Subscriber access provided by American Chemical Society

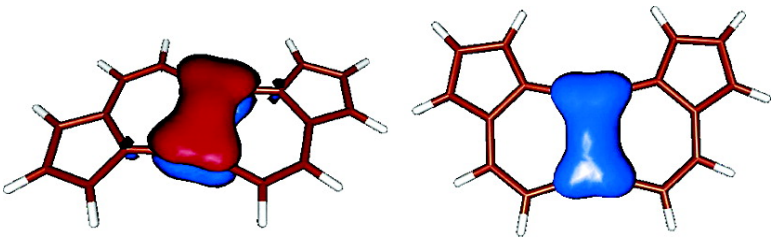
Article

Neutral Structures with a Planar Tetracoordinated Carbon Based on Spiropentadiene Analogues

Pierre M. Esteves, Narciso B. P. Ferreira, and Rodrigo J. Corra

J. Am. Chem. Soc., **2005**, 127 (24), 8680-8685• DOI: 10.1021/ja042971a • Publication Date (Web): 26 May 2005

Downloaded from http://pubs.acs.org on March 25, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 10 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

ACS Publications
High quality. High impact.

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
ARTICLES
Published on Web 05/26/2005

Neutral Structures with a Planar Tetracoordinated Carbon Based on Spiropentadiene Analogues

Pierre M. Esteves,* Narciso B. P. Ferreira, and Rodrigo J. Corrêa*

Contribution from the Instituto de Química, Universidade Federal do Rio de Janeiro, Cidade Universitária, CT Bloco A, 21949-900, Rio de Janeiro-RJ, Brazil

Received November 22, 2004; E-mail: pesteves@iq.ufrj.br; rcorrea@iq.ufrj.br

Abstract: Neutral hydrocarbon structures containing a planar tetracoordinated carbon atom are proposed on the basis of quantum chemical calculations. The planarity at the central carbon atom is achieved by using aromaticity for stabilizing a positively charged core moiety that contains the planar atom. This charge is compensated by negatively charged cyclopentadienyl rings fused on the structure, leading to neutral structures. These are found to be stable from a dynamic point of view and are potentially synthesizable through carbene chemistry. These structures can lead to new breakthroughs in the chemical structure theory. A family of species derived from this model is also presented.

Introduction

In 2004, the model proposed by van't Hoff and LeBel in 1874 of tetrahedral symmetry for tetracoordinated carbon celebrated 130 years.[1−3] The tetrahedral carbon was proposed independently by van't Hoff and LeBel and became a dogma in organic chemistry. In 1970, Hoffmann and co-workers made a theoretical proposal for the possibility of the existence of species containg a planar tetracoordinated carbon (ptC) atom.[4] These authors considered various models for chemical bonding that could stabilize the planar tetracoordinated carbon atom. However, due to the inherent instability of this species, its synthesis remains a challenge. According to these authors, bending methane to its planar form leads to the formation of two 2-center two-electron bonds (2c2e), one 3c-2e bond (CH_2), and a doubly occupied p orbital, perpendicular to the plane of the atoms (Chart 1).[4] This is the result of a rehybridization of the central carbon to a sp^2 hybrid. Molecular orbital calculations show that the tetrahedral carbon (T_d) is more stable than its planar (D_{4h}) geometry by 100−250 kcal/mol.[4]

The breakthrough for obtaining ptC systems would be to find a way to stabilize the planar tetracoordinated sp^2-hybridized carbon, relative to the tetrahedral structure. This can be achieved by mechanical and/or electronic stabilization strategies.[5−12] One such strategy was proposed by Radom and collaborators[5−8] where the planar geometry is reached by keeping the carbon atom inside rigid structures such as cycles and cages, for instance, pagodanes and related structures. Thus, the spatial restriction is responsible for keeping the central carbon atom in its (disfavored) planar form by making the energy barriers for decomposition into other products as high as possible.

Chart 1. Stereoelectronic Arrangement of a PtC Atom

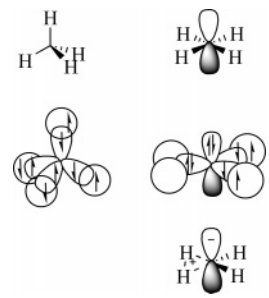
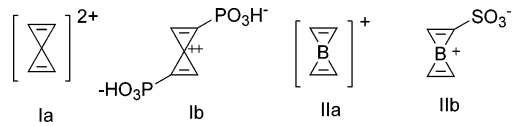


Chart 2. Systems Containing Planar Tetracoordinated Atoms Stabilized by Aromaticity



In a second approach, the stabilization is achieved by delocalizing the isolated electron pair located on the *p* orbital of the central planar carbon atom in a subsystem that can stabilize it, such as a π system. For instance, this electron pair can be part of an aromatic π-system. Following this idea, it was suggested that the coordination of the central carbon to silicon atoms and π-systems, such as those in anulenes, would allow the stabilization of a ptC that incorporates groups and atoms acting as good σ-electron donors and good π−electron acceptors.[13] Initially, boron and lithium were suggested as

(1) van't Hoff, J. H. *La Chimie dans L'Espace*; Bazendyk: Rotterdam, 1895.
(2) *The Rearrangement of Atoms in Space*, 2nd ed.; Longmans, Green and Co.: New York, 1898; pp 103−108.
(3) Le Bel, J. A. *Bull. Soc. Chim. Fr.* **1874**, *22*, 337.
(4) Hoffmann, R.; Alder, R. W.; Wilcox, C. F., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 4992.
(5) Wong, M. W.; Radom, L. *J. Am. Chem. Soc.* **1989**, *111*, 1155.
(6) McGrath, M. P.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 3320.
(7) McGrath, M. P.; Radom, L.; Schaefer, H. F., III. *J. Org. Chem.* **1992**, *57*, 4847.
(8) Radom, L.; Rasmussen, D. R. *Pure Appl. Chem.* **1998**, *70*, 1977.
(9) Sorger, K.; Schleyer, P. v. R. *THEOCHEM* **1995**, *338*, 317.
(10) Siebert, W.; Gunale, A. *Chem. Soc. Rev.* **1999**, *28*, 367.
(11) Rottger, D.; Erkert, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 813.
(12) Rasmussen, D. R.; Radom, L. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2876.
(13) 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.

10.1021/ja042971a CCC: $30.25 © 2005 American Chemical Society

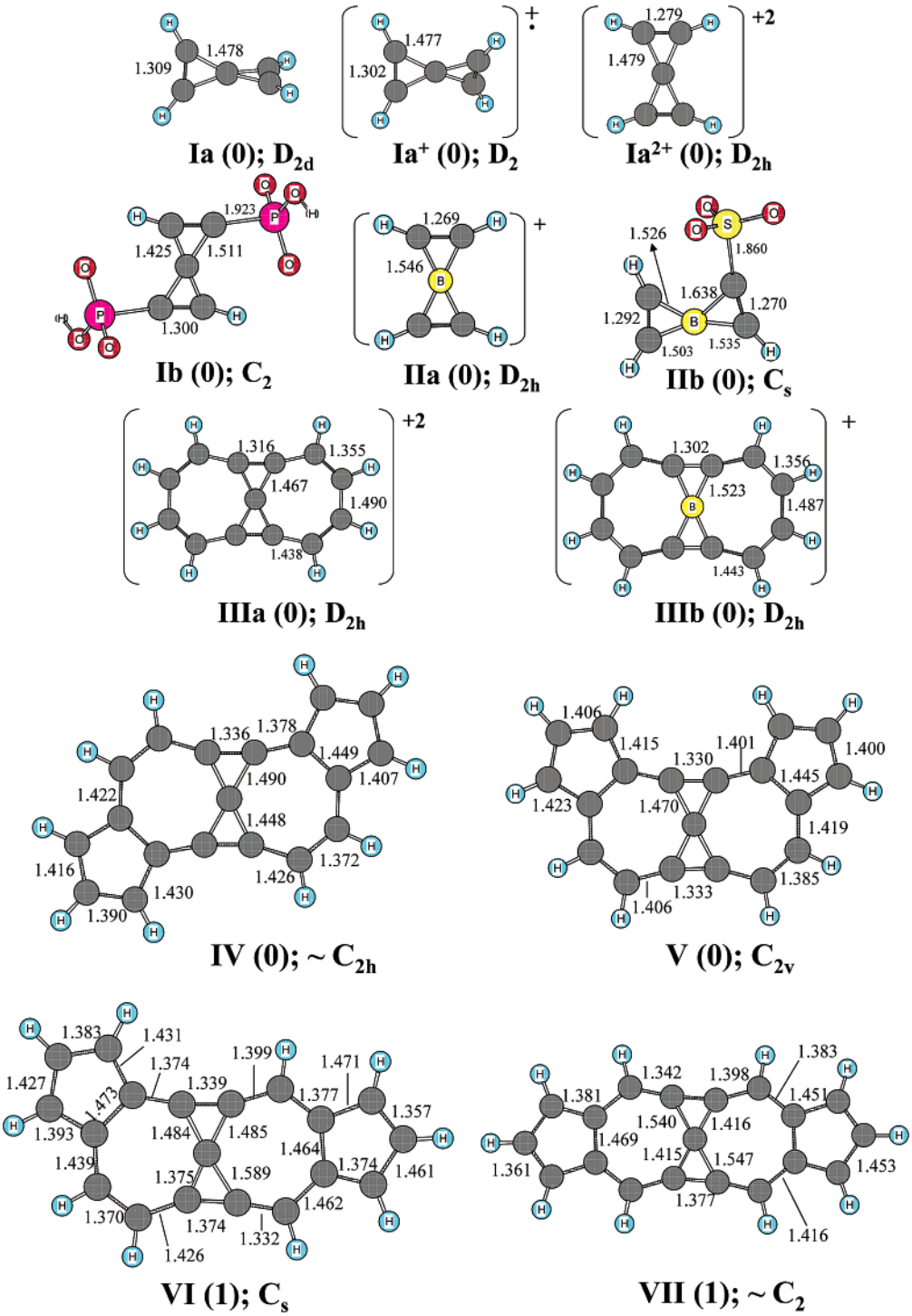


Figure 1. Optimized geometries of the structures **I** to **VII**. Number in parentheses is the number of imaginary frequencies found after vibrational analysis.

candidates, but the use of silicon has also been considered.[14−18] Boldyrev and collaborators have shown that surrounding the carbon atom by metal atoms (Al, Ge, etc.) leads to species containing ptC.[19−23] Lammertsma and Schleyer[24] related the neutral and the monocation of spiropentadiene as possible ptC structures, but neither of the structures are planar. However, their ab initio calculations showed that its dication contains a ptC. In this approach, the two electrons on the p orbital perpendicular to the ring plane are essentially removed, affording the planar dication. Priyakumar et al. showed that bicyclic analogues of spiropentadiene have a ptC atom,[25,26] but the

(14) Wang, Z. X.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2002**, *124*, 11979.
(15) Wang, Z. X.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2001**, *123*, 994.
(16) Exner, K.; Schleyer, P. v. R. *Science* **2000**, *290*, 1937.
(17) Wang, Z. X.; Schleyer, P. v. R. *Science* **2001**, *292*, 2465.
(18) Jespersen, M. B. K.; Chandrasekhar, J.; Würthwein, E. U.; Collins, J. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1980**, *102*, 2263.
(19) Boldyrev, A. I.; Simons, J. *J. Am. Chem. Soc.* **1998**, *120*, 7967.
(20) Li, X.; Wang, L. S.; Boldyrev, A. I.; Simons, J. *J. Am. Chem. Soc.* **1999**, *121*, 6033.
(21) Boldyrev, A. I.; Wang, L. S. *J. Phys. Chem. A* **2001**, *105*, 10759.
(22) Li, X.; Zhang, H. F.; Wang, L. S.; Geske, G. D.; Boldyrev, A. I. *Angew. Chem., Int. Ed.* **2000**, *39*, 3630.
(23) Wang, L. S.; Boldyrev, A. I.; Li, X.; Simons, J. *J. Am. Chem. Soc.* **2000**, *122*, 7681.
(24) Lammertsma, K.; Schleyer, P. v. R. *J. Phys. Chem.* **1988**, *92*, 881.

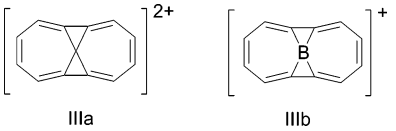
theoretical activation barriers for ring opening are not large enough to maintain a stable planar structure. Conversely, they have shown that a tricyclic dication structure also based on a spiropentadiene moiety is perfectly planar. The authors also show that for a $C_6H_6^{2+}$ isomer the structure is a minimum on the potential energy surface. Merino and collaborators have also shown that the C_5^{2-} moiety contains a ptC atom and that coordination of this moiety with metals leads to stable neutral molecules.[27−29]

In this work, we found a family of ptC structures using aromaticity as the driving force to stabilize the ptC in relation to the tetrahedral carbon. To accomplish this goal, the candidate structures were theoretically studied using DFT calculations (see Computational Details section).

As a first approach we studied the spiropentadiene family, as previous results showed it to be a promising structure, obeying an anti-van't Hoff rule.[24] The parent species, spiropentadiene, and derivatives have been successfully synthesized,[30,31] and thus they can serve as a starting point for the design of molecules containing a ptC. Our DFT calculations also predict that the dication (Chart 2) should be planar and corresponds to a true minimum on the potential energy surface, in agreement with previous studies.[24] Actually, by taking successively two electrons from the neutral spiropentadiene, affording the mono- and dicationic species, and optimizing their geometries we observed that the system naturally tends to planarity. Figure 1 shows the optimized geometries obtained for these species. The angle between the two three-member rings is 90° in neutral spiropentadiene **Ia**, around 60° for the $C_5H_4^+$ species, **Ia**$^+$ (a cation radical), and 0° for $C_5H_4^{+2}$, **Ia**$^{2+}$. In the dication, the electron pair of the ptC atom is involved in two aromatic subsystems, which stabilize the planar structure in relation to its tetrahedral form. It can be seen that the single bonds connecting the spiro atom to the other carbons are not affected by electron removal, since their bond lengths do not change significantly when going from the neutral to the dicationic form. Conversely, the bond between the external atoms is slightly shortened when going from the neutral to the dicationic form. Considering these results, the $C_5H_4^{+2}$ is a potentially interesting target for the synthesis of the first viable ptC containing only C and H atoms.

To make their neutral forms so they could be experimentally isolable or detectable, we propose replacing two hydrogen atoms with two negatively charged groups (HPO_3^-) in the structure, leading to structure **Ib** (Chart 2). As can be seen, results for the DFT calculations of the neutral structures show a ptC in this framework, and it corresponds to a true minimum on the potential energy surface (Figure 1). The bond lengths change slightly in relation to **Ia**$^{2+}$. We also performed calculations on the isoelectronic boron analogue, **IIa**, of the spiropentadiene **Ia**, which afforded the corresponding planar structure (Figure 1). In the boron case, a neutral molecule containing a tetracoordinated planar boron atom was found when one of the hydrogen atoms was substituted by a SO_3^- moiety.

Chart 3. Mono and Dicationic Structures Containing a Central Planar Atom



Scheme 1. Potential Methodological Synthetic Strategy for Obtaining PtC

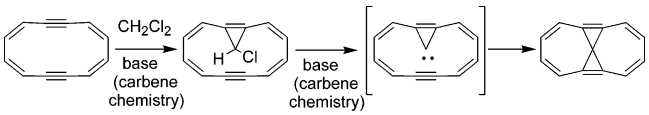


Chart 4. Neutral Structures Containing Only C and H with a PtC Atom

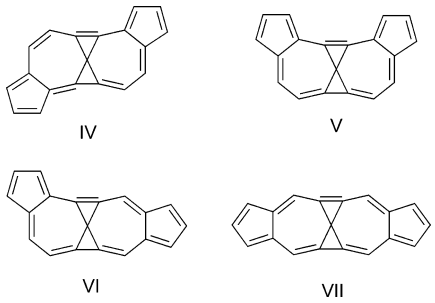
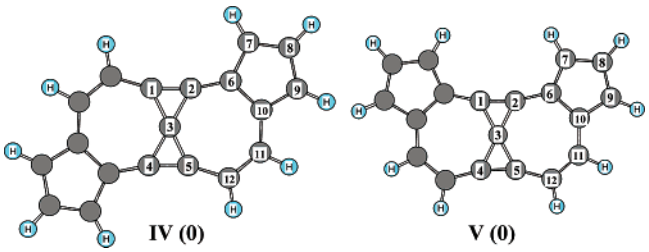


Table 1. Bond Order and Bond Lengths for Structures IV and V



pair of atoms	structure IV NBO bond order	structure IV bond length (Å)	structure V NBO bond order	structure V bond length (Å)
1−2; 4−5	1.46	1.336	1.47; 1.49	1.330; 1.333
1−3; 3−5	0.96	1.455	0.90	1.469
2−3; 3−4	0.84	1.490	0.90	1.465
2−6	1.24	1.378	1.15	1.401
6−7	1.24	1.430	1.34	1.415
7−8	1.52	1.391	1.40	1.406
8−9	1.33	1.416	1.44	1.400
9−10	1.42	1.407	1.31	1.423
10−11	1.16	1.433	1.24	1.411
11−12	1.65	1.372	1.53	1.385
12−5	1.11	1.426	1.17	1.406
6−10	1.14	1.449	1.15	1.445

We explored the delocalization of the positive charge in the perpendicular p orbital of the ptC by making it an essential component of multiring aromatic structures. A manner of doing this would be to fuse unsaturated seven-member rings (tropylium analogues) to the spiropentadienyl dication species, for example, structures **IIIa** and **IIIb** (Chart 3).

DFT calculations show that these structures, as well as their isoelectronic boron analogues, do present a planar tetracoordi-

(25) Priyakumar, U. D.; Sastry, G. N. *Tetrahedron Lett.* **2004**, *45*, 1515.
(26) Priyakumar, U. D.; Reddy, A. S.; Sastry, G. N. *Tetrahedron Lett.* **2004**, *45*, 2495.
(27) Merino, G.; Mendez-Rojas, M. A.; Vela, A. *J. Am. Chem Soc.* **2003**, *125*, 6026.
(28) Pancharatna, P. D.; Mendez-Rojas, M. A.; Merino, G.; Vela, A.; Hoffmann R. *J. Am. Chem. Soc.* **2004**, *126*, 15309.
(29) Merino G.; Mendez-Rojas, M. A.; Beltran, H. I.; Corminboeuf, C.; Heine, T.; Vela, A. *J. Am. Chem. Soc.* **2004**, *126*, 16160.
(30) Billups, W. E.; Haley, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 5084.
(31) Billups, W. E.; Haley, M. M. *Tetrahedron Lett.* **1999**, *40*, 6157.

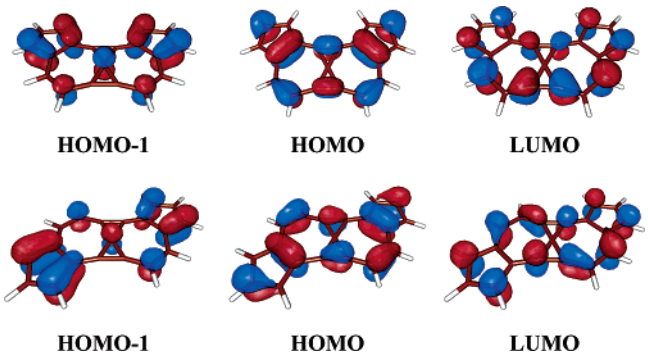
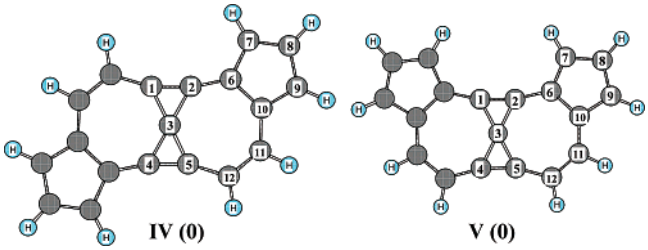


Figure 2. Selected molecular orbitals for structures **IV** and **V**.

Table 2. ^{13}C Chemical Shifts (GIAO/B3LYP/6-311++G**), CHelpG Charges and NICS Values for Structures IV and V



	structure IV		structure V	
atom	^{13}C chemical shifts	CHelpG charges	^{13}C chemical shifts	CHelpG charges
1	120.7	+0.30	131.0	+0.08
2	123.2	−0.09	131.5	+0.08
3	135.7	+0.10	146.8	+0.12
4	123.6	−0.09	130.1	+0.13
5	120.0	+0.30	130.8	+0.15
6	102.2	+0.10	112.9	−0.05
7	147.0	−0.29	160.5	−0.18
8	128.2	−0.03	135.7	−0.09
9	151.5	−0.23	161.0	−0.22
10	133.5	0.00	140.8	+0.06
11	145.8	−0.01	159.4	−0.06
12	90.8	−0.42	91.9	−0.32
NICS (0) five-member ring	−9.7; −9.8		−13.6; −13.6	
NICS (0) seven-member ring	−17.0; −17.4		−18.6; −19.2	

nated atom and are minima on the potential energy surface (Figure 1). The positive charge is better delocalized through resonance with the other two rings, as expressed by the bond lengths. The main advantage of using such systems is that they can be potentially prepared, for instance, from large ring acetylenic precursors using carbene/carbenoid chemistry (e.g., Scheme 1).

With the objective of constructing a neutral framework consisting of only carbon and hydrogen atoms, we fused two cyclopentadienyl anions to the dicationic species **IIIa**. From this procedure, some neutral hydrocarbon structures containing a perfectly planar tetracoordinated carbon atom were calculated as true minima on the potential energy surface, making these structures very interesting synthetic targets (Chart 4). Our calculations showed that of the four considered isomers, **IV**−**VII**, only **IV** and **V** are minima on the electronic potential energy surface (Figure 1). The two remaining structures have imaginary frequencies, which characterize them as transition states for the twist of the spiropentadiene moiety. Among

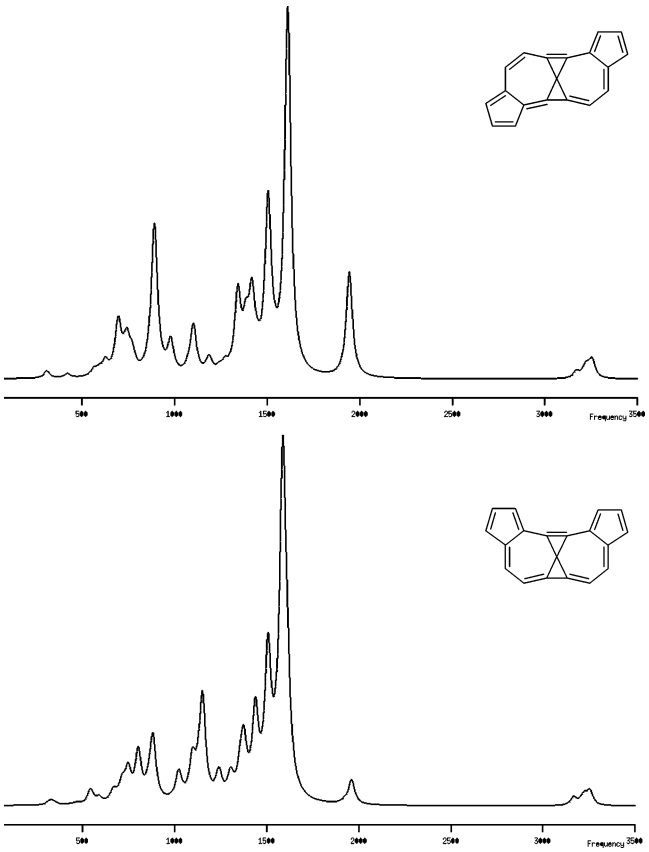


Figure 3. Theoretically derived infrared spectra (IR) of species **IV** and **V**.

isomers **IV**−**VII**, structure **IV** was found to be the most stable. It is 1.0 kcal/mol more stable than **V**, possibly due to a steric interaction. Their geometries (see Figure 1 and Table 1) show that most of the carbon−carbon bond lengths are similar to aromatic carbon−carbon bond lengths (e.g. the azulene computed at the same level; see Supporting Information). In the optimized structures of **IV** and **V**, one can observe that these molecules have a perfectly planar tetracoordinated central atom carbon. The bond lengths between the ptC atom and the surrounding carbon atoms in the spiropentadiene moiety have single bond character. We carried out a natural bond orbital (NBO) calculation for **IV** and **V** at the HF/6-311G(d,p)//B3LYP/6-31++G(d,p) level (Table 1) and found that the bond order is in the range of 0.84−0.97 for the chemical bonds and connected to the ptC atom in **IV** and 0.90 for **V**. On the other hand, the bond order calculated for the peripheric bond lengths confirms the aromatic character of these bonds, with bond orders similar to those ones found for azulene. It is noteworthy that these systems obey the Hückel $4n + 2$ rule (18-π electrons; $n = 4$).

Analysis of the frontier orbitals in these two molecules (Figure 2), calculated at the RHF/6-31G*//B3LYP/6-31G* level, indicates that the perpendicular p orbital formed in planar methane, which corresponds to the HOMO in this case (see Chart 1), is now stabilized by the aromatic system, becoming the HOMO-1 orbital of these systems. Analysis of the HOMO indicates that this orbital presents typically aromatic behavior, being a cyclic conjugated π-system. The same is observed for the LUMO. This shows that aromaticity is a key factor in the stabilization of the ptC system. The lowering of the energy of the electron pair in the p orbital in the ptC atom reinforces the fact that the electronic effect-based strategies for obtaining ptC atoms is appropriate

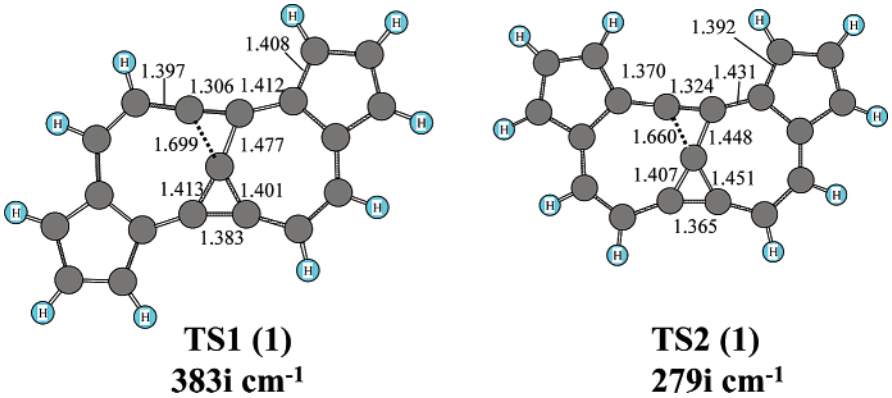


Figure 4. Transition states geometries for three-member ring opening for **IV** and **V**, obtained at B3LYP/6-31G* level. Number in parentheses is the number of imaginary frequencies found after vibrational analysis.

and should be taken into account when proposing new ptC-containing structures.

The aromatic character of the carbon atoms surrounding the central ptC atom is also evidenced by the calculated ^{13}C chemical shifts (GIAO/B3LYP/6-311++G**/B3LYP/6-31G* level) and are summarized in Table 2. The values around 120 ppm do agree with typical aromatic chemical shifts, such as those of azulene. Nucleus-independent chemical shift (NICS)[32] calculations on the five- and seven-member rings were performed to check whether these rings present aromatic character. The NICS of three-member rings was not taken into account since local shielding of its σ-bonds complicates the analysis (see ref 32 for details). The NICS calculations present negative values for both five- and seven-member rings (see Table 2), denoting aromaticity. CHelpG charge analysis in the spiropentadiene moiety is +0.52e, indicating that the charge has been spread over the molecule. The charge on the ptC atom is, respectively, +0.10e and +0.12e for structures **IV** and **V**.

The theoretically derived IR spectra are shown in Figure 3 for structures **IV** and **V**. The bands correlate well with the computed spectrum at the same level of calculation obtained for azulene. Low-frequency vibrational modes (~700 cm^{-1}) correspond to the breathing modes of the spiropentadiene moiety. The (uncorrected) band around 2000 cm^{-1}, when corrected by a factor of 0.96 (for correcting anharmonicity and other approximations on the calculations of IR spectrum), affords a band around 1920 cm^{-1}, which corresponds to the vibration associated with the C=C stretching mode of the outer bonds of the spiropentadiene moiety. It is noteworthy that the intensity of this band decreases in **V** in comparison to **IV**, due to the more symmetric structure of the former. The dipole change associated with the stretching modes in **V** change less significantly than that in **IV**, thus leading to a smaller oscillator strength and a smaller IR band on the latter.

We next considered whether these species were thermally stable. We found the transition states for opening of the three-member rings in **IV** (**TS1**) and **V** (**TS2**) (Figure 4). Analysis of the vibrational mode corresponding to the imaginary frequency showed that these transition states correspond to the ring opening through breaking of only one of the bonds connecting the ptC to the spiropentadiene moiety atoms. The breaking bond is 1.699 Å (**TS1**) and 1.660 Å (**TS2**). NBO bond orders for these bonds are, respectively, 0.45 and 0.52, showing that these bonds are about half broken in these transition states. Interestingly, most of the open forms of structure **IV**, when submitted to DFT calculations, return to the corresponding planar structure. Nevertheless, we found a open form structure, **VIII** (see Supporting Information). The barrier ($\Delta H^{\ddagger}$) for opening the trans (**IV**) and cis (**V**) structures is, respectively, 2.2 and 1.4 kcal/mol. The small barrier of ring opening indicates that potential synthetical strategies for these molecules must use low-temperature procedures (e.g., argon matrix). Reaction enthalpy for the formation of the open structure from **IV** is −25.3 kcal/mol.

Conclusion

In conclusion, we have proposed a family of compounds that, according to DFT calculations, present a tetracoordinated planar carbon atom. Some of them are neutral and made exclusively of carbon and hydrogen atoms and are potentially synthesizable through carbene chemistry. We hope that this will stimulate synthetic groups to achieve the synthesis of the first hydrocarbon that violates the 130-year-old dogma, which states that tetracoordinated carbon has only tetrahedral arrangement. This achievement will surely be a landmark for the advancement of the structural theory in chemistry.

Computational Details

The geometry of several species was optimized using standard techniques,[33] and, after geometry optimization, vibrational analysis was performed and the resulting geometries were checked with respect of being true minima on the potential energy surface, shown by the absence of imaginary frequencies. Calculations were performed at B3LYP/6-311++G(3df,3pd) for structures **I** and **II**. Structures **III**−**VIII** were calculated at the B3LYP/6-311++G**//B3LYP/6-31G* level, as well as transition states **TS1** and **TS2**. Chemical shifts were obtained at the GIAO/B3LYP/6-311++G**//B3LYP/6-31G* level. NICS values were computed for the nonweighted Cartesian coordinates of the heavy atoms in each ring system.[32] All energy differences correpond to enthalpy differences at 298 K and 1 atm and take into account zero-point energy and thermal corrections. In all structures charges at the atomic centers were calculated by fitting to density-derived electrostatic potential using the CHelpG scheme.[34,35] NBO[36] calculations were performed at RHF/

(32) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.
(33) Fletcher, R. *Practical Methods of Optimization*; Wiley: New York, 1980; Vol. 1
(34) Chirlian, L. E.; Francl, M. M. *J. Comput. Chem* **1997**, *8*, 894.
(35) Breneman, C. M.; Wiberb, K. B. *J. Comput. Chem* **1991**, *11*, 361.
(36) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

6-311G**//B3LYP/6-31G*. All calculations were performed with Gaussian 98 package of programs.[37]

Acknowledgment. Authors acknowledge Profs. G. K. S. Prakash, Simon J. Garden, W. Bruce Kover for helpful discussions, and to CNPq and FAPERJ for financial support. This article is dedicated to the memory of Prof. Luiz C. Trugo.

(37) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

Supporting Information Available: Table containing bond order and bond lengths for azulene, IR spectrum of azulene, and the optimized geometry for an open form of **IV**. Table containing the comparison of ring-opening barrier for **IV**, obtained at several levels of theory, and π-molecular orbital for structures **IV** and **V**. Total energies and geometry coordinates are also included. This material is available free of charge via the Internet at http://pubs.acs.org.

JA042971A