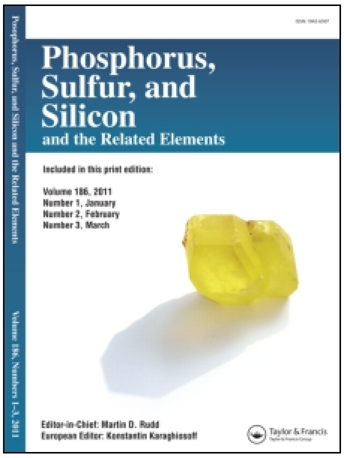

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Configurational and Conformational Properties of 1,3,7,9-Tetraphospha-Cyclododeca-1,2,7,8-tetraene: An Ab Initio Study and NBO Analysis

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Configurational and Conformational Properties of 1,3,7,9-Tetraphospha-Cyclododeca-1,2,7,8-tetraene: An Ab Initio Study and NBO Analysis

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An investigation employing the ab initio molecular orbital (MO) and density functional theory (DFT) methods to calculate structural optimization and conformational interconversion pathways for the two diastereoisomeric forms, (±) and meso *configurations of 1,3,7,9-tetraphospha-cyclododeca-1,2,7,8-tetraene (**1**) was undertaken. Two axial symmetrical conformations are found for (±)-**1** configuration. (±)-**1**-TB axial symmetrical form is found to be about 0.35 and 0.99 kcal mol^{-1} more stable than (±)-**1**-Crown axial symmetrical conformation, as calculated by HF/6-31G*//HF/6-31G* and B3LYP/6-31G*//HF/6-31G* levels of theory, respectively. The unsymmetrical* meso-**1**-*TBCC form is found to be the most stable geometry, among the various conformations of* meso-**1** *configuration. HF/6-31G*//HF/6-31G* and B3LYP/6-31G*//HF/6-31G* results showed that between the two most stable conformations of (±) and* meso *configurations, (±)-**1**-TB is more stable than* meso-**1**-*TBCC by about 3.35 and 2.43 kcal mol^{-1}, respectively. In addition, MP2/6-31G* and B3LYP/6-311+G** results showed that the (±)-**1**-TB form is about 1.10 and 2.36 kcal mol^{-1} more stable than the* meso-**1**-*TBCC form. Further, NBO results revealed that in the most stable form of* meso *configuration (*meso-**1**-*TBCC), the sum of the π^* allenic antibonding orbital occupancies ($\Sigma\pi^*_{occupancy}$) is greater than* dl *configuration ((±)-**1**-TB). Also, NBO results indicated that in the (±)-**1**-TB conformer, the sum of σ and π allenic moieties bonding orbital deviations ($\Sigma\sigma_{dev}+\Sigma\pi_{dev}$) from their normal values, is lower than in the* meso-**1**-*TBCC form.*

Keywords Ab initio; conformational analysis; cyclic phosphadiimide; DFT; molecular modeling; NBO analysis

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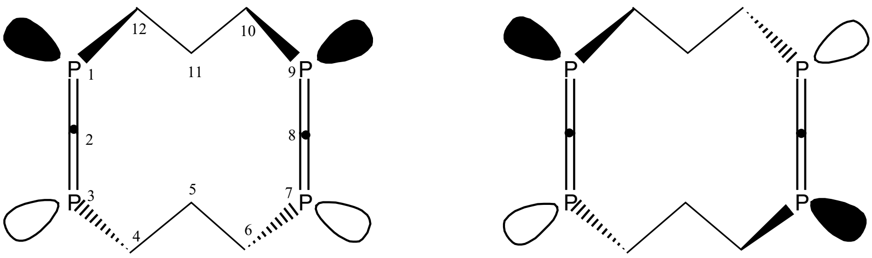
INTRODUCTION

Cyclic phosphadiimides possess two torsional constraints, but there is an unusual strain where the constrained bonds are adjacent to one another with perpendicular geometries. Monocyclic medium-rings containing two phosphadiimides (P=C=P) moieties are strained compounds, the detailed structural and dynamic features of which are largely unexplored.[1,2] Ring constraints bend and twist the normally linear perpendicular cumulene-type bonds and engender substantial strain and resultant kinetic reactivity.[3] It seems these compounds such as those parent hydrocarbons[4–7] possess two chiral centers and should exist in two diastereoisomeric forms, one diasereisomer being racemic and the other a *meso* compound.

Recently, we reported ab initio calculations and NBO for the configurational and conformational properties of Cyclododeca-1,2,7,8-tetraene.[8] We now report a detailed ab initio MO, DFT calculations, and NBO analysis on the conformational and configurational features of *meso*-and (±)-isomers of 1,3,7,9-tetraphospha-cyclododeca-1,2,7,8-tetraene (1) (see Scheme 1).

In this work, we have investigated computationally the structural, conformational properties of compound **1**, by both ab initio MO and DFT methods, using the GAUSSIAN 98 package of programs.[9–13] In addition, the cumulative bonds nature (population and bonding orbital deviation) and the stability of various conformations of (±) and *meso* configurations of compound **1**, was systematically and quantitatively correlated using NBO analysis.[14,15]

In view of the limited information concerning the phosphadiimide cumulative bonds, it is possible to learn something about it by using



meso-**1** (±)-**1**

[Numbering used for *meso* and (±) configurations of compound **1**]

SCHEME 1

theoretical methods that have proved to be reliable in other applications. Effectively, the successful application of density functional theory (DFT) based methods broadened the applicability of the computational methods and now represents an interesting approach for determining activation barrier and molecular energies.[10,11,13] Also, the B3LYP functional method combines Becke's three-parameter exchange function with the correlation function of Lee et al.[10,11]

Computational Details

In this work, the potential energy diagram of conformational properties of (±) and *meso*-configurations of compound **1** were investigated using HF/6-31G*//HF/6-31G ab initio molecular orbital (MO) and B3LYP/6-31G*//HF/6-31G* density functional theory (DFT) methods. These calculations were performed using GAUSSIAN 98 package of programs[16] implemented on a Pentium–PC computer with 1.7 GHz processor.

More time consuming MP2/6-31G* and B3LYP/6-311+G** levels of theory were also used to optimize the structures and minimize the energies of (±)-**1**-TB, *meso*-1-TBCC, *meso*-**1**-TBBC, *meso*-**1**-TCCC and *meso*-1-TBCB geometries, in order to compare them with the HF/6-31G* results.

Initial estimation of structural geometries of (±) and *meso*-configurations of compound **1**, was obtained by PCMODEL (88.0)[20] molecular mechanic program. PM3 method of MOPAC 7.0 computer program was used[21,22] for further geometry optimizations. GAUSSIAN 98 program was finally used to perform ab initio calculations at the HF/6-31G* level of theory for geometry optimization. Energy minimum molecular geometries were located by minimizing energy, with respect to all geometrical coordinates without imposing any symmetrical constraints. The nature of the stationary points has been fixed by means of the number of imaginary frequencies. For minimum state structures, only real frequency values, and in the transition-state, only single imaginary frequency value was accepted.[23,24] The structures of the molecular transition state geometries were located using the optimized geometries of the equilibrium molecular structures according to the Dewar et al procedure (keyword SADDLE).[25] The transition state geometry structures were obtained by QST2 or QST3 subroutines at the HF/6-31G* level. The vibrational frequencies of ground states and transition states were calculated by FREQ subroutine. Finally, based on the HF/6-31G* optimized geometries, NBO analysis was performed by the NBO 3.1 program,[18] included in GAUSSIAN 98 package of programs.

RESULTS AND DISCUSSION

Corrected zero point (ZPE^c) and total electronic (E_{el}) energies ($E_o = E_{el}+ZPE^c$) for important conformations of *meso* and *dl* configurations of compound **1**, as calculated by the ab initio molecular orbital (HF/6-31G*//HF/6-31G*) and density functional theory (B3LYP/6-31G*//HF/6-31G*) methods, are used to compare these forms (see Figures 1 and 2). In addition, in order to evaluate the quality of the HF/6-31G*//HF/6-31G* and B3LYP/6-31G*//HF/6-31G* results, higher MP2/6-31G* and B3LYP/6-311+G** levels of theory were also used for energy minimization of the more stable conformations of (±) and *meso* configurations of compound **1** (namely: (±)-**1**-TB, *meso*-**1**-TBCC, *meso*-**1**-TBBC, *meso*-**1**-TCCC and *meso*-**1**-TBCB), (see Table I).

The π bonding and π^* antibonding orbital occupancies and also the deviations of σ and π bonding orbitals of phophadiimide moieties in the most stable conformations of (±)-**1** and *meso*-**1** configurations of compound **1**, were calculated using NBO analysis.

The energy surfaces for the interconversion of the energy-minimum conformations of (±)-**1** and *meso*-**1**, were obtained by changing different torsional angles, as shown in Figures 1 and 2.

Three ground state geometries were found to be necessary for a description of the conformational properties of (±)-1,3,7,9-tetraphospha-cyclododeca-1,2,7,8-tetraene (**1**). Also, there are two distinct transition states (excluding the mirror images), which are required to describe the dynamic conformational properties of (±)-**1**. The most stable conformation of (±)-**1** is found to be an axial symmetrical twist-boat geometry (Figure 1). The calculated energy for the second lowest energy-minimum conformation, viz. twist (C_1) is 1.16 and 0.97 kcal mol^1, as calculated by HF/6-31G*//HF/6-31G* and B3LYP/6-31G*//HF//6-31G* levels of theory, respectively. The structure of the transition state (TS) is obtained from QST3 subroutine using the optimized geometries of (±)-**1**-Twist-Boat and (±)-**1**-Twist conformations. The calculated energy barrier for interconversion of these two forms is 11.58 and 9.97 kcal mol^1, as calculated by HF/6-31G*//HF/6-31G* and B3LYP/6-31G*//HF//6-31G* levels of theory, respectively.

Third lowest energy-minimum structure of (±)-1,3,7,9-tetraphospha-cyclododeca-1,2,7,8-tetraene (**1**) is the axial symmetrical crown form, (±)-**1**-crown, having nonintersecting C_2 symmetry element. The (±)-**1**-crown conformation is found to be less stable than the (±)-**1**-T conformer by about 0.99 and 0.35 kcal mol^1, as calculated by HF/6-31G*//HF/6-31G* and B3LYP/6-31G*//HF//6-31G* levels of theory, respectively (Figure 1). The calculated energy barrier for interconversion of (±)-**1**-Twist and (±)-**1**-Crown forms is 8.56

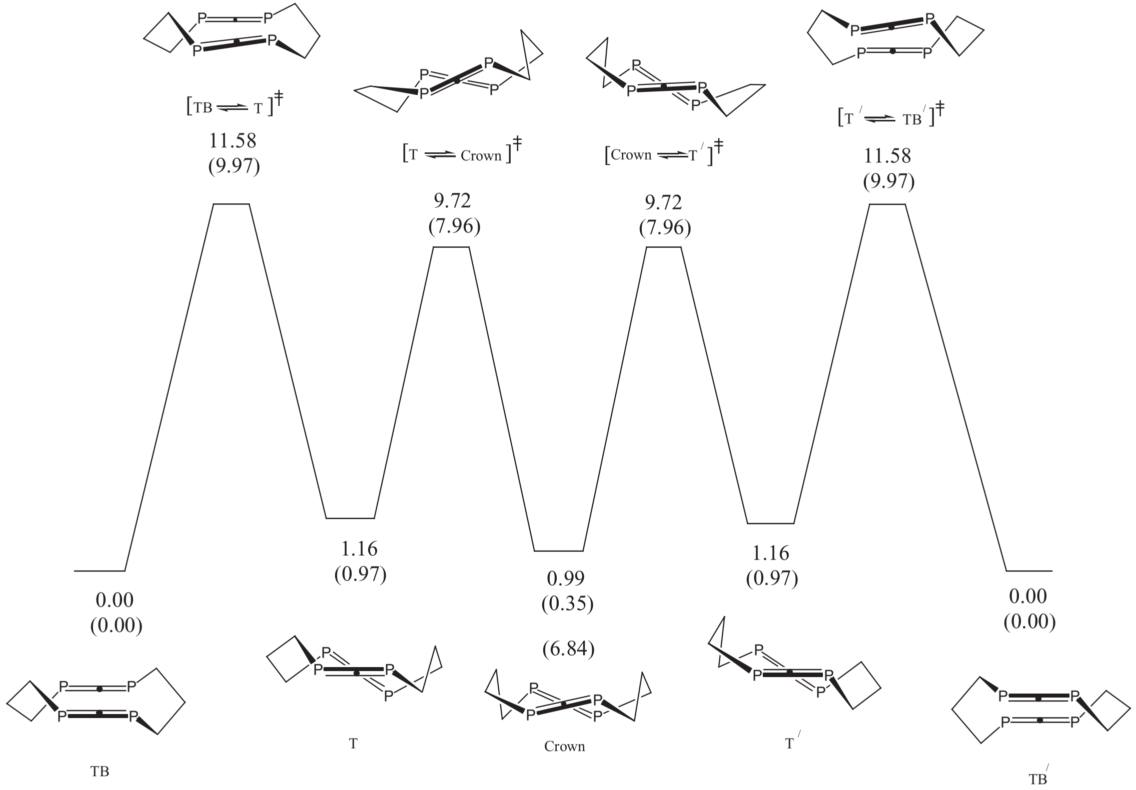


FIGURE 2 HF/6-31G* calculated conformational interconversion profile of (±)-**1**. The values in the parenthesis are obtained by B3LYP/6-31G*//HF/6-31G*level of theory.

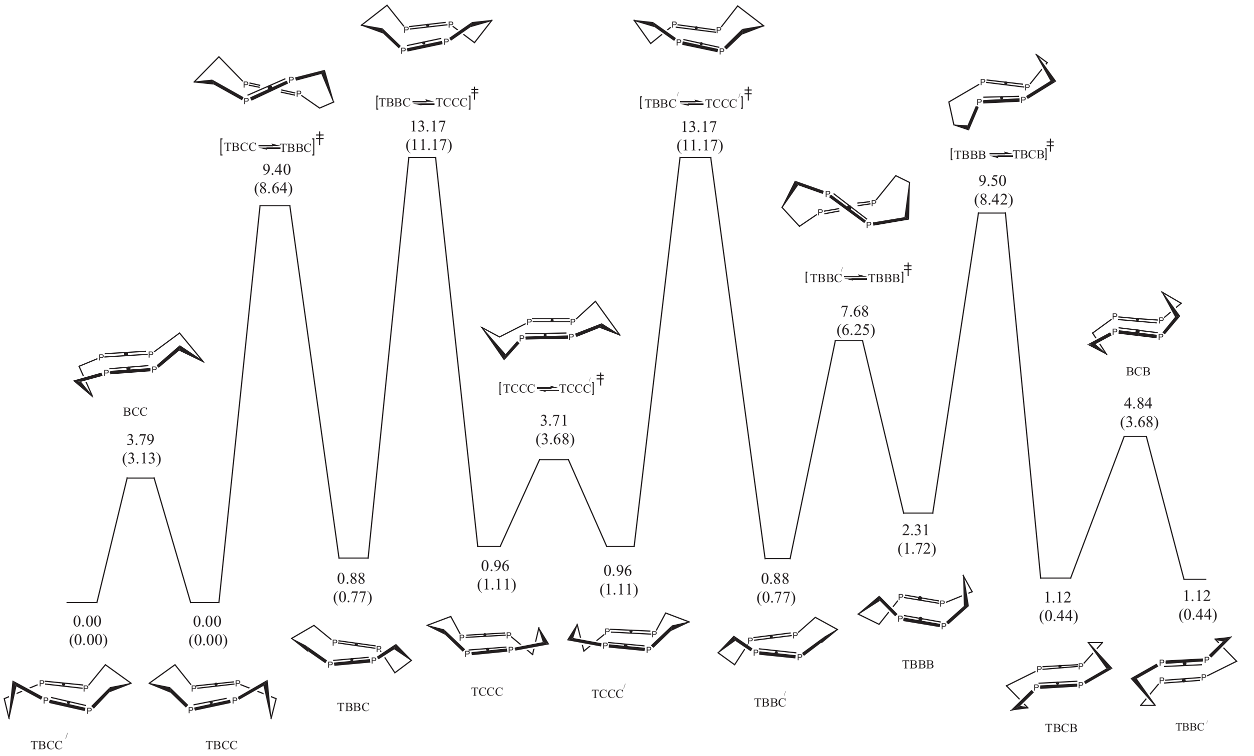


FIGURE 3 HF/6-31G* calculated conformational interconversion profile of *meso*-**1**. The values in the parenthesis are obtained by B3LYP/6-31G*//HF/6-31G*level of theory.

TABLE I MP2/6-31G* and B3LYP/6-311+G Calculated Energies (in Hartree) for the More Stable Energy-Minimum Geometries of (±) and *Meso* Configurations of Compound 1**

	MP2/6-31G*				B3LYP/6-311+G**			
Method compound	$ZPE^{c,d}$	E_{el}	E_0	ΔE_0^{a}	ZPE	E_{el}	E_0	ΔE_0^{a}
(±)−1−**TB**	0.180633	−1674.151436	−1673.970803	0.00000 (0.000000)[b]	0.166725	−1677.553991	−1677.387266	0.000000 (0.000000)[b]
meso-1-**TBCC**	0.180555	−1674.149605	−1673.969050	0.001753 (1.100025)[b]	0.166577	−1677.550077	−1677.383500	0.003766 (2.363203)[b]
meso-1-**TBBC**	0.180615	−1674.148603	−1673.967988	0.002815 (1.766441)[b]	0.166623	−1677.548895	−1677.382272	0.004994 (3.133785)[b]
meso-1-**TCCC**	0.180482	−1674.147028	−1673.966546	0.004257 (2.671310)[b]	0.166584	−1677.548474	−1677.381890	0.005376 (3.373494)[b]
meso-1-**TBCB**	0.180761	−1674.148945	−1673.968184	0.002619 (1.643449)[b]	0.166818	−1677.549256	−1677.382438	0.004828 (3.029618)[b]

[a] Relative to the ground state; [b] numbers in parenthesis are the corresponding ΔE values in kcal mol^{1}; [c] corrected by multiplying by a scaling factor (0.9135); and [d] from HF/6-31G*.

and 6.99 kcal mol^1, as calculated by HF/6-31G*//HF/6-31G* and B3LYP/6-31G*//HF//6-31G* levels of theory, respectively.

The unsymmetrical TBCC conformation is the most stable form of *meso*-**1** configuration (Figure 2). Conformational racemization of *meso*-**1**-TBCC form can take place via the plane symmetrical BCC geometry, and requires an energy about 5.35 kcal mol^1, as calculated by B3LYP/6-31G*//HF/6-31G* method. Also, conformational interconversion barrier height between *meso*-**1**-TBCC and *meso*-1-TBBC forms is 8.64 kcal mol^1, as calculated by B3LYP/6-31G*//HF/6-31G* method. On the other hand, the*meso*-**1**-TBCC racemization could take place via another plane symmetrical BCB conformation. For this purpose, *meso*-**1**-TBBC conformation should, first, be converted to *meso*-**1**-TBCB conformation, via a minimum geometry, namely *meso*-**1**-TBBB conformation. The racemization process could be completed, if the *meso*-**1**-TBCB conformation could be converted to its mirror image (e.g., *meso*-**1**-TBCB'), via the plane symmetrical BCB conformation (Figure 2).

Based on the obtained energy profile (Figure 2), the required energy for the racemization process via the plane symmetrical BCC form is found to be less than BCB conformation.

The use of higher level but more time consuming MP2/6-31G* and B3LYP/6-311+G** methods, have also confirmed, quantitatively, the results obtained by HF/6-31G*//HF/6-31G* and B3LYP/6-31G*//HF/6-31G* methods concerning the energy difference between the most stable forms of (±) and *meso* configurations of compound **1** [(±)-**1**-TB and *meso*-**1**-TBCC conformations, respectively].

Accordingly, MP2/6-31G* and B3LYP/6-311+G** results showed, respectively, that the (±)-**1**-TB form is about 1.10 and 2.36 kcal mol^1 more stable than the *meso*-**1**-TBBC form. These results are in agreement with those obtained by HF/6-31G*//HF/6-31G* and B3LYP/6-31G*//HF/6-31G* levels of theory (see Table I).

Based on the energetic results, it could be concluded that, all the various conformations of *meso* and (±) configurations of compound **1**, could be significantly populated at room temperature.

As the geometrical strain on the phosohadiimide moieties are expected to have an impact on the bonding nature in the (±)-**1**-TB and *meso*-**1**-TBCC forms, therefore, NBO analysis was also used to investigate this aspect. Accordingly, NBO analysis was used to investigate the π and π^* bonding and antibonding orbital occupancies and also the deviations of σ andπ bonding orbitals of phosphadiimide moieties. Effectively, NBO results revealed that the sum of the π^* allenic antibonding orbital occupancies ($\Sigma\pi^*_{\text{occupancy}}$), in the most stable form of *meso* configuration, is greater than (±) configuration (see Table II). NBO results

TABLE II NBO Calculated π Bonds Occupancies of Allenic Moieties of Compound 1, Based on the HF/6-31G* Calculated Geometries

Geometry	**1**-TB-(±)	*meso*-**1**-TBCC
Occupancies		
$\Sigma\pi_{\text{occupancy}}$	7.87052	7.87004
$\Sigma\pi^*{}_{\text{occupancy}}$	0.27692	0.28407
$\Delta(\Sigma\pi_{\text{occupancy}} - \Sigma\pi^*{}_{\text{occupancy}})$	7.59360	7.58597

indicate also that the deviations of σ andπ bonding orbitals of allenic moieties ($\Sigma\sigma_{dev}+\Sigma\pi_{dev}$) in the (±)-**1**-TB conformer, are less than in the *meso*-**1**-TBBC form (see Table III).

Both, the lower occupancy of the antibonding π^* orbitals and lower deviations of σ and π hybridized bonding orbitals, should increase the strength of the σ and π bonds, and should therefore have an impact on the molecular stability. These facts could explain the relative stability of (±)-**1**-TB conformer, as compared to the *meso*-1-TBCC form.

Structural parameters for various conformations of (±)-1 and *meso*-1 configurations are calculated by HF/6-31G* level of theory. Although, due to the nature of the various approximations involved in theoretical calculations, it is not expected, in principal, to obtain exactly the experimental values;[27] however, it is possible to carry out theoretical calculations, from which many properties and structures can be obtained with an accuracy that is competitive with experiments.[28–31]

HF/6-31G* results showed that $\phi_{4\text{-}3\text{-}1\text{-}12}$ torsion angles (ϕ $_{\text{Csp3}-\text{P}=\text{C}=\text{P}-\text{Csp3}}$) in (±)-**1**-TB and (±)-**1**-T conformers, are 93.2° and 98.3°, respectively. It is clear that, in phosphadiimide moieties, the deviation of $\phi_{\text{Csp3}-\text{P}=\text{C}=\text{P}-\text{Csp3}}$ torsion angle from the normal (91.0° for Dimethylphosphadiimide) value would affect the relative stability of these compounds due to the increase of torsional strain energy.

TABLE III NBO Calculated σ Bonds Deviation of Cyclododeca-1,2,7,8-tetraene Ring, and π Bonds of Allenic Moieties, Based on the HF/6-31G* Calculated Geometries

	(±)-**1**-TB	*meso*-**1**-TBCC
Deviations		
$\Sigma\sigma_{dev}$	76.4	92.7
$\Sigma\pi_{Dev}$	38.8	32.2
$\Sigma\sigma_{dev}+\Sigma\pi_{dev}$	115.2	124.9

Therefore, the higher deviation of $\phi_{\mathrm{Csp3-P=C=P-Csp3}}$ torsion angles, from the normal value in (±)-1-T as compared to (±)-1-TB conformer, would explain the relative instability of the former conformer.

HF/6-31G* results showed that $\phi_{4\text{-}3\text{-}1\text{-}12}$ and $\phi_{6\text{-}7\text{-}9\text{-}10}$ torsion angles in (±)-1-TB is 93.2° and for *meso*-1-TBCC form are 87.7 and 91.3°, respectively. Therefore, based on the HF/6-31G* results, the deviation of this torsion angle from its normal 91.0° value, in *meso*-1-TBCC form, is more than in (±)-1-TB form. The increase of the π^* antibonding orbital occupancies could also be regarded as a result of the increase of strain due to the resulting deviation of the torsion angle from its normal value. It is clear that the decrease of strain (e.g., lower deviation of structural parameters from their normal values) should increase the molecular structural stability. Consequently, the presence of lower strain in (±)-**1**-TB form, explain fairly its more relative stability, as compared to *meso*-**1**-TBBC conformation.

CONCLUSION

Ab initio MO, DFT calculations and NBO analysis provided a reasonable picture from structural, energetic and bonding points of view for the various conformations of two diastereoisomeric forms ((±) and *meso* configurations) of 1,3,7,9-tetraphospha-cyclododeca-1,2,7,8-tetraene (**1**). Effectively, the results showed mainly that:

- between the two axial symmetrical conformations, namely (±)-**1**-TB and(±)-**1**-crown, the former is found to be the more stable form;
- among the various conformations of *meso*-**1** configuration, the unsymmetrical TBCC form was found also to be the most stable geometry;
- the conformational racemization of *meso*-**1**-TBCC can take place via the plane symmetrical BCC geometry; and
- all the various conformations of *meso* and (±) configurations of compound **1**, could be significantly populated at room temperature.

In addition, NBO results revealed also that:

- the sum of the π^* allenic antibonding orbital occupancies ($\Sigma\pi^*_{occupancy}$) in the most stable form of *meso* configuration is greater than in (±) configuration; and
- the deviations of σ and π bonding orbitals of allenic moieties ($\Sigma\sigma_{dev}+\Sigma\pi_{dev}$), in the (±)-**1**-TB conformer, is lower than in the *meso*-**1**-TBBC form.

In summary, these facts could fairly explain the relative more stability of (±)-**1**-TB conformer compared to the *meso*-**1**-TBCC form.

REFERENCES

[1] A. Greenberg and J. F. Liebman, *Strained Organic Molecules* (Academic Press, New York, 1979).

[2] M. Traetteberg, P. Bakken, and A. Almenningen, *J. Mol. Struct.*, **70,** 287 (1981).

[3] R. P. Johnson, *Chem. Rev.*, **89,** 1111 (1989).

[4] I. Yavari, R. Baharfar, D. Nori-Shargh, and A. Shaabani, *J. Chem. Res. (S)*, 162 (1997).

[5] I. Yavari, R. Baharfar, and D. Nori-Shargh, *J. Mol. Struct. (Theochem)*, **393,** 167 (1997).

[6] I. Yavari, D. Nori-Shargh, and K. Najafian, *J. Mol. Struct. (Theochem)*, **467,** 147 (1999).

[7] D. Nori-Sgargh, N. Saroogh-Farahani, S. Jameh-Bozorghi, F. Deyhimi, M.-R. Talei Bavil Oliai, and F. R. Ghanizadeh, *J. Chem. Res. (S)*, 384 (2003).

[8] D. Nori-Shargh, F. R. Ghanizadeh, M. Malak Hosseini, and F. Deyhimi, *J. Mol. Struct. (Theochem)*, **808,** 135 (2007).

[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, Jr. 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, M. Head-Gordon, E. S. Replogle, and J. A. Pople. *GAUSSIAN 98* (Gaussian Inc. Pittsburgh, PA, 1998), Revision A.3.

[10] A. D. Becke*, J. Chem. Phys.*, **98,** 5648 (1993).

[11] C. Lee, W. Yang, and R. G. Parr, *Phys. Rev*. B, **37,** 785 (1988).

[12] W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab initio Molecular Orbital Theory* (Wiley, New York, 1986).

[13] J. M. Seminario and P. Politzer, Eds., *Modern Density Function Theory, A Tool for Chemistry* (Elsevier, Amsterdam, 1995).

[14] E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold, NBO Version 3.1.

[15] E. Reed, L. A. Curtiss, and F. Weinhold, *Chem. Rev.*, **88,** 899 (1988).

[16] Program available from Serena Software, P.O. Box 3076, Bloomington, IN 47402-3076, USA.

[17] J. J. P. Stewart, *QCPE 581*, Department of Chemistry, Indiana University, Bloomington, IN, USA.

[18] M. J. S. Dewar, E. F. Heally, and J. J. P. Stewart, *J. Chem. Soc, Faraday Trans.*, **80,** 227 (1984).

[19] F. Freeman, A. Phornvoranunt, and W. J. Hehre, *J. Phys. Org. Chem.*, **11,** 831 (1998).

[20] T. M. Gilbert, *Tetrahedron Lett.*, **39,** 9147 (1998).

[21] M. Remko, P. D. Lyne and W. G. Richards, *Phys. Chem. Chem. Phys.*, **1,** 5353 (1999).

[22] A. D. Strickland and R. A. Caldwell, *J. Phys. Chem.*, **97,** 13394 (1993).

[23] I. Arnason, G. K. Thorarinson, and E. Matern, *J. Mol. Struct. (Theochem).*, **91,** 454 (1998).