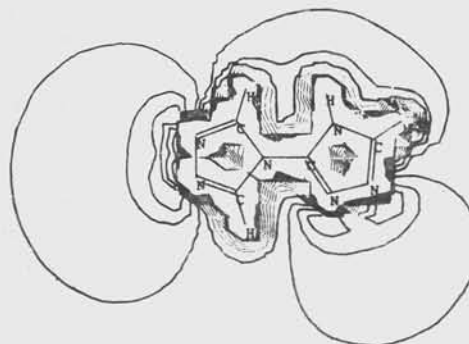Fig. 1—Electron density contour map of 3, 4'-bi(4H-1,2,4-triazole)

Fig. 2—Electrostatic potential contour map of 3,4'-bi(4H-1,2,4-triazole)

Table 2—Ionisation potential (in eV), dipole moment (in Debye) and energies of frontier molecular orbitals (in eV) of 3, 4'-bi(4H-1,2,4-triazole)

Method	IP	μ	E_{HOMO}	E_{LUMO}
MNDO	10.023	5.905	−10.023	−0.683
AM1	9.976	5.870	−9.976	−0.775
PM3	10.139	6.597	−10.139	−1.099

Table 3—The values of electron densities of HOMO (q_i) and full atomic charges (Q_i) for 3,4'-bi(4H-1,2,4-triazole)

	N-1	N-1'	N-2	N-2'	N-4	N-4'	C-3	C-5
q_i	0.120	0.040	0.173	0.017	0.004	0.130	0.221	0.269
Q_i	−0.112	−0.109	−0.127	−0.134	−0.0256	−0.220	0.154	0.022

reveals that the stable conformations of mono protonated species have planar structures.

The cations formed by the protonation of N-1' or N-2' atoms of the molecule can exist in *anti* or *syn* conformation according to the position of NH group relative to C_3-N_4 central bond. The protonation of N-1' and N-2' atoms of the molecule (Scheme 1-A) results in the formation of *syn* and *anti* monocations, respectively. The data obtained show that the *anti* conformation is relatively more stable than the other. The total energy difference between the two conformations is found to be 8.368 kJ/mol by AM1 method and 6.568 kJ/mol by PM3 method.

The proton affinity (PA) values for the different nitrogen atoms of 3,4'-bi(4H-1,2,4-triazole) molecule were calculated using the equation given below. The results obtained are presented in Table 5.

$$PA = \Delta H_f^0 (H^+) + \Delta H_f^0 (B) - \Delta H_f^0 (BH^+)$$

Here PA is the proton affinity, $\Delta H_f^0 (B)$ is the heat of formation for the molecule, $\Delta H_f^0 (BH^+)$ is the heat of formation for the cation and $\Delta H_f^0 (H^+)$ is the heat of formation for proton (367.2 kcal/mol)[37].

A comparison of the results shown in Table 5 reveals that the proton affinities of 3,4'-bi(4H-1,2,4-triazole) molecule calculated for N-2' and N-1' atoms are higher than those of the other nitrogens. According to Scheme 1-A, the protonation of N-2' atom leads to the formation of *anti* conformation of the monocation, and for this reason, the proton affinity of the molecule corresponding to this nitrogen atom is higher than that of N-1'. Hence, 3,4'-bi(4H-1,2,4-triazole) molecule is predicted to protonate at N-2'. In other words, the electrophilic attack of proton on N-2' atom of 4H-1,2,4-triazole ring placed in *anti* position according to NH group of the other triazole ring is easier.

Although the atomic charge at N-4 atom is relatively higher than that at the other nitrogen atoms (Scheme 2 and Table 3), the proton affinity of the molecule calculated for N-4 has a lower value. As a result of N-4 protonation of the bitriazole molecule, 4H-1,2,4-triazole ring becomes non-aromatic. Thus, the stability of the formed cation is relatively lower than that of the others, and its heat of formation is relatively higher (Table 4). N_4-C_3 bond length (Scheme 1-A) of the N-4 protonated species is 1.558Å.

It is plausible to consider that the interaction between two 4H-1,2,4-triazole rings affects the basicity of the molecule. Hence, the proton affinities of 3,4'-bi(4H-1,2,4-triazole) and 4H-1,2,4-triazole molecules were calculated for the same nitrogens in position (Table 5). A comparison of the results presented in Table 5, clearly shows that the proton affinities of the bitriazole molecule are relatively lower than those of 4H-1,2,4-triazole. According to the data obtained for the proton affinities, the 3,4'-bi(4H-1,2,4-triazole) is predicted to be less basic than 4H-1,2,4-triazole molecule.

In our previous study[2], the proton affinity values of 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole molecule have been calculated for the different nitrogen atoms, and the proton affinity related to N-1' (Scheme1-B) has been determined as the

Table 4—Heats of formation (in kcal/mol) for the protonated forms of 3,4'-bi(4H-1,2,4-triazole)

Protonated nitrogens →	N-1	N-2	N-4	N-1'	N-2'
AM1	336.793	337.906	370.029	332.684	330.678
PM3	281.361	284.218	325.471	273.837	272.273

Table 5—Proton affinities (in kcal/mol) of 4H-1,2,4-triazole (1) and 3,4'-bi(4H-1,2,4-triazole) (2) calculated for different nitrogens

Protonated nitrogens →	N-1	N-2	N-4	N-1'	N-2'
AM1					
1			170.88	206.34	206.34
2	197.50	196.39	164.26	201.61	203.62
PM3					
1			164.05	207.15	207.15
2	198.14	195.28	154.03	205.66	207.12

highest value: 210.76 kcal/mol (AM1) and 213.67 kcal/mol (PM3). Comparing these values with those of 3,4'-bi(4H-1,2,4-triazole) molecule calculated for N-2' atom (Table 5) it is easy to see that 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole is a more basic tautomer than 3,4'-bi(4H-1,2,4-triazole). Moreover, the heats of formation of the cations formed by the N-1' protonation of 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole and by the N-2' protonation of 3,4'-bi(4H-1,2,4-triazole) molecule were found to be 262.684 kcal/mol (PM3) and 272.273 kcal/mol (PM3) respectively. According to these results, it is obvious that the former cation is more stable than the latter. On the other hand, it is possible to say that 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole is a more basic molecule than 4H-1,2,4-triazole, according to the proton affinity values related to N-1' atom. Consequently, it can be said that 1H-1,2,4-triazole ring acts as an electron-donor towards the 4H-1,2,4-triazole ring in 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole molecule, and so renders the molecule more basic (Scheme 1-B). Similarly, one 4H-1,2,4-triazole ring acts as an electron-acceptor towards the other ring in 3,4'-bi(4H-1,2,4-triazole) molecule, and renders it less basic.

As expected, the protonation of a nitrogen of 3,4'-bi(4H-1;2,4-triazole) molecule affects the further protonation of the other centers. Thus, the proton affinities of the N-2' protonated cation for N-1 and N-1' atoms are calculated to be 122.975 kcal/mol (AM1) and 80.242 kcal/mol (AM1), respectively. These values are lower than the corresponding values for the neutral molecule (Table 5). Among the diprotonated species of the bitriazole molecule, the dication formed by protonation of N-2' and N-1 atoms is found to be most stable dication, according to AM1 and PM3 methods. The internal rotation angle (ϕ) for the most stable conformation of the dication is calculated as 34.89° (AM1). Furthermore, the dication formed by the protonation of N-1' and N-2' atoms is found to be 24.970 kJ/mol (AM1) more stable than the one formed by N-1 and N-2 diprotonation.

In addition, the complex formation ability of 3,4'-bi(4H-1, 2, 4-triazole) molecule with metal ions has been considered in the study. It is plausible to consider that N-2' and N-1' atoms having higher proton affinities act as coordination centers in the metal complexes. In order to support this consideration, the electronic properties of the predicted metal complexes were also investigated using semiempirical methods. The electronic properties of Mg^{2+} complexes of the bitriazole molecule were investigated by PM3 method.

The complex containing Mg^{2+} ion attached to N-2' and N-1' atoms is found to be 24.970 kJ/mol more stable than the one having N-1 and N-2 coordination centers. This stable complex approximately has a planar structure. The $r_{(Mg-N2')}$ and $r_{(Mg-N1')}$ bond lengths in this complex are 1.871 and 1.874 Å, respectively.

Apart from this, the electronic properties of Fe^{2+} complexes of 3, 4'-bi(4H-1, 2, 4-triazole) molecule were also investigated with full geometry optimization using ZINDO/1 method. Total energies (E_{tot}), heats of formation (ΔH_f°), positive charge densities of iron (Q_{Fe}) and bond lengths (r_{Fe-N}) for the complexes containing Fe^{2+} ion attached to N-1/N-2 (I) and N-2'/N-1' (II) are given in Table 6, respectively. Both the complexes are found to have approximately planar structures. But complex II is 16.209 kJ/mol more stable than the other.

So, the coordinating ability of N-2' and N-1' atoms for 3, 4'-bi(4H-1, 2, 4-triazole) molecule is confirmed by the investigation of electronic properties of the predicted metal complexes.

Moreover, the electronic properties of the complex (III) containing Fe^{2+} ion attached to N-1' and N-2' atoms of 3-(4H-1, 2, 4-triazol-4-yl)-1H-1, 2, 4-triazole (Scheme I-B) were investigated by ZINDO/1 method. This investigation revealed that complex III is more stable than complex II. According to the results obtained, it can be established that 3-(4H-1, 2, 4-triazol-4-yl)-1H-1, 2, 4-triazole molecule has a higher reactivity and a higher complex formation ability than that of 3, 4'-bi(4H-1, 2, 4-triazole).

Table 6—Total energies (in kcal/mol), heats of formation (in kcal/mol), positive charge densities of iron (Q_{Fe}) and Fe-N bond lengths (in Å) of complexes I and II

Complexes	E_{tot}	ΔH_f°	Q_{Fe}	r			
				Fe-N$_1$	Fe-N$_2$	Fe-N$_{1'}$	Fe-N$_{2'}$
I	−71866.227	−2552.096	1.110	2.035	1.993		
II	−71870.101	−2555.970	1.127			2.020	2.016

References

1 Saltek N, Abbasoglu R & Ikizler A A, *Acta chim, hung, Models in Chemistry*, 133 (1996) 43.
2 Abbasoglu R, Saltek N & Ikizler A A (submitted for publication).
3 Aoniali P M, Viallefont Ph & Ammari L E, *Acta Crystallo*, c47 (1991) 1866.
4 Fos E, Vilerros J & Fernandez J, *J org Chem*, 50 (1985) 4894.
5 Ostrovskiy V A, Erusalimsky G B & Serbinin M B, *Zh org Chim*, 29 (1993) 1297.
6 Atkinson M R & Polya J B, *J chem Soc*, 141 (1954).
7 Schofield K, Grimmett M R & Keene B R T, *Heteroaromatic nitrogen compounds—The azoles* (Cambridge University Press, Cambridge, England) 1975.
8 Pojarsky A F, *Fundamentals of heterocyclic chemistry*, (Moscow State University Press, Moscow) 1985.
9 Balotin V A, (*Ph*) *Doktora Dissertion* (Moscow State University Press, Moscow) 1980.
10 Sirokova N P, Mityukova N B, Pevxner M S, Ostrovsky V A, Kaldovskiy G I & Erusalimskiy G B, *Zh org Chem*, 25 (1989) 2003.
11 Orti E, Sancher-Marin J & Tomas F, *Theochem—J molec Struc*, 124 (1985) 307.
12 Orti E, Sancher-Marin J, Merchan M & Tomas F, *J phys Chem*, 91 (1987) 545.
13 Russo N, Toscana M, Baroni V & Minichino C, *J chim Phys*, 84 (1987) 735.
14 Fabian W M F, *J comp Chem*, 9 (1989) 369.
15 Begtrup M, Nielsen C J, Nyguard L, Samdal S, Sjorgen C E & Sorensen G O, *Acta chem Scand*, A42 (1989) 500.
16 Barone V, Leli F, Minichino C, Fliszar S, Russo N & Toscana M, *J chem Soc (Perkin)*, (1988) 1975.
17 Barone V, Minichino C, Fliszar S & Russo N, *Can J Chem*, 66 (1988) 1313.
18 Ritche J P, *J org Chem*, 54 (1989) 3553.
19 Catalan J, Sanchez-Cabezudo M, de Paz J L G, Elguero J, Taft R W & Anvia F J, *J comput Chem*, 10 (1989) 426.
20 Voets R, Francois J P, Martin J M L, Mullens J, Yeperman Y & Poucice L S, *J comput Chem*, 10 (1989) 449.
21 Tomas F, Abbout J L G, Loynez J, Notario R, Soutos L, Nilsson S O, Catalan J, Claramunt R M & Elguero J, *J Am chem Soc*, 111 (1989) 7348.
22 Katrizky A R, Szafron M & Stevens J, *Theochem—J molec Struc*, 184 (1989) 179.
23 Catalan J, de Paz J L G, Yanez M, Claramunt R M, Lopez C, Elguero J, Anvia F, Quian J H, Taagepera M & Taft R W, *J Am chem Soc*, 112 (1990) 1303.
24 William J W, *J comput Chem*, 11 (1990) 694.
25 Kodaka M, *Chem Express*, 6 (1991) 89.
26 Abboud J L M, Cabildo T, Canada T, Catalan J, Claramunt R M, de Paz J L G, Elguero J, Homan H, Notavia R, Tairan C & Yrazo G I, *J org Chem*, 57 (1992) 3938.
27 Anders E, Katrizky A R, Malhotra N & Stevens J, *J org Chem*, 57 (1992) 3698.
28 Sigalov M V, Schmidt E Y, Trofimov A B & Trofimov B A, *J org Chem*, 57 (1992) 3934.
29 Turchaninov V K & Yeroshcenco S V, *Theochem—J molec Struc*, 253 (1992) 371.
30 Del Valle J C & De Faz J L G, *Theochem—J molec Struc*, 254 (1992) 481.
31 Ivashkevich O A, Gaponik P N, Koren A O, Bubel O N & Fronchek E V, *Int J quant Chem*, 43 (1992) 813.
32 Enriz R D, Jauregui E A & Tomas-Vert F, *Theochem—J molec Struc*, 306 (1994) 115.
33 Dewar M J S & Thiel W, *J Am chem Soc*, 99 (1977) 4899.
34 Dewar M J S, Zocbish E G, Healy E F. & Steawart J J P, *Am chem Soc*, 107 (1985) 3902.
35 Steawart J J P, *J comput Chem*, 10 (1989) 209.
36 *HyperChem Reference Manual*, Chapter 2 (Hypercube Inc, Canada) 1993, 7.
37 Dewar M J S & Dieter K M, *J Am chem Soc*, 108 (1986) 8075.