

Recent Advances in Planar Tetracoordinate Carbon Chemistry

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Received 28 March 2006; Accepted 26 April 2006

DOI 10.1002/jcc.20515

Published online in Wiley InterScience (www.interscience.wiley.com).

Abstract: We summarize our contributions on the quest of new planar tetracoordinate carbon entities (new carbon molecules with exotic chemical structures and strange bonding schemes). We give special emphasis on the rationalization why in this type of molecules the planar configuration is favored over the tetrahedral one. We will concentrate on the latter and will show that molecules containing planar tetracoordinate carbons have a stabilizing system of delocalized π electrons, which shows similar properties as π systems in aromatic molecules.

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Key words: planar tetracoordinate carbon; aromaticity; magnetic properties; electron delocalization

Background

It is fascinating to see and to understand the chemical structure of molecules. The chemical structure is a consequence not only of their constituent elements but also of the way those atoms are connected to each other, and what their special arrangement is. So, the chemical structure and the connection between atoms—the chemical bond—are intimately related. Any change in the spatial distribution of the nuclei will modify the nature of the chemical bond and vice versa.

Our knowledge about chemical structure begins in the XIX-th century. Now, chemists use “familiar” symbols to represent chemical reality. For example, Scheme 1 represents the chemical structure of benzene.

Every vertex in the structural representation is a carbon. Since the valence of carbon is typically four, we know that only one hydrogen atom is bonded to each carbon. The tetravalence of carbon was proposed by Kekulé and Couper, and it represents the first step towards understanding the chemical structure of organic molecules.^{1,2}

In 1850, Pasteur found a curious phenomenon related to optical rotation. He recrystallized a salt of racemic acid and noted that the crystals came in two identical, but not superimposable, arrays. Pasteur patiently separated the crystals under microscopy and observed that the solution of the two crystal forms rotated the plane of polarized light in opposite directions. How to explain this phenomenon in terms of molecular structure?

In 1872, van't Hoff and LeBel found a solution for this problem.^{3,4} They proposed that the four carbon bonds point to the

vertices of a tetrahedron. If four different groups are linked to carbon, the mirror image is not identical to the original one. It established a relationship between optical activity and the atomic spatial arrangement. Chemists realized that they needed to think in three dimensions.

It took almost a century to find an example that refutes the tetravalence of carbon. In 1951, Tal'roze and Lyubimova suggested the existence of CH_5^+ .⁵ Immediately, a huge set of molecules containing a carbon surrounded by more than four ligands (hypercarbons) were proposed on paper, but were also synthesized and characterized.^{6–9} The fascinating chemistry of hypercarbons is summarized in Olah's Nobel lecture.¹⁰

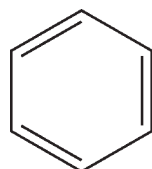
Almost a century after the publication of the van't Hoff-LeBel model, Hoffmann et al. suggested rules to stabilize molecules containing a planar tetracoordinate carbon (ptC) atom,¹¹ challenging the second structural foundation of Organic Chemistry. Inspired on Hoffmann's ideas, several groups have successfully suggested and experimentally characterized molecules containing ptCs.^{12–17} It is not pretentious to say that the works around ptCs opened a new age of carbon chemistry.

In this article, we summarize our contributions on the quest of new ptC entities (new carbon molecules with exotic chemical

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Contract/grant sponsor: PROMEP; contract/grant number: UGTO-PTC-079

Contract/grant sponsor: DINPO; Conacyt; Deutsche Forschungsgemeinschaft (DFG)



Scheme 1.

structures and strange bonding schemes). We give special emphasis on the rationalization why in this type of molecules the planar configuration is favored over the tetrahedral one. There are two ways to achieve this goal: mechanical and electronic stabilization. We will concentrate on the latter and will show that, similar to aromatic structures, molecules containing ptCs have a stabilizing system of delocalized π electrons, which shows similar properties as π systems in aromatic molecules.

How to Stabilize a Planar Tetracoordinate Carbon?

The simplest hypothetical molecule containing a ptC is planar methane. The symmetry lowering from T_d to D_{4h} induces a change in the hybridization of carbon from sp^3 to sp^2 . By construction, there is a lone pair perpendicular to the molecular plane (the a_{2u} orbital in Fig. 1). Therefore, only six electrons occupy bonding orbitals (orbitals e_u and a_{1g} , Fig. 1), in contrast to the four bonding pairs present in T_d structure. Actually, the planar

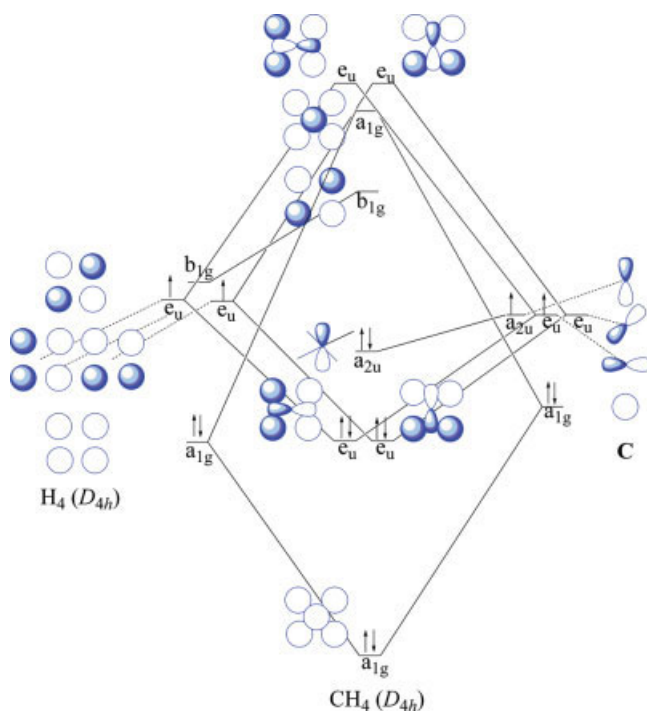


Figure 1. Molecular diagram of planar methane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

conformation is destabilized by a considerable amount of energy (around 600 kJ mol^{-1}). The strategy suggested by Hoffmann et al. to stabilize a ptC entity electronically was based on the replacement of the hydrogens by ligands that are (1) σ -donors (to assist electron transfer to the electron deficient carbon), and (2) π -acceptors (to delocalize the p or π -type lone pair), or by incorporating the lone pair into a $(4n + 2)\pi$ delocalized system.¹¹

Using Hoffmann's strategy (also called the *electronic approach*), several ptC molecules have been proposed *in silico*^{14,18–37} and/or experimentally detected.^{38–48} A few realized compounds of nonclassical structures containing ptCs are shown in Figure 2. In order to achieve electronic stabilization they share a common feature: there is at least one atom *different from carbon* linked to the ptC.

CSi_2Ga_2 is a special case. It is a five atomic molecule and in fact it is the simplest possible ptC molecule. In this case, planar geometries can be favored over tetrahedral when (1) Jahn–Teller instability (even if within the ligand–ligand interactions only) makes the latter locally unstable and (2) the number of valence electrons allows for maximum C–ligand and ligand–ligand bonding. The optimal case for planar structures occurs with 18 valence electrons, where three σ and one π bond occur as well as one ligand–ligand bond.²⁰ When the theoretical prediction of the CSi_2Al_2 planarity was published in 1991, the community met it with a great skepticism. It took a lot of time to convince experimentalists to try to test this prediction. However, molecules CAL_4^- and CAL_3Si^- (isoelectronic to CSi_2Ga_2) have been made in molecular beams and their planarity has been experimentally verified.^{22,48,49}

There is a second general strategy to promote a ptC molecule stabilization based on steric enforcement of the planar orientation of the bonds, the so-called mechanical approach. The idea looks quite simple: the central carbon and its nearest neighbors are forced to be in a plane using several geometrical constraints. Alkylanes are the best examples.^{16,50–55} However, so far attempts to synthesize a ptC molecule using the mechanical approach have failed.

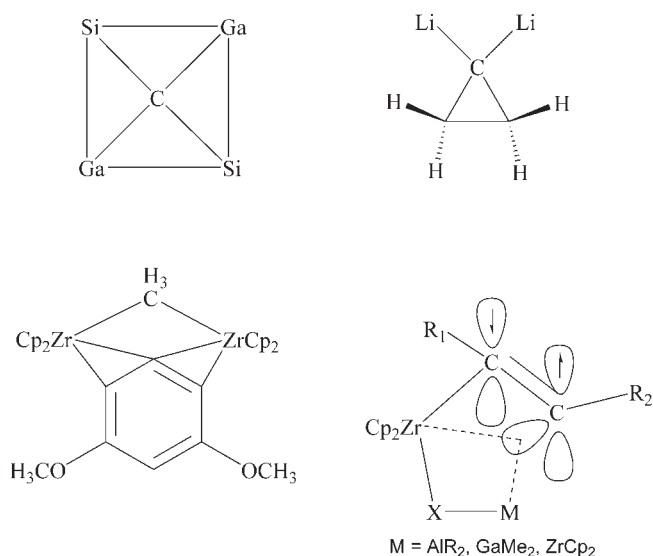


Figure 2. Selected examples of molecules containing a ptC.

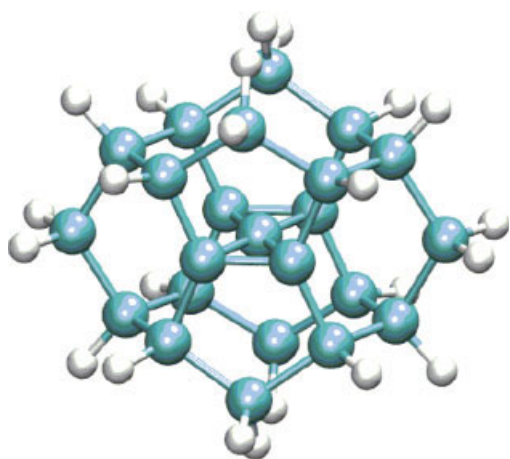


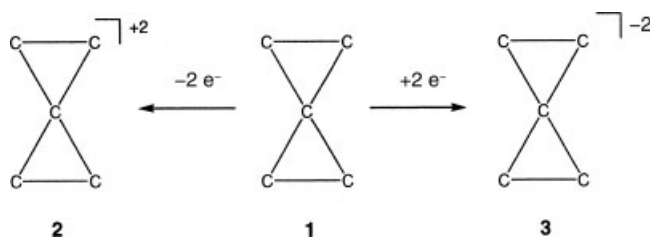
Figure 3. Alkplane proposed by Rasmussen and Radom.⁵¹ [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In 1999, Keese and coworkers noted that “despite considerable computational efforts no structures with a planar tetracoordinate C(C)₄ substructure have been found.”⁵⁶ Rasmussen and Radom designed the first molecule with a ptC surrounded only by carbons, the dimethanospiro[2.2]octaplane (Fig. 3).⁵¹ Using a similar approach, Wang and Schleyer found a set of boron spiroalkanes with a planar C(C)₄ core through substitution of carbon by boron atoms.^{24,57} Both suggestions are based on the mechanical approach.

In 2003, a novel family of molecules based on a C₅²⁻ moiety was proposed by us, which constituted the simplest set of molecules containing a C(C)₄ core stabilized purely by electronic factors.²⁶

The Smallest Planar Tetracoordinate Carbon Containing a C(C)₄ Core, C₅²⁻

The smallest hypothetical cluster containing a C(C)₄ skeleton is C₅, **1**. Experimental and theoretical studies have shown that the linear structure of C₅ is the global minimum energy structure.^{58,59} Hoping that the removal or the addition of electrons might encourage the formation of ptC, we explored both options. No minimum with a ptC could be found in the first case. Gratifyingly, the addition of two electrons to **1** stabilizes a local minimum with the desired ptC atom.



The optimized geometry of C₅²⁻ at different levels of theory is shown in Figure 4. All methodologies yield very similar values

for the geometrical parameters. The largest C—C bond length (151 pm) is comparable with those calculated for dimethanospiro [2.2]octaplane (150.4 pm)¹⁴ and several [4.4.4.5]fenestrene derivatives (149.3–152.9 pm).⁶⁰

The experimental observation of any molecule is only possible if the molecule is stable for a certain detection period. Depending on the experimental technique of characterisation, the necessary detection time ranges from the microsecond scale to a couple of seconds. The mean life time of a molecule strongly depends on the topography of the PES that drives the dynamics of the system, and thus to gain a better idea about the stability or metastability of the parental skeleton C₅²⁻, an extensive exploration of its PES was performed (see Fig. 5). Among all the stationary points located on the PES, only four were local minima, including **3**. Two of them (**3A** and **3B**) are lower in energy than **3** (202.4 and 184.8 kJ mol⁻¹, respectively), whereas the three dimensional D_{3h} structure, **3C**, is 179.5 kJ mol⁻¹ higher in energy. Structure **3D** is the transition state involved in the rearrangement that isomerizes **3B** into **3**, and vice versa. It should be noted that structure **3D** is not planar and lies very close in energy to **3** (12.6 kJ mol⁻¹). Structures **3E–3H** have one imaginary frequency, and they are not connected to the ptC molecule.

Why is C₅²⁻ a local minimum? Consider a neutral spiro-pentadiene as a starting structure (Fig. 6). After removing four protons C₅⁴⁻ is obtained. This process generates four lone pairs, one on each terminal carbon and pointing outwards, roughly in the direction where the hydrogen nuclei were located in the original structure. Now, after rotating one cyclopropenyl ring against the other, all five carbon atoms are in the same plane, and one ends up with the planar C₅⁴⁻.

The central π-type lone pair, a characteristic feature of square planar carbon systems, will be surely destabilized. Vacating this MO will result in C₅²⁻ for which there are four lone pairs pointing outwards and a π-system of two occupied orbitals. A careful examination of the MOs for C₅²⁻ show that the four localized pairs of **1** transform as a_g + b_{1u} + b_{2u} + b_{3g}. Their delocalized equivalents are to be found in 1b_{2u}, b_{eg}, 2a_g, and 2b_{1u} (Fig. 7). Two very low-lying MOs (a_g and b_{1u}) have mainly s character and are omitted in the diagram. The destabilization of 2a_g and 2b_{1u} (mostly bonding) over 1b_{2u} and b_{3g} (mostly antibonding) is

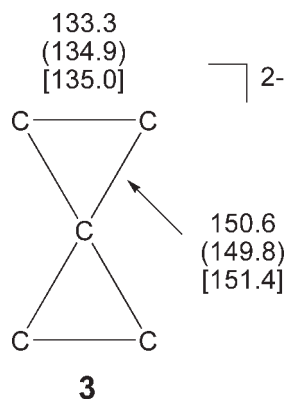


Figure 4. Optimized geometry of the parental skeleton C₅²⁻ using B3LYP, (MP2), and [CCSD(T)] levels.

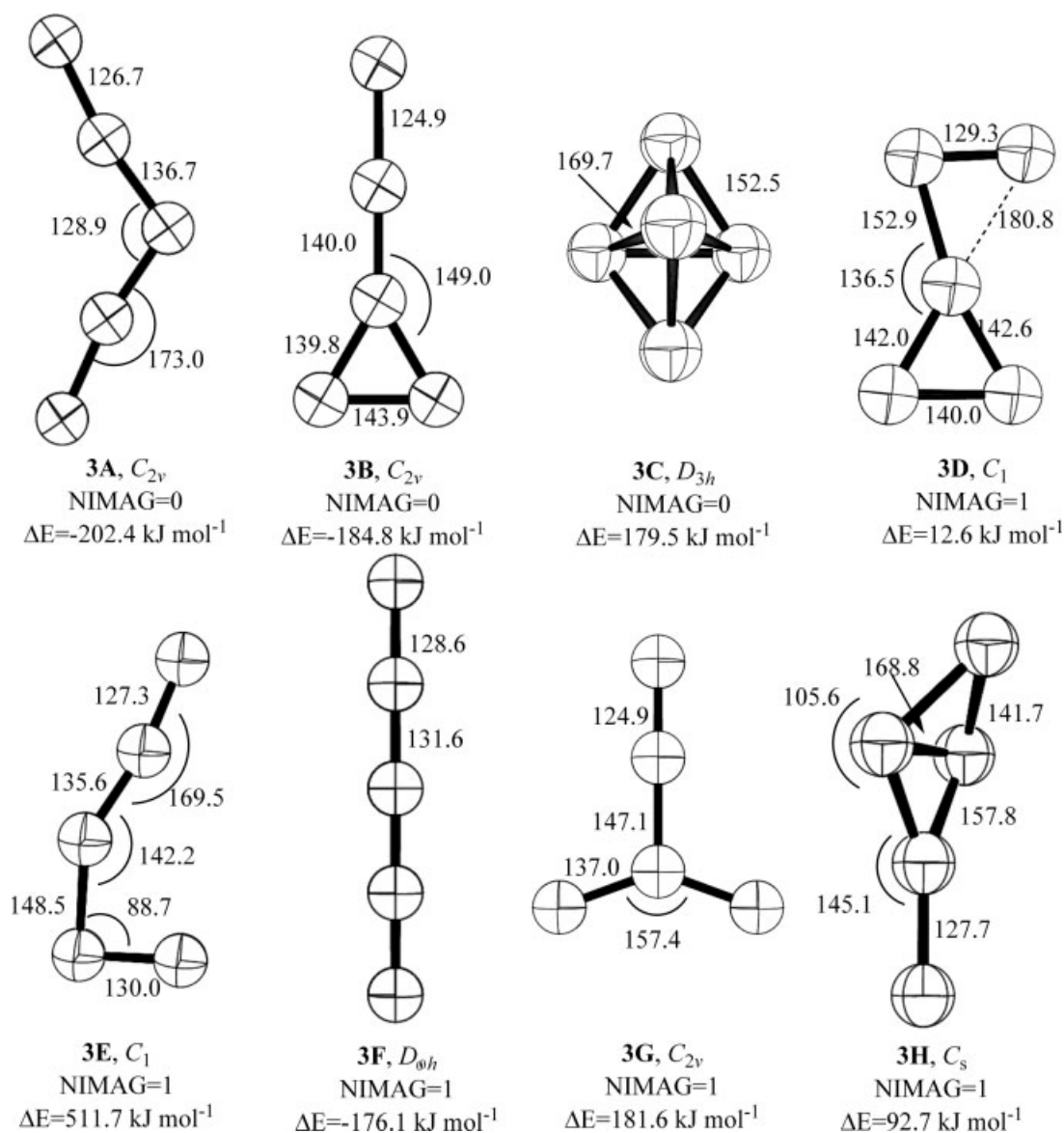


Figure 5. Stationary points of the C_5^{2-} skeleton calculated at the B3LYP/6-311++G(2d) level. NIMAG is the number of imaginary frequencies, and ΔE is the energy difference between the corresponding structure and 3, including the scaled ZPE (0.9806). All distances are in picometers and angles in degrees.²⁹

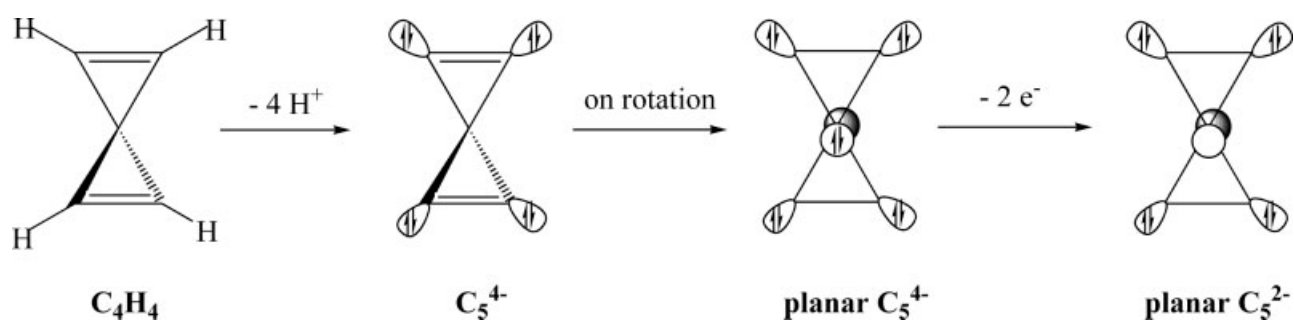


Figure 6. Simplified picture of the construction of the MOs of C_5^{2-} from C_5H_4 .

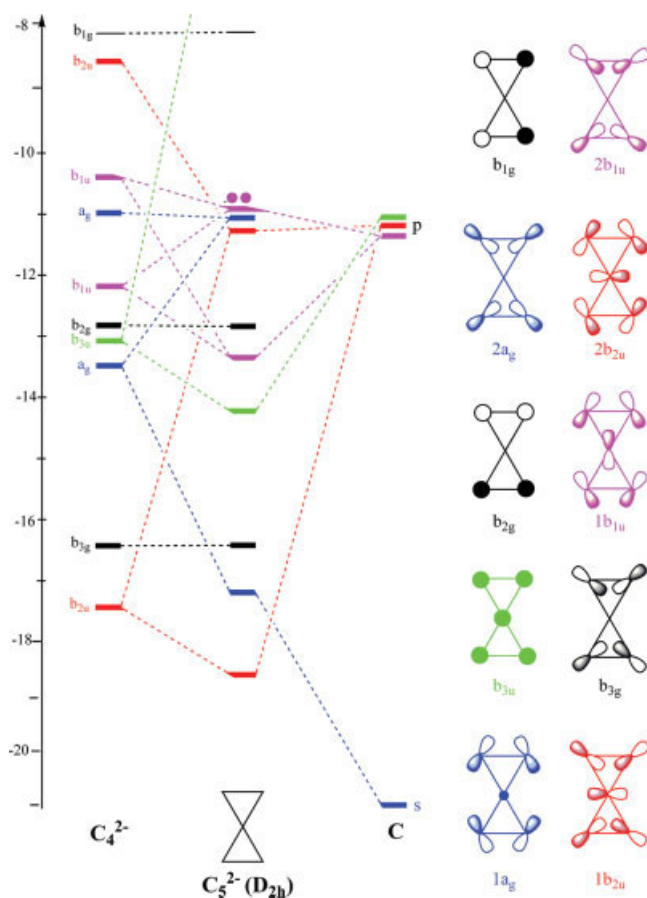


Figure 7. Correlation diagram between the fragment orbitals of the four “outside” carbon atoms and the central ptC using extended Hückel theory (EHT). The bold and thin lines distinguish between filled and empty molecular orbitals. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

due to the interaction with the σ set of MOs. Since these radial MOs mix with the tangential MOs ($1a_g$, $1b_{1u}$, and $2b_{2u}$) due to their common symmetry, the orientation of the canonical orbitals differs slightly from those shown schematically in Figure 7. The p orbitals perpendicular to the plane, which are involved in the formation of π MOs, are shown as circles, symbolizing their “top” (above the plane) phase. The two π MOs are identified as b_{3u} and b_{2g} in Figure 7. The corresponding antibonding combination lies above the LUMO (b_{1g}). Note that the p-orbital of the central carbon atom is the lowest-lying p-orbital of the carbon framework, covering completely the $C(C)_4$ skeleton and contributing to the double-bond character of the C_2-C_2' bond, which turns out to be the fundamental reason to understand the stability of the C_5^{2-} structure.

Similar to other dianions, the HOMO and four other occupied MOs of **3** have positive energies at any correlated level of theory. To prevent immediate bond breaking in these structures, it is mandatory to stabilize these orbitals. One option is to introduce positive charges into the parent dianion. With this in mind, we explored the influence of adding several metals (Li^+ , Na^+ , K^+ ,

Cu^{2+} , Be^{2+} , Mg^{2+} , Ca^{2+} , Zn^{2+}) to the parental structure C_5^{2-} (Fig. 8). Interestingly, the addition of one (**4**) or two cations (**5**) does not destroy the planarity of the molecules.

To gain further insight into the bonding mechanism prevailing in these systems, we perform the analysis of several molecular fields: the electron density $\rho(\mathbf{r})$,⁶¹ the electron localization function (ELF(\mathbf{r})),⁶² and the magnetic response to an applied external magnetic field given by the locally induced magnetic field, $\mathbf{B}^{ind}(\mathbf{r})$.⁶³ We find that the interaction of the parental C_5^{2-} skeleton with the alkaline and alkaline earth atoms is basically ionic, with a remarkable transferability of properties from the isolated dianion to the C_5M_2 salts. The study of the magnetic response shows that, indeed, electron delocalization plays a very significant role in stabilizing these ptC containing compounds.

Our results indicate that planar C_5Li_2 is an excellent candidate for experimental isolation. However, the experimental observation of C_5Li_2 also depends on the possible rearrangements to more stable isomers. For C_5^{2-} , the rearrangement barrier is only 12.6 kJ mol⁻¹, including the zero-point energy correction, but the inclusion of two lithium cations increases this barrier to 58.3 kJ mol⁻¹ (Fig. 9). Furthermore, the energy difference between the planar structure of C_5^{2-} and the closest isomer is -184.0 kJ mol⁻¹, while for C_5Li_2 this value is appreciably smaller (-17.4 kJ mol⁻¹). Therefore, the isomerization barrier in C_5Li_2 is sufficiently high to support our optimism that this molecule can be experimentally detected.

How to build polymers containing a C_5^{2-} core? The design of a fragment containing two C_5^{2-} units (a dimer) would require the inclusion of four monocations to keep the system neutral. The relative stabilities of the monomers give an idea on how one can arrange the metal ions around the C_5 units (Fig. 10). The most stable isomer in the C_5Li_2 series was **6**, suggesting two alternative arrangements for a $C_{10}Li_3^-$ dimer; one where both C_5^{2-} units are coplanar, **7**, and another, where the units are perpendicular to each other, **8** (Fig 10). Structure **8** is a minimum on the PES, while **7** has two imaginary frequencies. In the optimized structure of $C_{10}Li_4$, **9**, two of the Li^+ occupy positions between the terminal carbons which are not linked to each other. To gain further insight on the preferred position of the metal, a trimer $C_{15}Li_6$, **10**, was also constructed. Both **9** and **10** are minima and continue the bonding motif found for $C_5Li_4^{2+}$, **11**. These results provided clues for designing extended systems in two and three dimensions containing a ptC.

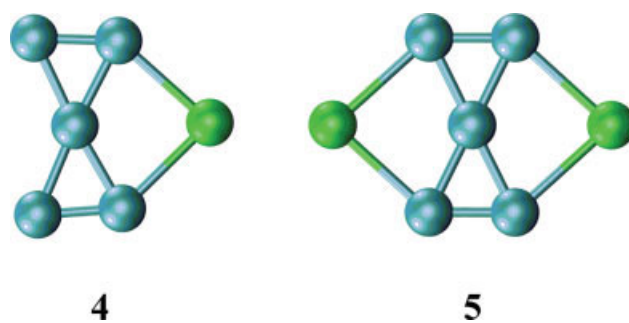


Figure 8. Schematic representation of **4** and **5**. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

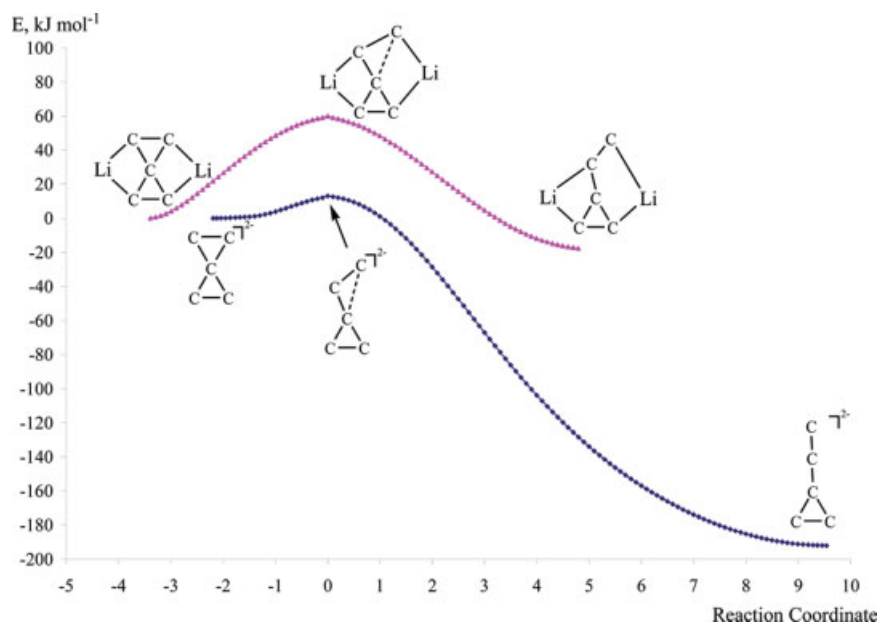


Figure 9. Energy profiles for the isomerization of C_5^{2-} and C_5Li_2 . The origin of both reaction paths is the corresponding planar structure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

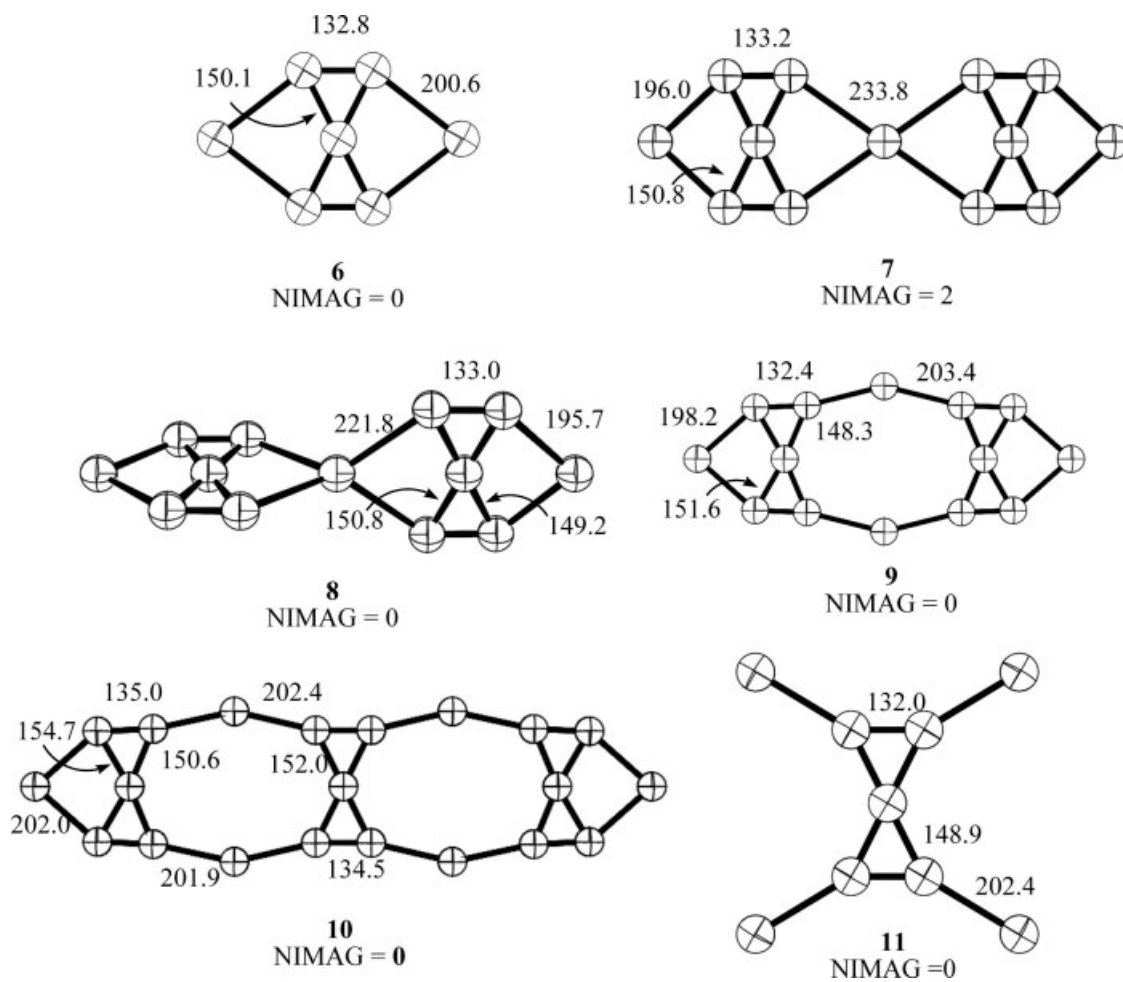


Figure 10. Optimized structures of C_5Li_2 , $C_{10}Li_3^-$, $C_{10}Li_4$, and $C_{15}Li_6$.

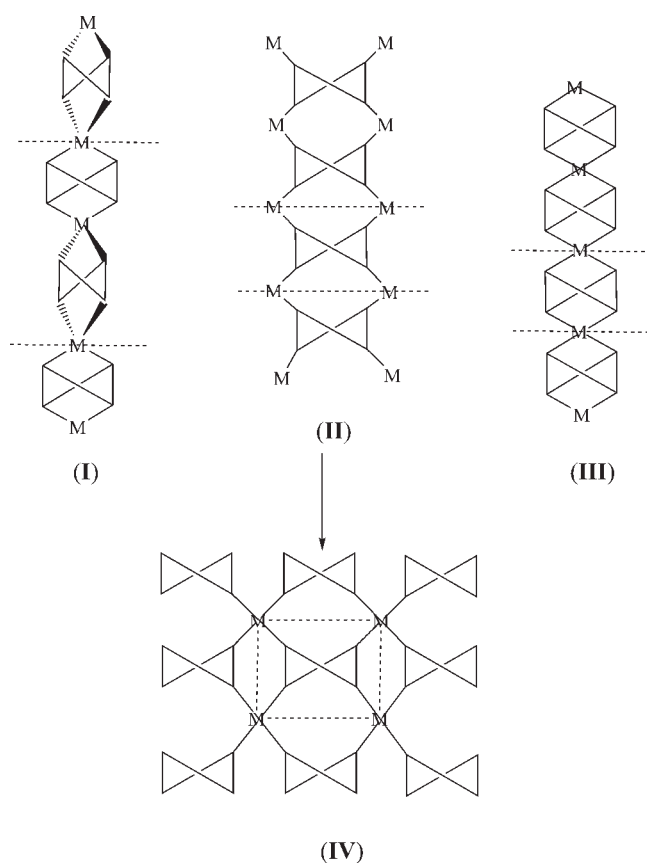


Figure 11. Schematic diagram for a 1-D (**I**, **II**, **III**) and a 2-D (**IV**) pattern of C_5^{2-} units bridged by appropriate metal ions. The repeating units are shown by dashed lines.

ptCs in Extended Systems³⁰

Based on our previous calculations on the stability of dimeric and trimeric structures, different 1-D and 2-D networks were built. The stable dimers **8** and **9** as well as structure **6**, lend themselves to extension to 1-D chains of C_5 units. These polymeric chains are depicted in Figure 11 as **I**, **II**, and **III**. Since the ratio of a C_5 unit to the metal in a unit cell of **I** and **III** is 1:1, a divalent metal ion is needed to compensate for the -2 charge on C_5 . In the case of **II**, the 1:2 C_5 to metal ratio requires a singly charged cation like Li^+ . If Li^+ is replaced by a divalent tetra-coordinate metal ion, **II** can be converted into a 2-D network **IV**, as shown in Figure 11.

Structure **I** requires a tetrahedral coordination around the metal and a divalent metal ion (Zn^{2+} or Be^{2+} , for example, as these ions have been found before in similar systems such as $[Zn(CN)_2]_n$ and $[CBe_2]_n$).^{64,65} Structure **II** may use Li^+ ions, while Pt^{2+} may be the right choice for structures **III** and **IV**, as it often exists in a square planar arrangement. In fact, the theoretical analysis showed that compounds **I**- Zn^{2+} and **II**- Li^+ were stable, having a tetragonal and orthorhombic unit cell, respectively (Fig. 12), but not **I**- Be^{2+} , which even failed to converge. The optimized lattice parameters of the different $[C_5M_x]_n$ systems studied are given in Table 1.

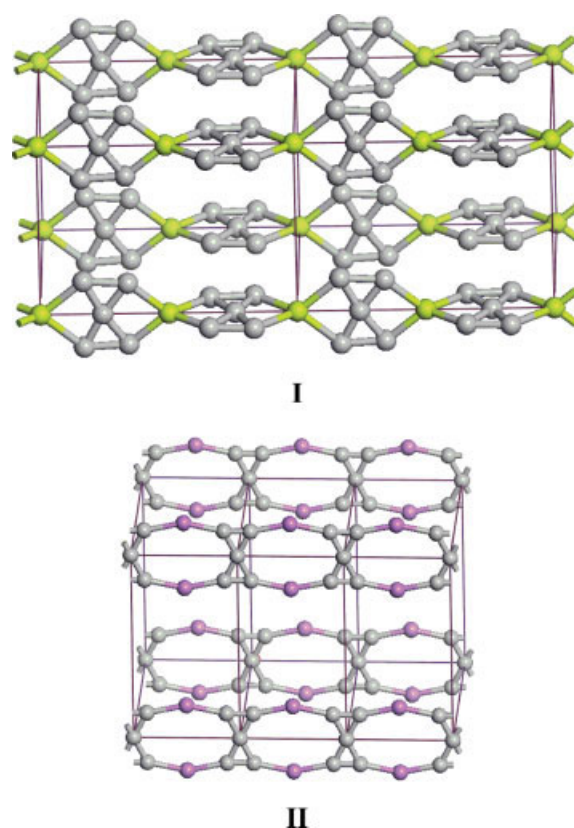


Figure 12. Optimized lattice of (**I**) C_5Zn and (**II**) C_5Li_2 . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

VASP calculations of the band structure and density of states (DOS) for $[C_5Zn]_n$ and $[C_5Li_2]_n$ show large band gaps, suggesting that these solids have semiconducting or insulating behavior. The same situation happens for all other extended network systems. For $[C_5Pt]_n$, it was found that **III** in Figure 13 was preferred over **IV**, which agrees with the relative stabilities of the isomeric forms of $C_5Li_4^{2+}$.

Thus, this study shows that C_5^{2-} is a building block that generates interesting crystal structures having ptCs and semiconducting–insulating properties.

Table 1. Cell Parameters (a , b , c in Å) and V (Volume in Å³) of the Different C_5M_x Systems.

System	a	b	c	V
$C_5Zn(I)$	9.90	9.90	9.33	915.14
C_5Li_2	5.33	9.91	9.97	526.80
C_5Pt	3.84	4.46	5.22	89.32
$C_5Zn(V)$	4.76	4.76	9.14	206.56
C_5Be	4.45	4.45	8.82	174.83
$C_5Zn(VII)$	3.78	3.78	10.53	150.46
C_5Ni	3.82	3.82	10.44	152.04

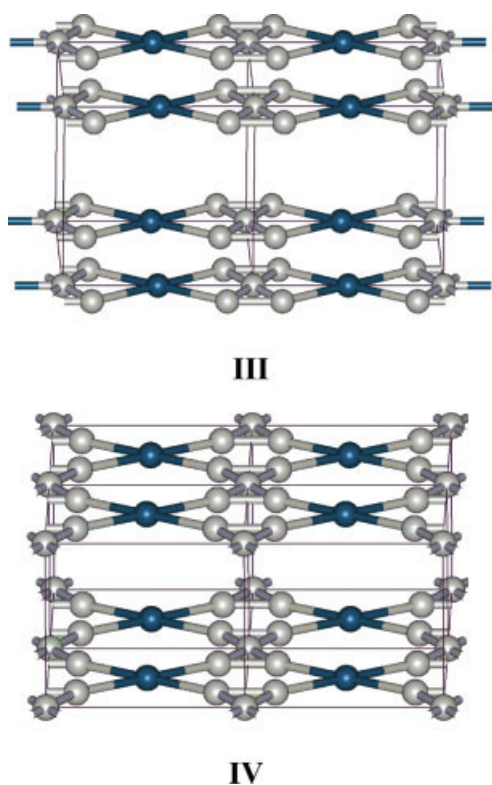


Figure 13. The 3-D unit cells of the **III** and **IV** forms of C_5Pt are shown. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ptCs in Cyclic Hydrocarbons⁶⁶

As the electronic strategy to stabilize a ptC derived from the C_5^{2-} unit was shown to be successful, the next step was to build hydro-

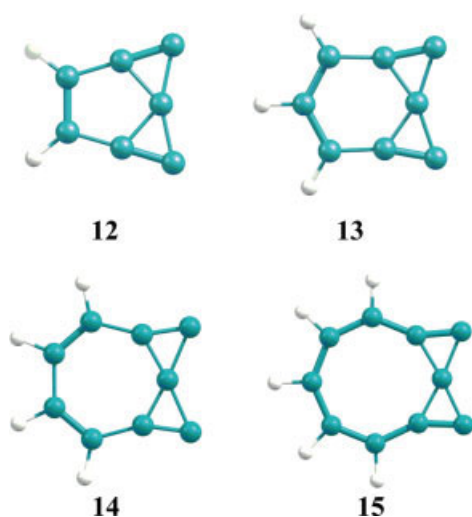


Figure 14. Optimized structures of cyclic hydrocarbons containing a ptC. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 2. Smallest Frequencies, Energy Difference between the ptC Molecule and Its Closest Isomer (ΔE), and Its Corresponding Activation Energy, E_a .

	Frequency (cm^{-1})	ΔE	E_a
12	246.3	-42.4	38
13	169	-28.9	23.1
14	102	-52.1	30.7
15	150.1	-110.7	10.7

All energies are in kilojoules per mole.

carbons containing a ptC. The main goal for their design is to avoid the isomerization process which energetically favors linear carbon chains. Very recently, we started to explore a series of cyclic hydrocarbons containing a planar $C(C)_4$ core.⁶⁶ Candidates were obtained by combining the parental C_5^{2-} anion with an unsaturated fragment: two hydrogens from ethane and 1,3-dibutadiene were removed, providing the corresponding dications which interact with C_5^{2-} , yielding five- and seven-membered ring systems C_7H_2 , **12**, and C_9H_4 , **13**, respectively. The same strategy was used to build the six- and eight-membered anionic rings $C_8H_3^-$, **14**, and $C_{10}H_5^-$, **15**, from allyl and pentadienyl anions. Their structures are depicted in Figure 14. The harmonic analysis shows that all of them are local minima on their respective PES with an appreciable positive lowest vibrational frequencies ($\gg 100 \text{ cm}^{-1}$).

To explore the possibility of experimental detection we estimated of the mean life times of these species by a series of Born–Oppenheimer molecular dynamic (BO-MD) simulations. As reported in Table 2, and as expected, ring-opening is accompanied by small activation barriers of the range of $10\text{--}40 \text{ kJ mol}^{-1}$. Figure 15 shows a typical MD trajectory of **15**, which has the lowest activation barrier. Here, the planar structure preserves its geome-

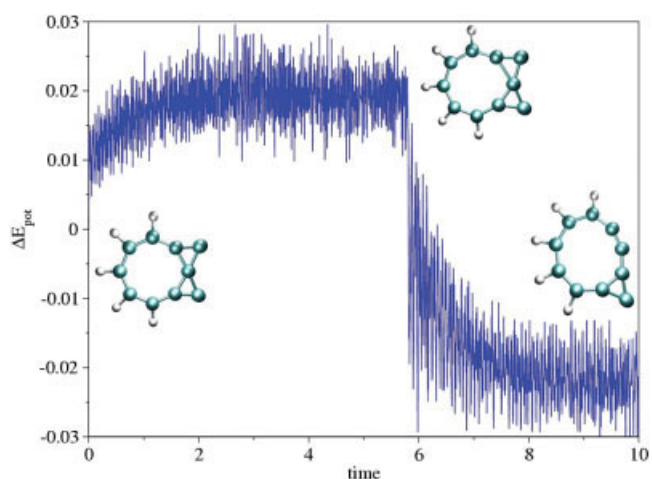


Figure 15. BO-MD simulation of molecule **15**. Relative potential energy (ΔE_{pot}) (in au) versus time (in ps). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

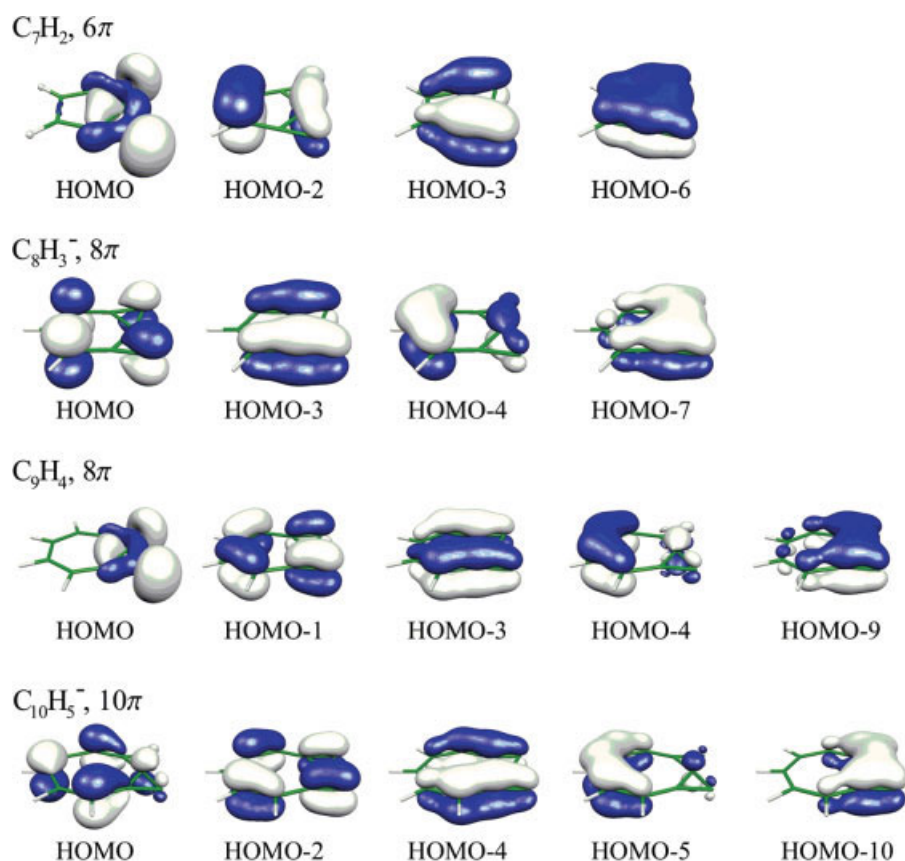


Figure 16. HOMOs and π -MOs ($|\phi| = 0.05$ au) for **12–14**. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

try for about 6.0 ps at 300 K. This is a very short lifetime, but considering that it corresponds to the hydrocarbon with the smallest activation energy, one can be optimistic that the lifetimes of **12–14** can be large enough for its experimental detection.

The MOs of these molecules that contribute more to their stability are shown in Figure 16. Clearly, the lowest-lying π -orbitals have an important contribution from the central π -type lone pair, and it is essentially distributed over the entire $C(C)_4$ skeleton. The HOMOs of the neutral species **12** and **14** are in-plane lone pairs of the carbon atoms labeled as C_3 . In contrast, in the anions **13** and **15**, the HOMOs are π orbitals. The number of π electrons in each molecule is 6 in **12**, 8 in **13** and **14**, and 10 in **15**. It should be noted that cyclic hydrocarbons containing $(4n + 2)\pi$ electrons (**10** and **13**) preserve the C_5^{2-} fragment almost intact.

We have also explored the electron delocalization and magnetic response of these molecules. All planar hydrocarbons have strong diatropic contributions inside the three-membered rings that constitute the C_5 skeleton. For the $(4n + 2)\pi$ electron species (**12** and **15**), the main cycles of the molecules have an aromatic response, while they show an antiaromatic response for the 8 π -electron cycles (**13** and **14**). B_z^{ind} and isosurfaces of the z -component of B^{ind} (B_z^{ind}) of **12** and **13** are shown in Figure 17. The aromatic molecules have a strongly shielding region close to the carbons inside the ring, which resembles the form of the car-

bon π orbitals. The antiaromatic molecules show a deshielding cone outside the ring, with the carbon atoms just inside the deshielding region.

We are currently exploring the electronic, magnetic, and structural characteristics of several new members of this cyclic hydrocarbon family. Symmetric and asymmetric systems with rings of different size at each side are showing an increased stability due to the size and symmetry of these hydrocarbons.

Perspectives on ptCs Derived from C_5^{2-}

The most important messages that we have learned from our studies about ptC containing molecules are that the delocalization of the lone pair located in the central carbon atom and the size of the energy barriers that prevent the isomerization of the molecule are the most important factors to be considered in the molecular engineering of these species. Taking into account these crucial factors, we are presently studying systems where these rearrangements are decreased, or even better, stopped completely. By learning these theoretical “know-hows,” we are optimistic that we will see *in vitro*, and in our lifetimes, the experimental detection of some of these *in silico* designed molecules that challenge one of the paradigms of Organic Chemistry.

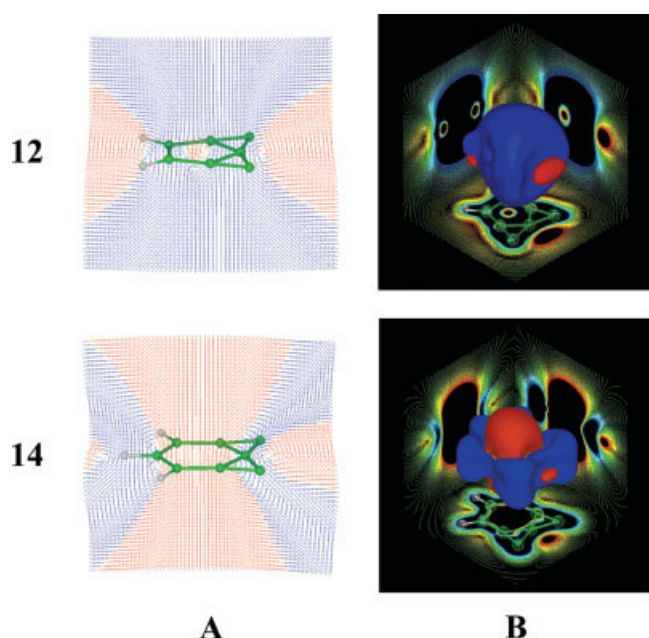


Figure 17. (A) \mathbf{B}^{ind} of **13** and **14**. Blue and red areas denote diatropic (shielding) and paratropic (deshielding) regions, respectively. (B) Isosurfaces of the z -component of the induced magnetic field, $\mathbf{B}_z^{\text{ind}}$; $|\mathbf{B}_z^{\text{ind}}| = 9.0 \mu\text{T}$ and $|\mathbf{B}^{\text{ext}}| = 1.0 \text{T}$, perpendicular to the molecular plane. Blue and red indicate shielding ($|\mathbf{B}_z^{\text{ind}}| < 0$) and deshielding areas, respectively.

Acknowledgments

We are grateful to many colleagues for their collaboration in this project: Gotthard Seifert and Robert Barthel from Technische Universität Dresden, Pattath D. Pancharatna from Cornell University, Clemence Corminboeuf from University of Geneva, Nancy Perez from Universidad de las Americas, and Hiram I. Beltrán from Instituto de Química in UNAM. We owe special thanks to Prof. Roald Hoffmann for his thorough and thoughtful inspiration of this work.

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