Int. J. Electrochem. Sci., 5 **(2010)** 955 - 966

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Effect of Herbicide Terbutryn on the DNA Base Pairs: Design of New Herbicide with the Minimum Toxicity

S. Riahi[1,2,*], *A. Mashhadi*[2], *S. Eynollahi*[2], *M.R. Ganjali*[2], *P. Norouzi*[2]

[1] Institute of Petroleum Engineering, Faculty of Engineering, University of Tehran, P. O. Box 11365-4563, Tehran, Iran
[2] Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, P. O. Box 14155-6455, Tehran, Iran
[*]E-mail: riahisv@khayam.ut.ac.ir

Received: 16 June 2010 / *Accepted:* 29 June 2010 / *Published:* 15 July 2010

Terbutryn [2-(t-butylamino)-4-(ethylamino)-6-(methylthio)-s-triazine] (TB) is a widely used pre-emergence and post-emergence s-triazine carcinogen herbicide in agriculture as a control agent for most grasses and many annual broadleaf weeds in cereal and legume fields, and also under fruit trees. Current effort of this research is to investigate how the structure and dynamics of DNA-binding is affected by TB. Molecular modeling on the complex formed between TB and DNA has shown that this complex is indeed fully capable of participating in the formation of a stable intercalation site. Therefore, molecular geometries of TB and the canonical Watson-Crick base pairs (adenine (A) forms a base pair with thymine (T), as does guanine (G) with cytosine (C) in DNA) were optimized using DFT/B3LYP method. Properties of the isolated intercalator and its stacking interactions with A=T and G≡C nucleic acid base pairs were studied using DFTB method, an approximate version of the DFT method, which was extended to cover London dispersion energy. B3LYP/6-31G* stabilization energies of intercalator···base pair complexes were obtained to be -20.31 kcal/mol and -36.23 kcal/mol for A=T···TB and G≡C···TB, respectively. At the end, It was concluded that, dispersion energy and electrostatic interaction contribute to the stability of intercalator···DNA base pair complexes.

Keywords: Triazine, herbicide terbutryn, toxicity, chemometrics, DNA, DFTB

1. INTRODUCTION

The extensive use of pesticides in agricultural practice to control pests and weeds has undoubtedly increased crop yields and reduced post-harvest losses. At the same time, as a consequence of the massive use of these compounds in the environment, residual amounts of pesticides and their metabolites have been found in drinking water and foods [1], which have led to a risk.

Substituted symmetrical triazines (with chemical structures centered about a common six-membered ring composed of three nitrogens and three carbons arranged symmetrically about the ring) constitute a group of herbicides used extensively in agriculture for local weedkilling. The International Agency for Research on Cancer (IARC) initially ranked atrazine, the prototypic s-triazine compound, in category 2B (i.e. possibly carcinogenic to humans) [2]. Following this evaluation, atrazine was banned in some European countries [3], and substituted by novel s-triazine herbicides, such as simazine and terbutryn. Atrazine was subsequently re-evaluated and then ranked in category 3 (i.e. not classifiable as to its carcinogenicity to humans), likewise simazine [4].

TB belongs to the group of triazine herbicides which inhibits photosynthesis by interrupting the electron transport system, and is a powerful tool for weed control in agriculture [5]. This herbicide is used as a selective pre- and early post-emergence control agent for most grasses and many annual broadleaf weeds on a variety of crops, such as cereals, legumes, and under fruit trees. It is also used as an aquatic herbicide to control submerged and free- floating weeds and algae in water courses, reservoirs and fish ponds [6]. According to U.S. EPA-OPP list, TB belongs to the C-Possible human carcinogen category, whereas the Italian National Advisory Toxicological Committee (CCTN) has classified TB in the 4B category [7], but this pesticide has not yet been evaluated by IARC. In other words, this substance is not evaluable for incomplete or inappropriate mutagenicity studies.

In recent years, DFT method is applied in different branches of chemistry. In the presented paper, we have used the recently introduced approximate DFT method, DFTB (density functional tight-binding), extended by the empirical London dispersion energy term, which is accurate and reliable for computational studies [8] and the recent calculations performed using the DFTB technique for the H-bonded and the stacked DNA base pairs. Furthermore, this computationally very efficient technique can yet be used in quantum mechanical (QM) and QM/molecular mechanical (MM) MD simulations very conveniently and accurately [9].

Study of the respective cancers has been an important research line in our group during recent years [10]. In this paper we have reported a quantum mechanical description of the interactions between the herbicide TB and the DNA base pairs (*Watson-Crick base pairing*) employing DFTB method. To achieve this goal, TB and the DNA base pairs were simulated, and atomic charges, geometrical values (bond lengths, bond angles and dihedral angles), dipole moment, polarizability, and energies of the frontier molecular orbitals (HOMO and LUMO) were obtained. According to the literature survey, this is the first paper which studies TB and the DNA base pairs intercalations using DFT method.

2. COMPUTATIONAL METHODS

GAUSSIAN 98 package and HyperChem (Version 7.0 Hypercube, Inc) softwares have been used in this research [9].

The chemical structure of TB, A, G, C, T, G≡C, and A=T were drawn with the Hyperchem software and optimized using Gaussian 98. Each species was initially optimized with PM3 method. Finally, full geometry optimizations and frequency calculations were performed employing B3LYP/6-

31G* level of theory. Each species was found to be minima by having no negative eigenvalues in the frequency calculations [11]. The frequency calculations on the studied structures verified that they were true minima, providing the necessary thermal corrections to calculate *H* (Enthalpy energy) and *G* (Gibbs energy) [12].

TB structure and geometry were optimized at the B3LYP level using the 6-31G* basis set. The structure of the Watson-Crick base pairs was strong-minded at the B3LYP/6-31G* level with the assumption of their planarity. The structures of the TB···G≡C and TB···A=T complexes used ideal geometries, prepared in the following way. The intercalator and the base pairs were situated in coplanar planes in such a way that the major system axes were parallel. The intersystem separation (vertical) and the in-plane displacements were optimized. In all cases, the quantum mechanical optimized geometries of the base pairs and the intercalators were used for the quantum mechanical calculations. Thus, when the idealized geometries were utilized, the interacting molecules were overlaid by their B3LYP/6-31G optimized geometries, based on the least-squares fitting method. In the case of the empirical potential calculations, either the subsystem geometries were relaxed by the empirical potential or the quantum mechanical optimized geometries were saved. This difference had not a significant effect on the calculated energies.

The other one-electron properties (dipole moment, polarizability, energies of the frontier molecular orbital) were also determined at the B3LYP/6-31G* level of theory. For the charged species, the dipole moment was derived with respect to their mass center, because for the non-neutral molecules the calculated dipole moment depends on the origin of the coordinate system.

The stabilization energies of the selected complexes were determined using a recently introduced method, based on the combination of the approximate tight-binding DFTB with the empirical dispersion energy. The DFT methods are known to be inherently very deficient for stacking interactions, as they basically ignore the dispersion attraction [13-34]. Consequently, their enlargement by an empirical dispersion term currently appears to be a very reasonable way to improve the major deficiency of the DFT method for the evaluation of the molecular complexes. It should also be mentioned that the interaction energies were obtained as the difference between the complex energy and the combined energies of the molecules in isolation [35].

3. RESULTS AND DISCUSSION

3.1. TB characteristics

The optimized structure, the atom numbering and the atom charges of TB are shown in Figure 1a. The equilibrium geometries of the TB subsystems were determined and confirmed by subsequent calculations of the vibrational frequencies. The geometrical optimizations were performed using the DFT method and the significant computed geometrical parameters are available in Table 1. This Table contains some significant geometrical values including bond lengths, bond angles and dihedral angles for herbicide and the base pairs, before and after the complex formation (TB with G≡C and A=T).

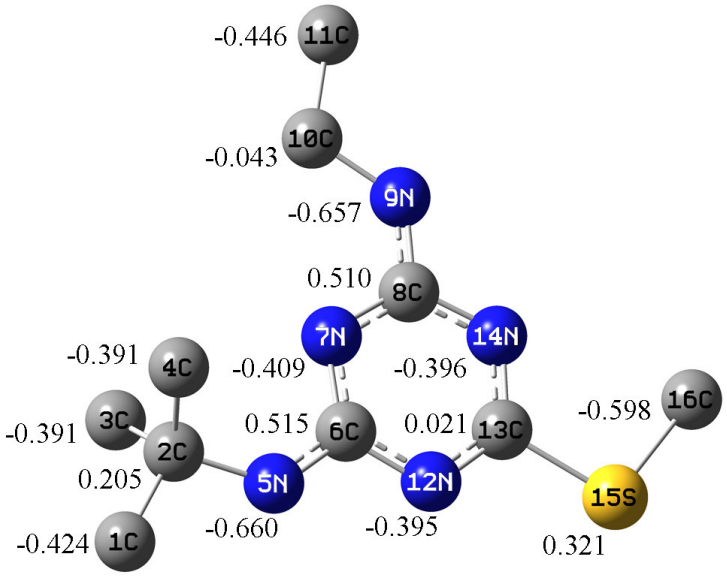


Figure 1(a). The optimized structure and the atom charges of TB

Table 1. Significant computed geometrical parameters for TB before and after the complex formation

Bond (Å)	TB	TB[a]		Angle(°)	TB	TB[a]		Dihedral(°)	TB	TB[a]	
		A=T	G≡C			A=T	G≡C			A=T	G≡C
(2,5)	1.487	1.491	1.491	(1,2,5)	105.7	105.6	109.6	(1,2,5,6)	-180.0	173.1	61.5
(3,21)	1.096	1.096	1.091	(4,2,5)	110.4	111.4	105.3	(4,2,5,6)	-61.4	-68.1	179.6
(4,23)	1.092	1.092	1.097	(8,9,27)	115.8	114.6	115.5	(4,2,5,26)	118.6	126.4	8.7
(5,6)	1.354	1.356	1.353	(9,10,11)	110.2	111.7	110.1	(8,9,10,11)	180.0	111.4	161.6
(6,12)	1.370	1.371	1.374	(9,10,29)	109.5	106.7	108.5	(8,9,10,28)	-58.2	-126.0	-76.2
(7,8)	1.355	1.354	1.354	(30,11,31)	107.8	109.2	108.8	(27,9,10,11)	0.0	-56.9	-16.9
(8,9)	1.353	1.356	1.352	(15,16,33)	105.4	105.4	108.6	(27,9,10,28)	121.8	65.6	105.3
(8,14)	1.370	1.372	1.372	(15,16,35)	109.7	109.8	105.9	(9,10,11,32)	60.4	64.8	179.1
(10,11)	1.530	1.536	1.531					(28,10,11,30)	58.9	62.3	177.2
(10,29)	1.097	1.091	1.094					(28,10,11,31)	178.4	-176.7	-61.9
(11,32)	1.097	1.098	1.095					(29,10,11,31)	60.7	64.1	179.9
(13,15)	1.825	1.825	1.831					(29,10,11,32)	-178.4	-176.3	-61.0
(13,14)	1.341	1.342	1.338					(13,15,16,33)	180.0	177.5	-43.2
(15,16)	1.886	1.886	1.889								

[a]after the complex formation with A=T or G≡C

Carbons 6 and 8 demonstrate the highest positive charges which is due to their bonding to the three nitrogen atoms with high electronegativity and most heteroatoms have the maximum negative

charge (Figure 1b). Existence of electronegative elements in TB has facilitated its interaction with DNA molecule through hydrogen bonding with the G≡C and A=T hydrogen. Essentially, there are two kinds of interactions between TB and DNA; electrostatic interactions and dispersion interactions, being discussed in the next paragraphs.

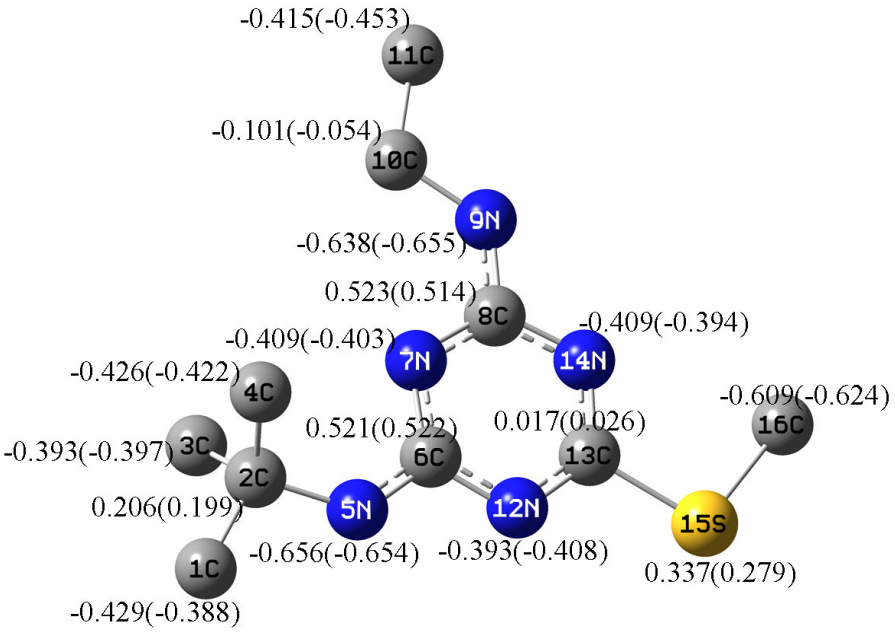


Figure 1(b). The optimized structure and the atom charges of TB after the complex formation with A=T and G≡C (Parentheses include the changes after the complex formation with G≡C)

Table 2 represents the one-electron properties (dipole moment and polarizability) and the energies of the frontier molecular orbital (HOMO and LUMO) of TB using the DFT computational method. The dipole moment is the first derivative of the energy with respect to an applied electric field as a measure of asymmetry in the molecular charge distribution. The high values of the dipole moment and the polarizability present that the electrostatic and the dispersion contribution will play a key role in the interaction with the nucleobases.

Table 2. Dipole moments, polarizibility, HOMO and LUMO energies of the hebricide, the bases and the base pairs

Compound	HOMO	LUMO	Dipole moment	Polarizability
A=T	-8.64	3.01	1.28	213.2
G≡C	-7.35	2.74	2.51	223.4
TB	-6.06	-0.23	3.96	216.285
A	-8.83	3.12	2.49	101.17
T	-9.53	2.94	3.88	89.14
G	-8.45	3.52	2.76	109.19
C	-9.93	3.01	6.12	80.41

3.2. Base pairs characteristics

The optimized structures of the G≡C and A=T in the Watson-Crick structures are visualized in Figures 2 and 3, respectively. Table 2 shows the significant computed geometrical parameters, using the DFT method before and after the complex formation. In addition, from Table 2, it is clear that all the bases and base pairs are very poor electron acceptors (all LUMO energies are positive in contrast to the LUMO energy of TB which is negative). The bases and the base pairs are in fact good electron donors and among the isolated bases the best one is guanine. The electron donating ability of all bases is further magnified by base pairing. For example, the HOMO energy of guanine (-8.45 eV) increases by 1.1 eV upon pairing by cytosine. Moreover, the high polarizability and dipole moment values of A=T and G≡C expose that the electrostatic and dispersion contributions significantly have influence on the interaction with the intercalator.

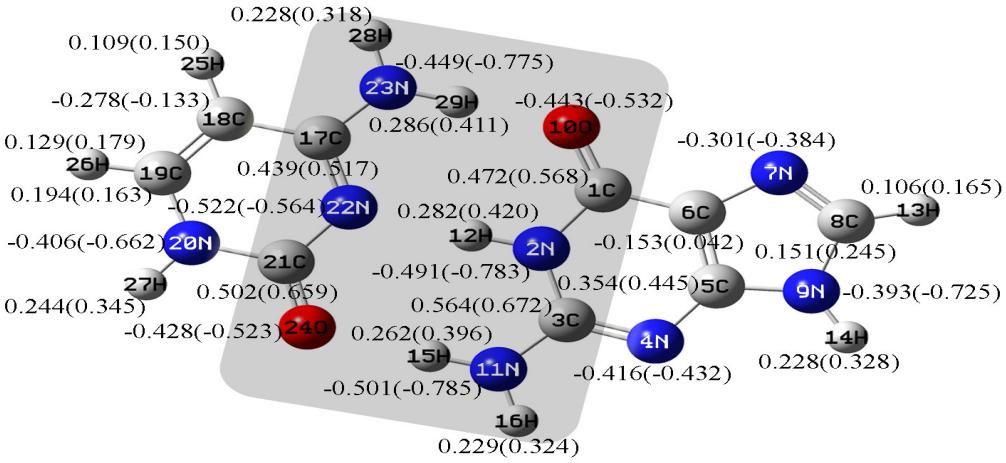


Figure 2. Optimized structure and charge of G≡C base pair & TB···G≡C, before and after the complex formation (Parentheses include the changes after the complex formation)

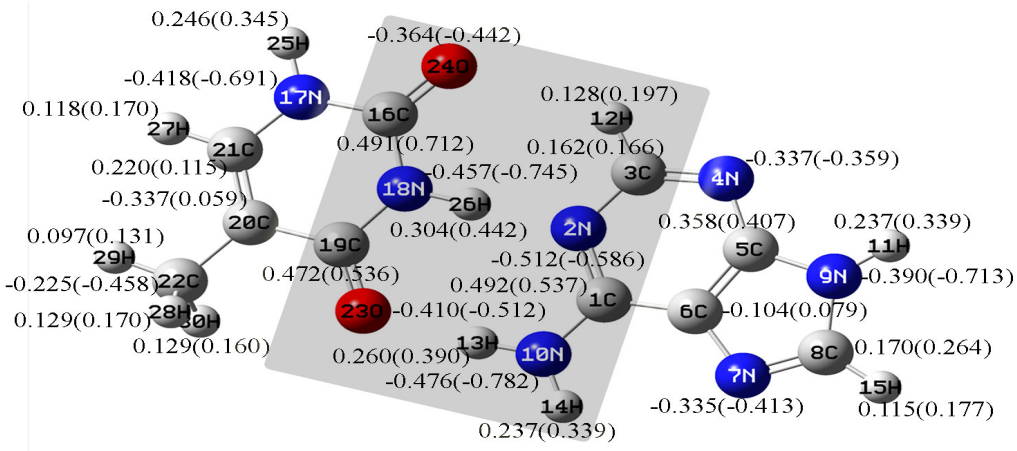
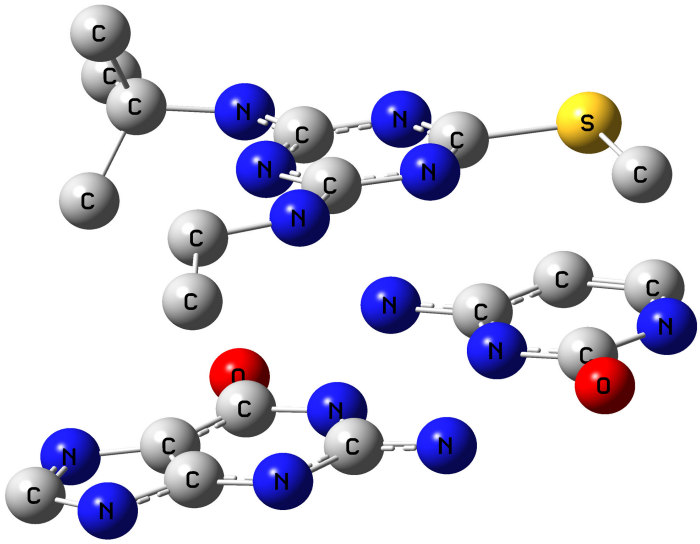


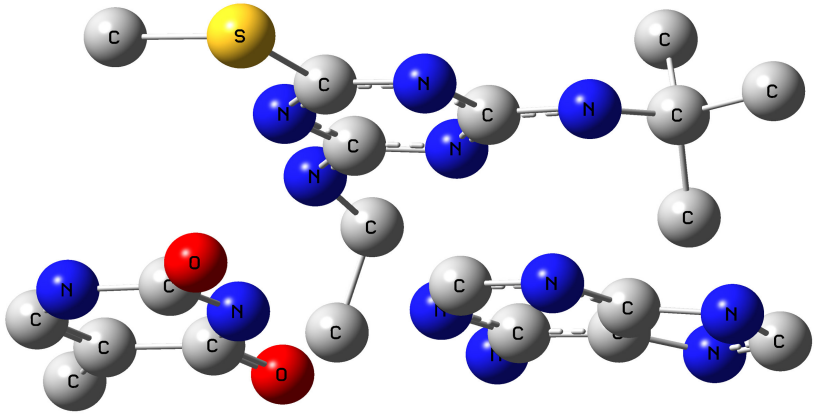
Figure 3. Optimized structure and charge of A=T base pair & TB···A=T before and after the complex formation (Parentheses include the changes after the complex formation)

3.3. Complex characteristics

The TB···G≡C and TB···A=T optimized geometries are summarized in Figures 4a and 4b, respectively. The atomic charge differences of TB, A=T and G≡C are accessible in Figures 1(1a and 1b), 2 and 3, respectively. From Figure1 (a, b), it is clear that the charge difference is tangible in TB after the complex formation, because a number of atoms have wasted some of their charges in hydrogen bonding. For instance, in TB···A=T, the atomic charges for N_9 differs from -0.657 to -0.638 and for S_{15}, from 0.321 to 0.337. Therefore, a stronger hydrogen bonding was formed between TB and A=T.



(a)



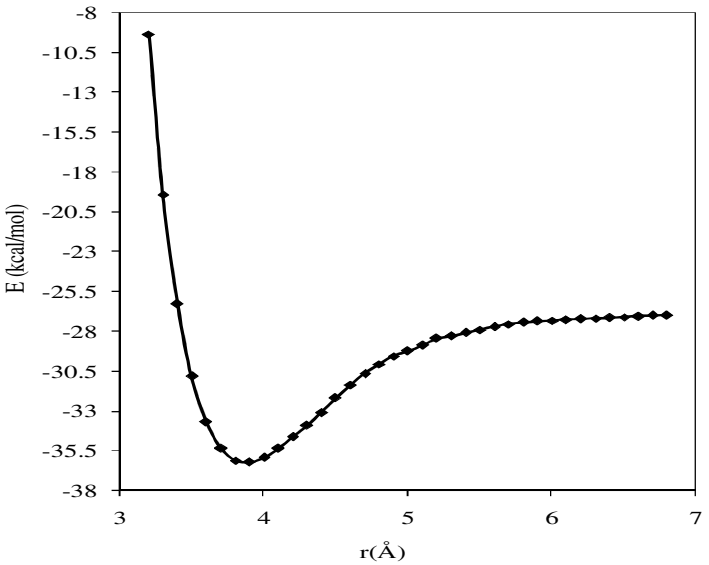
(b)

Figure 4(a,b). Optimized structures of TB···G≡C and TB···A=T, respectively

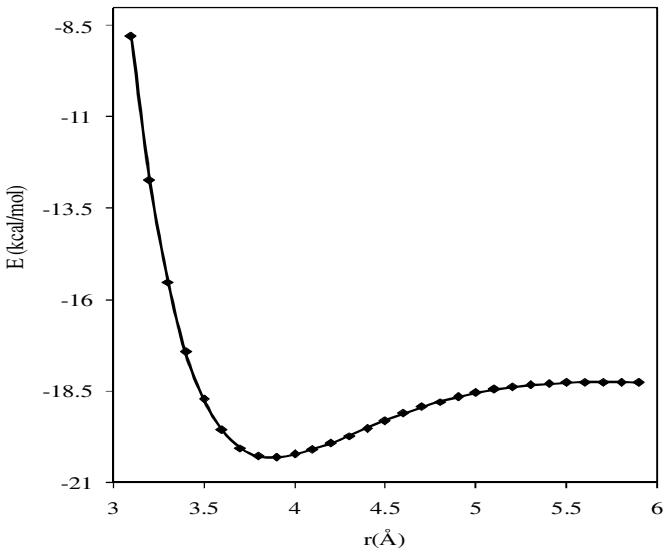
Study of the charges in G≡C and TB···G≡C exhibits that the part, shown with High Light (the only part which is going to be discussed afterwards), displays the highest changes, because of the TB and G≡C interactions. Similar changes have also been obtained in A=T. Since the TB heteroatom interact with the G≡C hydrogen in the mentioned region, the charge changes are not significant for the other heteroatom of the G≡C or A=T bases pairs. Alternatively, an increase in the G≡C hydrogen charges in the area proves the fact that the hydrogen bonding has become stronger, i.e. H_{15} has shifted from 0.262 to 0.396 and its bond length (R (15, 24)) has decreased from 1.915 Å to 1.840 Å. After interacting with the TB molecule, the bond angles of the base pairs have changed in the mentioned area, i.e. in G≡C, A (11, 15, 24) shifted from 178.2 to 176.3. The changes in the dihedral angles denote that the base pairs structure have shifted from the planar, i.e., D (3, 11, 15, 24) in G≡C exhibits the highest difference. As it is apparent from Tables 1 and 3, bond lengths, bond angles and the dihedral angles alter notably in a way that the hydrogen bonding becomes stronger, causing changes in the DNA molecule structure. Therefore, we should attempt to design herbicides which bring about the least changes in the above mentioned area. To evade repetition, the results attained for A=T are only listed in Tables 1, 3 and Figure 3, which are in agreement with those of G≡C.

To evaluate the dependence of the Intercalator-Base Pair Stacking interaction energy on their vertical separation, we started investigating the vertical distance between the interacting systems. The interaction energies were corrected for the basis set superposition error using the counterpoise method [36].

Figures 5a and 5b illustrate the investigated structures for A=T and G≡C with TB, respectively. As it is apparent from Figures 5a and 5b, the minimum values of the respective potential energy curve for TB···G≡C and TB···A=T were found at 3.9 Å, both. The stabilization energies (energy necessary to separate TB and the A=T pair to infinity) of TB···A=T and TB···G≡C were equal to -20.31 kcal/mol and -36.23 kcal /mol, respectively. Consequently, as the interaction energy increases, the distance between the DNA molecule and TB reduces.



(a)



(b)

Figure 5(a,b). Stabilization energies (ΔE) of TB···G≡C and TB···A=T, respectively

Furthermore the intercalation reaction between the TB and different double base pairs of DNA (A=T/A=T, A=T/T=A, A=T/G≡C, A=T/C≡G, C≡G/G≡C, C≡G/C≡G) was also studied using PM3 method. Figure 6 (A=T/G≡C) is a sample related to this study.

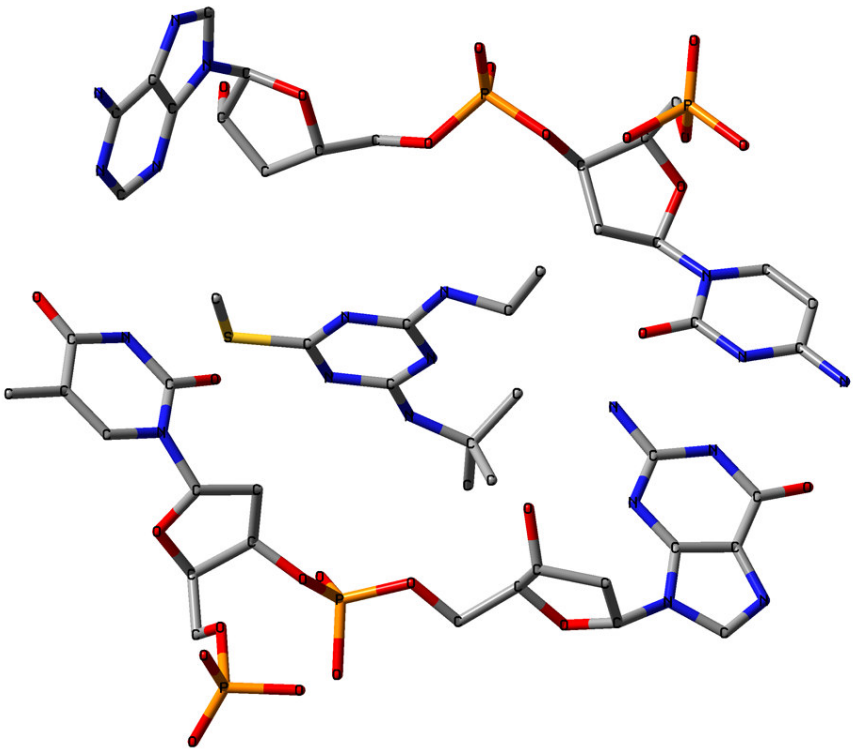


Figure 6. Optimized structures of TB with different DNA double base pair

Table 3. Significant computed geometrical parameters for DNA base pairs before and after the complex formation

Bond (Å)	G≡C	G≡C···TB	Angle(°)	G≡C	G≡C···TB	Dihedral(°)	G≡C	G≡C···TB
(1,2)	1.410	1.410	(2,1,10)	119.9	119.7	(10,1,2,3)	-180.0	-177.9
(1,10)	1.234	1.266	(1,2,3)	125.9	125.1	(10,1,2,12)	0.0	-2.7
(2,3)	1.373	1.384	(1,2,12)	115.2	115.6	(2,1,10,29)	0.0	-1.8
(2,12)	1.032	1.043	(3,2,12)	118.9	119.1	(1,2,3,11)	-180.0	177.7
(3,11)	1.349	1.350	(2,3,11)	116.8	117.4	(1,2,12,22)	-0.5	-48.5
(10,29)	1.765	1.723	(2,12,22)	177.1	176.3	(1,10,29,23)	1.8	77.0
(11,15)	1.020	1.026	(10,29,23)	179.1	177.2	(3,11,15,24)	-0.1	-55.2
(11,16)	1.005	1.006	(11,15,24)	178.2	176.3	(12,2,3,11)	0.0	2.6
(12,22)	1.910	1.842	(1,10,29)	127.2	126.2	(2,3,11,15)	-0.1	-2.5
(15,24)	1.915	1.840	(3,11,15)	123.1	123.0	(2,3,11,16)	-180.0	-179.3
(17,22)	1.336	1.354	(3,11,16)	116.7	116.9	(23,17,22,21)	-180.0	-176.4
(17,23)	1.335	1.339	(15,11,16)	120.3	120.0	(22,17,23,28)	-180.0	179.8
(21,22)	1.357	1.365	(22,17,23)	117.9	117.8	(22,17,23,29)	0.0	-1.2
(21,24)	1.229	1.264	(22,21,24)	124.6	124.0	(24,21,22,17)	-180.0	175.5
(23,28)	1.006	1.007	(17,22,21)	121.4	121.2			
(23,29)	1.035	1.037	(17,23,28)	120.1	120.4			
(23,29)	1.035	1.037	(17,23,29)	120.6	120.7			
			(28,23,29)	119.3	118.9			

Bond (Å)	A=T	A=T···TB	Angle(°)	A=T	A=T···TB	Dihedral(°)	A=T	A=T···TB
(1,2)	1.351	1.366	(2,1,10)	119.7	119.0	(10,1,2,3)	180.0	-178.4
(1,10)	1.341	1.344	(1,2,3)	119.7	120.8	(10,1,2,26)	0.0	1.7
(2,3)	1.346	1.358	(1,2,26)	123.2	123.0	(2,1,10,13)	0.0	-5.2
(2,26)	1.823	1.700	(3,2,26)	117.1	116.2	(2,1,10,14)	180.0	176.4
(3,12)	1.086	1.082	(2,3,12)	114.8	115.2	(2,3,12,24)	0.0	4.3
(10,13)	1.020	1.024	(1,10,13)	120.7	120.4	(1,2,3,12)	180.0	177.9
(10,14)	1.006	1.007	(1,10,14)	118.6	119.6	(26,2,3,12)	0.0	-2.2
(12,24)	2.852	2.641	(2,26,18)	179.3	177.6	(1,2,18,16)	-180.0	179.9
(13,23)	1.929	1.885	(10,13,23)	173.4	172.4	(1,2,18,19)	0.0	5.7
(16,18)	1.380	1.384	(3,12,24)	132.7	134.5	(3,2,18,19)	179.9	-173.3
(16,24)	1.214	1.246	(13,10,14)	120.6	119.9	(10,1,2,26)	0.0	1.7
(18,19)	1.389	1.388	(18,16,24)	124.4	124.2	(24,16,18,19)	-180.0	174.3
(18,26)	1.046	1.062	(16,18,19)	127.1	126.4	(24,16,18,26)	0.0	-0.9
(19,23)	1.229	1.265	(16,18,26)	115.9	115.7	(16,18,19,23)	-180.0	-173.8
			(19,18,26)	117.0	117.7	(19,18,26,2)	4.2	-108.6
			(18,19,23)	120.8	120.6	(26,18,19,23)	0.0	1.3

[a]after the complex formation with A=T or G≡C

4. CONCLUSIONS

1. In this research, it was demonstrated that TB is a good electron doner with high polarizability and dipole moment. While in contrast, A=T and G≡C base pairs are good electron acceptors.
2. These conclusions are favorable for the aromatic stacking interactions between these two systems. It was also found that the theoretical procedures could properly examine the dispersion and the polarization effects. Subsequently, they could be used for the study of the intercalation processes.

3. Additionally, charge differences, geometric changes (bond length, bond angle and dihedral angle) and also the calculated interaction energies (-20.31 kcal/mol and -36.23 kcal /mol for TB···A=T and TB···G≡C, respectively) prove the strong intercalation of TB and DNA base pairs.
4. The designed herbicide should exhibit the least interaction with DNA to decrease the side effects which means it should be designed in a way that it would have the least polarizability and dipole moment in order to decrease the interactions between DNA and the herbicides.

ACKNOWLEDGEMENTS
We gratefully acknowledge generous allocations of computing from the Institute of Petroleum Engineering, University of Tehran for Advanced Computing and Supercomputing Facilities.

References

1. Al-Saleh, *J. Environ. Pathol. Tox.,* 13 (1994) 151
2. IARC, Internation al Agency for Research on Cancer, IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Vol. 53, Occupational Exposure in Insecticide Application and Some Pesticides, International Agency for Research on Cancer, Lyon, p. 441, 1991.
3. Italian Health Ministry, D.M. 705/475, Rome, 1991.
4. IARC, Internation al Agency for Research on Cancer, IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Vol. 73, Some Chemicals that Cause Tumours of the Kidney or Urinary Bladder in Rodents and Some Other Substances, International Agency for Research on Cancer, Lyon, p. 59, 1999.
5. K. E. Steinback, L. McIntosh, L. Bogorad and C. J. Arntzen, *Proc. Natl. Acad. Sci. USA,* 78 (1981) 7463
6. E. L. Nilson and R. F. Unz, *Appl. Environ. Microb.,* 34 (1977) 815
7. National Health Institute, Guidelines of the Italian CCTN (National Advisory Toxicological Committee) for the classification of some effects of chemical substances. In: N. Mucci and I. Camoni (Eds.), National Health Institute Report Series 96/2. National Health Institute, Rome, 1996.
8. M. Elstner, P. Hobza, T. Frauenheim, S. Suhai and E. Kaxiras, *J. Chem. Phys.,* 114 (2001) 5149
9. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, 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, 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 and J. A. Pople, Gaussian Inc. Pittsburgh PA, 1998.
10. S. Riahi, M. R. Ganjali, R. Dinarvand, S. Karamdoust, K. Bagherzadeh and P. Norouzi, *Chem. Biol. Drug. Des.,* 71 (2008) 474
11. J. J. P. Stewart, *J. Comp. Chem.,* 10 (1989) 209
12. R. G. Parr and W. Yang, *Annu. Rev. Phys. Chem.,* 46 (1995) 701
13. F. B. Vanduijneveldt, J. G. C. M. Vanduijneveldtvanderijdt and J. H. Vanlenthe, *Chem. Rev.,* 94 (1994) 1873

14. Riahi, A. B. Moghaddam, M. R. Ganjali, P. Norouzi and M. Latifi, *J. Theor. Comput. Chem. (JTCC),* 6 (2007) 255.
15. S. Riahi, P. Norouzi, A. B. Moghaddam, M. R. Ganjali, G. R. Karimipour and H. Sharghi, *Chem. Phys.* 337 (2007) 33.
16. S. Riahi, A. B. Moghaddam, M. R. Ganjali and P. Norouzi, *J. Mol. Struct. (THEOCHEM),* 814 (2007) 131.
17. S. Riahi, M. R. Ganjali, A. B. Moghaddam, P. Norouzi and S. S. Hosseiny Davarani, *Spectrochim Acta, Part A,* 70 (2008) 94
18. S. Riahi, M. R. Ganjali, P. Norouzi and F. Jafari, *Sens. Actuators B,* 132 (2008) 13.
19. S. Riahi, A. Beheshti, M. R. Ganjali and P. Norouzi, *Spectrochim. Acta Part A,* 74 (2009) 1077.
20. M. R. Ganjali, A. Alipour, S. Riahi, B. Larijani and P. Norouzi, *Int. J. Electrochem. Sci.,* 4 (2009) 1262.
21. Riahi, M. R. Ganjali, A. B. Moghaddam and P. Norouzi, *J. Theor. Comput. Chem. (JTCC),* 6 (2007) 331.
22. S. Riahi, M. R. Ganjali, A. B. Moghaddam and P. Norouzi, *J. Theor. Comput Chem. (JTCC),* 6 (2007) 255.
23. S. Riahi, S. Eynollahi and M. R. Ganjali, *Int. J. Electrochem. Sci.,* 4 (2009) 1407.
24. S. Riahi, S. Eynollahi and M. R. Ganjali, *Int. J. Electrochem. Sci.,* 4 (2009) 1128.
25. S. Riahi, S. Eynollahi, M. R. Ganjali, *Int. J. Electrochem. Sci.,* 4 (2009) 551.
26. S. Riahi, M. R. Ganjali, A. B. Moghaddam, P. Norouzi and M. Niasari, *J. Mol. Struct. (Theochem)*, 774 (2006) 107.
27. S. Riahi, A. B. Moghaddam, P. Norouzi and M. R. Ganjali, *J. Mol. Struct. (Theochem)*, 814 (2007) 131.
28. S. Riahi, F. Jalali Farahani, M. R. Ganjali, A. B. Moghaddam and P. Norouzi, *J. Mol. Struct. (Theochem)*, 850 (2008) 48.
29. S. Riahi, M. R. Ganjali, P. Norouzi and F. Jafari, *Sens. Actuators, B*, 132, (2008) 13.
30. S. Riahi, A. B. Moghaddam, M. R. Ganjali and P. Norouzi, *J. Mol. Struct. (Theochem)*, 896 (2009) 63.
31. M.R. Ganjali, T. Razavi, F. Faridbod, S. Riahi and P. Norouzi, Curr. Pharm. Anal, 5 (2009) 28.
32. S. Riahi, P. Pourhossein, A. Zolfaghari, M.R. Ganjali and H. Z. Jooya, Fuller Nanotub Car N, 17 (2009) 159.
33. F. Faridbod, M.R. Ganjali, R. Dinarvand, S. Riahi and P. Norouzi, *J Food Drug Anal*, 17 (2009) 264.
34. S. Riahi, S. Eynollahi, M.R. Ganjali and P. Norouzi, *Int. J. Electrochem. Sci.,* 5 (2010) 355.
35. P. Hobza and R. Zahradnik, Intermolecular Complexes, Elsevier, Amsterdam, 1988.
36. M. J. Frisch, J. E. Del Bene, J. S. Binkley and H. F. Schaefer, *J. Chem. Phys.,* 84 (1986) 2279

© 2009 by ESG (www.electrochemsci.org)