ORGANIC
LETTERS

2005
Vol. 7, No. 8
1509−1512

Planar Tetracoordinate Carbons in Cyclic Hydrocarbons

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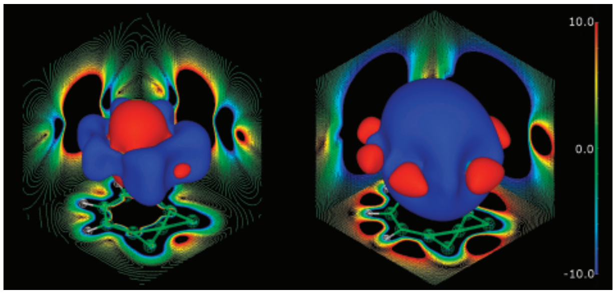
Received January 25, 2005

ABSTRACT



A series of cyclic hydrocarbons containing a planar tetracoordinate carbon atom is proposed. To rationalize the electronic factors contributing to the stability of these molecules, an analysis of the molecular orbitals and the induced magnetic field is presented.

Since the seminal paper entitled “Tetracoordinate Carbon Atom” of Hoffmann, Alder, and Wilcox,[1] several molecules with a planar tetracoordinate carbon (ptC) atom have been proposed in silico and characterized experimentally.[2] Two main approaches were pursued to stabilize such systems. The first mechanism arises from the delocalization of the electrons in the p orbital, which is located at the central carbon and perpendicular to the molecular plane. This can be accomplished by attaching electron acceptors to carbon (for example, metals). However, in most cases the ptC is linked to at least one atom different from carbon.[3a−e] (Beautiful examples of pentaatomic molecules have been predicted and detected by Boldyrev and Wang).[3f−j] In 1999, Rasmussen and Radom reported the first ptC surrounded only by carbons [ptC(C)$_4$], using another strategy: a mechanical approach.[4] Even, through substitution of carbon by boron atoms, Wang and Schleyer designed a set of spiroalkanes with a ptC(C)$_4$ stabilized mechanically and electronically.[5]

The simplest molecule with a ptC surrounded by four carbon atoms is C_5^{2-}.[6] This cluster and its metallic salts were

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(1) Hoffmann, R.; Alder, R. W.; Wilcox, C. F. *J. Am. Chem. Soc.* **1970**, *92*, 4992.

(2) Recent reviews: (a) Sorger, K.; Schleyer, P. v. R. *Theochem. J. Mol. Struct.* **1995**, *338*, 317. (b) Minkin, V. I.; Minyaev, R. M.; Hoffmann, R. *Usp. Khim.* **2002**, *71*, 989. (c) Rottger, D.; Erker, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 813. (d) Radom, L.; Rasmussen, D. R. *Pure Appl. Chem.* **1998**, *70*, 1977.

(3) (a) Li, S.-D.; Ren, G.-M.; Miao, C.-Q.; Jin, Z.-H. *Angew. Chem., Int. Ed.* **2004**, *43*, 1371. (b) Li, S.-D.; Ren, G.-M.; Miao, C.-Q. *J. Phys. Chem. A* **2005**, 109, 259. (c) Schleyer, P. v. R.; Boldyrev, A. I. *Chem. Commun.* **1991**, 1536. (d) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5419. (e) Wang, Z. X.; Manojkumar, T. K.; Wannere, C.; Schleyer, P. v. R. *Org. Lett.* **2001**, *3*, 1249. (f) Boldyrev, A. I.; Simons, J. *J. Am. Chem. Soc.* **1998**, *120*, 7967. (g) Li, X.; Wang, L. S.; Boldyrev, A. I.; Simons, J. *J. Am. Chem. Soc.* **1999**, *121*, 6033. (h) Boldyrev, A. I.; Wang, L. S. *J. Phys. Chem. A* **2001**, *105*, 10759. (i) Li, X.; Zhang, H. F.; Wang, L. S.; Geske, G. D.; Boldyrev, A. I. *Angew. Chem., Int. Ed.* **2000**, *39*, 3630. (j) Wang, L. S.; Boldyrev, A. I.; Li, X.; Simons, J. *J. Am. Chem. Soc.* **2000**, *122*, 7681.

(4) Rasmussen, D. R.; Radom, L. *Angew. Chem., Int. Ed.* **1999**, *38*, 2876.

(5) Wang, Z. X.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2002**, *124*, 11979.

10.1021/ol050170m CCC: $30.25

the first examples of molecules containing a ptC stabilized exclusively by electronic factors.[7] Priyakumar et al. and Esteves have used this moiety to design small hydrocarbons.[8] In a recent paper, the possibility of an extended 3D network based on the C_5^{2-} framework was also explored.[9] We now report a series of cyclic hydrocarbons containing a ptC. The stability and bonding scheme are analyzed through the study of the molecular orbitals (MOs) and the induced magnetic field, $\mathbf{B}^{ind}$.[10]

Geometry optimizations were carried out with Gaussian 03[11] using the B3LYP functional[12a,b] and a 6-311++G(2d,2p) basis set.[12c,d] In each case, the nature of the stationary point was determined by calculating and diagonalizing the Hessian matrix.[13] In addition, $\mathbf{B}^{ind}$ was calculated using PW91/IGLO-III.[14] The shielding tensors, NICS[15a] (nucleus-independent chemical shifts), and NICS_π[15b] (contributions of the π-orbitals to NICS), were computed using the IGLO[16] method. deMon[17] and deMon-NMR[18] programs were employed to calculate the MOs and the shielding tensors, respectively.[19] Graphics were created employing VU and Molekel.[20]

Candidates were designed by combining C_5^{2-} with an unsaturated hydrocarbon fragment. The removal of two hydrides from ethene and 1,3-dibutadiene provides the corresponding dications, which interact with C_5^{2-}, yielding the five- and seven-membered ring systems (C_7H_2, **1**, and C_9H_4, **3**), respectively. The same strategy is employed to build the six- and eight-membered anionic rings ($C_9H_3^-$, **2**, and $C_{10}H_5^-$, **4**) from allyl and pentadienyl anions. The harmonic analysis shows that all of them are local minima on their respective potential energy surfaces with appreciable positive lowest vibrational frequencies (>100 cm^{-1}, see Table 1).

Table 1. Smallest Frequencies (in cm^{-1}), Relative Energies for Structures along the Ring-Opening Process (in kJ mol^{-1}), and NICS and NICS_π (in ppm)

	1	**2**	**3**	**4**
freq	246.3	169.0	102.0	150.1
isomer B	−42.4	−28.9	−52.1	−110.7
TS	38.0	23.1	30.7	10.7
		Main Ring		
NICS	0.9	24.0	20.9	−8.7
NICS_π	−19.7	14.0	8.4	−15.9
		3-MRs[a]		
NICS	−36.1	−24.4	−28.9	−42.7
NICS_π	−26.4	−7.9	−16.3	−28.5

[a] Refers to the $C_1{-}C_2{-}C_3$ rings.

Clearly, the seven-membered ring molecule shows the largest geometrical distortion of the C_5^{2-} framework (Figure 1).[21] While the $C_1{-}C_2$ bond lengths decrease by 8.7 pm with respect to the free dianion, the $C_1{-}C_3$ bonds increase by 5.7 pm. In contrast, molecules **1** and **4** are less distorted.

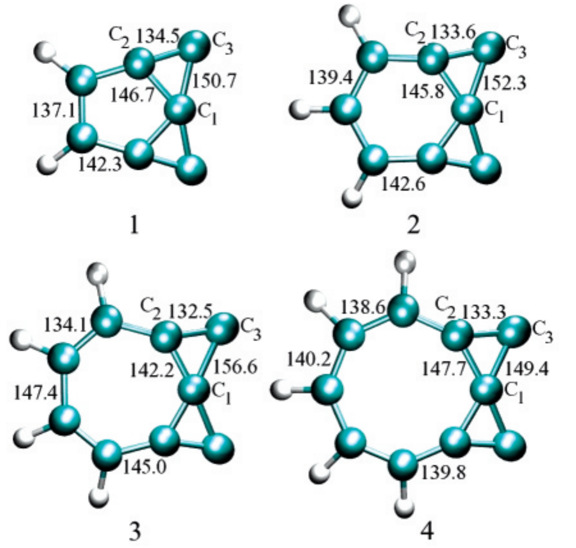

Figure 1. Optimized structures of cyclic hydrocarbons containing a ptC. Bond lengths are given in picometers.

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(6) Merino, G.; Mendez-Rojas, M. A.; Vela, A. *J. Am. Chem. Soc.* **2003**, *125*, 6026.

(7) Merino, G.; Mendez-Rojas, M. A.; Beltran, H. I.; Corminboeuf, C.; Heine, T.; Vela, A. *J. Am. Chem. Soc.* **2004**, *126*, 16160.

(8) (a) Priyakumar, U. D.; Reddy, A. S.; Sastry, G. N. *Tetrahedron Lett.* **2004**, *45*, 2495. (b) Priyakumar, U. D.; Sastry, G. N. *Tetrahedron Lett.* **2004**, *45*, 1515. (c) Esteves. P. M. Personal communication.

(9) Pancharatna, P. D.; Mendez-Rojas, M. A.; Merino, G.; Vela, A.; Hoffmann, R. *J. Am. Chem. Soc.* **2004**, *126*, 15309.

(10) Merino, G.; Heine, T.; Seifert, G. *Chem. Eur. J.* **2004**, *10*, 4367.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Gaussian Inc: Pittsburgh, PA, 2003.

(12) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. (d) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

(13) Minima connecting by transition state were confirmed by intrinsic reaction coordinate (IRC) calculations. Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363

(14) Kutzelnigg, W.; Fleischer, U.; Schindler, M. *The IGLO-Method: Ab Initio Calculation and Interpretation of NMR Chemical Shifts and Magnetic Susceptibilities*; Springer-Verlag: Heidelberg, 1990.

(15) (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. *J. Am. Chem. Soc.* **1996**, *118*, 6317. (b) Schleyer, P. v. R.; Jiao, H. J.; Hommes, N.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669.

(16) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193.

(17) Köster, A. M.; Flores, R.; Geudtner, G.; Goursot, A.; Heine, T.; Patchkovskii, S.; Reveles, J. U.; Vela, A.; Salahub, D. R. *deMon*; NRC: Ottawa, Canada, 2004.

(18) Malkin, V. G.; Malkina, O.; Salahub, D. R. *Chem. Phys. Lett.* **1993**, *204*, 80.

Note that in all cases the distance C_2-C_3 (a double bond) is almost constant.

Even though these structures are local minima, its experimental detection strongly depends on the magnitudes of the energy barriers that prevent them from distortion or fragmentation. To be experimentally detected in a given technique, the time needed to go from one minimum to another must be larger than the detection time. Certainly, the lifetimes of these species depends not only on the magnitudes of the energy barriers, but also on the detailed topography of the potential energy surface that drives the dynamics of the system. To analyze the energetic features, two isomers were considered for each molecule. Of the C_7H_2 isomers (Figure 2A), the first alternative (**1A**) converges to **1**, while **1B** is lower in energy than **1** by 42.4 kJ mol^{-1} (including the scaled ZPE correction).[22] The other hydrocarbons have an analogous trend (See Table 1).

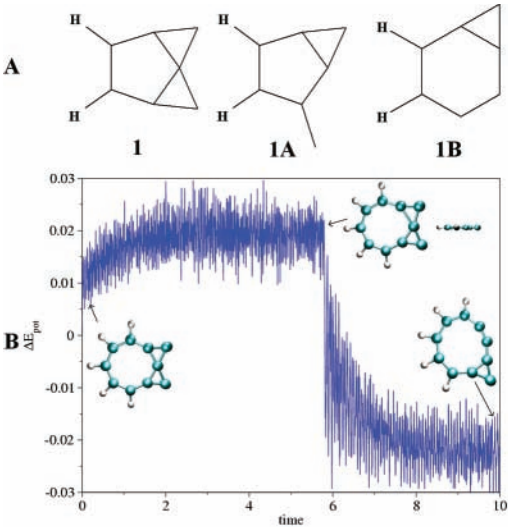

Figure 2. (A) Possible isomers of **1**. (B) BO-MD simulation for molecule **4**. Relative potential energy (ΔE_{pot}) (given in au) versus time (given in ps).

The starting points of the transitions state search involved in the ring opening were provided by the nudged elastic band method.[23] While the transition structures corresponding to **1** and **4** are planar (C_s symmetry), those for **2** and **3** are considerably distorted (geometries of the transition states and isomers are given in Figures 1-SI and 2-SI in Supporting Information). As expected, ring opening is accompanied by small activation barriers, lying in the range of 10−40 kJ mol^{-1} (Table 1). To obtain an estimate of the mean lifetimes of these molecules, a set of Born−Oppenheimer molecular dynamic (BO-MD) trajectories were done. For molecule **4** (the molecule with the lowest activation barrier), the planar structure preserves its geometry for about 6.0 ps at 300 K (Figure 2B).[24] Interestingly, an isomer of **1** has been detected in the interstellar medium.[25] Hence, organic molecules containing a ptC might be involved in different rearrangement reactions that occur in interstellar medium.

To gain a better understanding of the electronic structure, the MOs were analyzed. Figure 3 shows the HOMO and π-MOs of molecules **1**−**4**. Clearly, the lowest-lying π-orbitals (b_1 symmetry) have an important contribution from the central π-type lone pair. It is essentially distributed over the $C(C)_4$ skeleton. The HOMO of the neutral species **1** and **3** belong to a lone pair of the carbon atoms labeled as C_3. In contrast, in the anions **2** and **4** the HOMOs are π orbitals. The number of π electrons in each molecule is six in **1**, eight in **2** and **3**, and 10 in **4**. It should be noted that cyclic hydrocarbons containing (4n + 2) π electrons (**1** and **4**) preserve the C_5^{2-} fragment almost intact. Interestingly, the global hardness (η) in **1** and **4** is higher than in **2** and **3** (Figure 3).

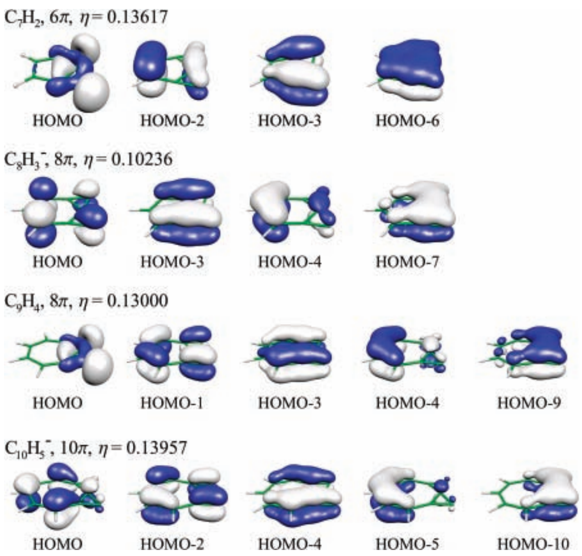

Figure 3. π-MOs ($|\varphi|$ = 0.05 au) and hardness (η) of **1**−**4**.

Electron delocalization and magnetic response of C_5^{2-} have been evaluated previously by graphical representation of the induced magnetic field, $\mathbf{B}^{ind}$.[7] It is important to emphasize that for a long time sketches of $\mathbf{B}^{ind}$ have been used to understand the modification of the local electronic environment induced by and applied external magnetic field

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(19) The external field is applied perpendicular to the molecular plane. When an external magnetic field of $|\mathbf{B}^{ext}|$ = 1.0 T is assumed, the unit of $\mathbf{B}^{ind}$ is 1.0 μT, which is equivalent to 1.0 ppm of the shielding tensor.

(20) The molecules were oriented in the following way: The center of mass is located at the origin of the coordinate system with the z-axis parallel to the highest order symmetry axis of the molecule. (a) Ozell, B.; Camarero, R.; Garon, A.; Guibault, F. *Finite Elem. Des.* **1995**, *19*, 295. (b) Portmann, S.; Luthi, H. P. *Chimia* **2000**, *54*, 766.

(21) In C_5^{2-} (D_{2h}), C_1-C_2 = 150.9 pm and C_2-C_3 = 133.4 pm.

(22) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502

(23) Mills, G.; Jönsonn, H. *Phys. Rev. Lett.* **1994**, *72*, 1124.

(24) MD simulations were carried out in deMon (See ref 17) using a PBE functional and TZVP/A2 basis. (a) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244. (b) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560.

(25) McCarthy, M. C.; Traves, M. J.; Gottlieb, C. A.; Thaddeus, P. *Astrophys. J.* **1997**, *483*, L139.

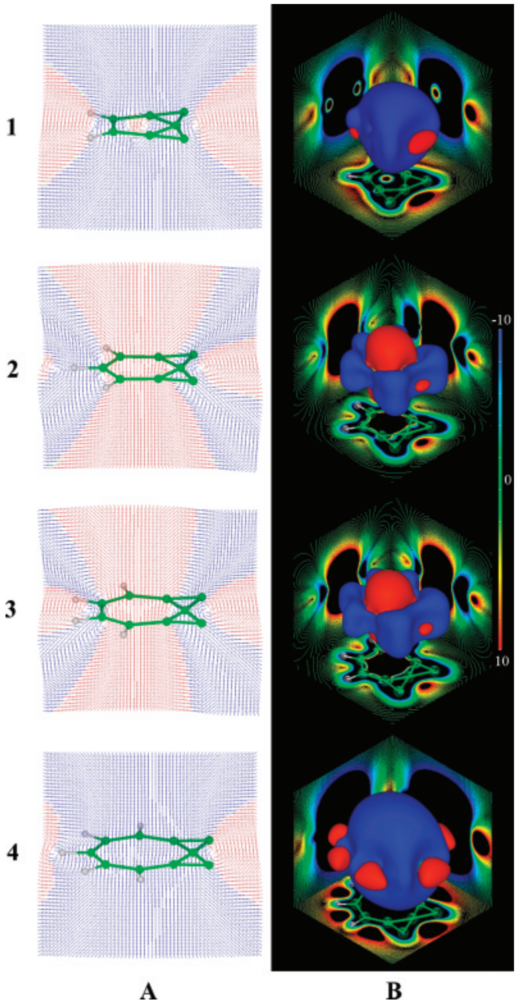

Figure 4. (A) Induced magnetic fields of an external field in z-direction to molecules located in the xy plane. Diatropic and paratropic contributions are given in blue and red, respectively. (B) Isosurfaces of the z-component of the induced magnetic field, $B^{\mathrm{ind}}{}_z$. $|B^{\mathrm{ind}}{}_z| = 9.0\ \mu\mathrm{T}$ and $\mathbf{B}^{\mathrm{ext}} = 1.0$ T perpendicular to the molecular plane. Blue and red indicate shielding and deshielding areas, respectively. Contour lines of $B^{\mathrm{ind}}{}_z$ in the molecular plane and perpendicular to the molecular planes through the origin.

in cyclic aromatic systems (The reader interested in further details is directed to refs 10 and 26). Figure 4 shows $\mathbf{B}^{\mathrm{ind}}$ of **1**−**4**. All molecules have strong diatropic contributions (in blue) inside of the three-membered rings. The five- and eight-membered ring in **1** and **4** shows an aromatic response for the $(4n + 2)$ π electron species, while an antiaromatic response for the 8 π-electron cycles **2** and **3** is observed. Note that **1** shows a weak paratropic contribution inside the ring.

Isosurfaces of the z-component of $\mathbf{B}^{\mathrm{ind}}$ ($B^{\mathrm{ind}}{}_z$) are given in Figure 4B. For **1** and **4**, the shielding isosurfaces (given in blue) are around the molecule, while deshielding regions are further outside (given in red). The opposite situation is observed in 8π molecules. We need to remark that the σ-framework is always surrounded by a diatropic region, independent of whether the system is classified as aromatic or antiaromatic. Contour lines for the z-component of the induced magnetic field allow the quantification of the magnetic response. The aromatic molecules have a strong shielding region close to the carbons inside the ring, which is similar to the form of the carbon π orbitals. The antiaromatic molecule shows a deshielding cone *outside* the ring, with the carbon atoms just inside the deshielding region (This detail cannot be observed by just looking at the isosurface plots).

As we showed previously, NICS and NICS_{zz}[27] are connected to $\mathbf{B}^{\mathrm{ind}}$. The NICS and NICS_{π} indexes were also calculated and are summarized in Table 1. All NICS values inside the three-membered rings are strongly diatropic. However, at the center of the main ring the NICS value is negligible for **1**, paratropic for **2** and **3**, and diatropic (with a value in the range of aromatic [n]-annulenes) for **4**. This fact is in complete agreement with the conclusions drawn from the analysis of $\mathbf{B}^{\mathrm{ind}}$. The NICS_{π} index gives also a clear picture of the role of the π system in these systems. Clearly, it distinguishes the π-aromatic systems (**1** and **4**) from the π-antiaromatic ones (**2** and **3**).

In conclusion, a series of cyclic hydrocarbons containing a ptC is proposed. From these examples it is seen that the balance between electron delocalization of the p-orbital and ring strain determines the metastability of these molecules. Preliminary calculations show that the combination of C_5^{2-} with two unsaturated fragments further increases the stability of the ptC structure. A detailed analysis will be published elsewhere.

Acknowledgment. This work was funded in part by grants from Deutsche Forschungsgemeinschaft (DFG), Conacyt (Projects G34037-E and G32710-E), and DIP-UDLA.

Supporting Information Available: Optimized geometries of the isomers and transition states involving in the ring-opening and an animation of the MD simulation of molecule **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) (a) Pople, J. A. *J. Chem. Phys.* **1956**, *24*, 1111. (b) Gomes, J. A. N. F.; Mallion, R. B. *Chem. Rev.* **2001**, *101*, 1349.

(27) Corminboeuf, C.; Heine, T.; Seifert, G.; Schleyer, P. v. R.; Weber, J. *Phys. Chem. Chem. Phys.* **2004**, *6*, 273.