J. Phys. Chem. A **2008,** *112,* 686−692

Understanding the Planar Tetracoordinate Carbon Atom: Spiropentadiene Dication

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Received: June 22, 2007; In Final Form: October 26, 2007

The atoms in molecule theory shows that the spiropentadiene dication has a planar tetracoordinate carbon (ptC) atom stabilized mainly through the σ bonds and this atom has a negative charge. The bonds to the ptC atom have less covalent character than the central carbon from neutral spiropentadiene. The total positive charge is spread along the structure skeleton. The analysis of the potential energy surface shows that the dication spiropentadiene has a 2.3 kcal/mol activation barrier for ring opening.

Introduction

Theoretical design and experimental characterization of molecules containing a planar tetracoordinate carbon (ptC) have been accomplished by several scientific groups to date.[1,2] Two major strategies to build them are derived from mechanical[3] (constraining the ptC in strained molecules) and electronic approaches[1b,c,4] (keeping the ptC surrounded by σ-donating and π-accepting groups).

It has been shown[5] that spiropentadiene analogues have a ptC atom when the structure is a dication. Merino et al.[6] also have shown that the related C_5^{-2} has a planar carbon atom and that the coordination of this system with metals leads to stable neutral structures. Our group[7] also has proposed a neutral hydrocarbon containing a ptC atom using the spiropentadiene dication moiety as an inspiration. It was inserted within an extended π system to neutralize its charge and originates the potentially synthesizable hydrocarbon.

The dianion C_5^{-2} can actually be thought of as a spiropentadiene without 4 protons and with a dication core.[8] The small energy barrier for ring opening (3.0 kcal/mol) would only prevent the isomerization of the dianion C_5^{-2} at low temperatures.[6c] Other small molecules with a ptC atom were successfully designed by Reddy and co-workers.[9]

As a consequence of Rasmussen and Radom's pioneering paper,[4b] it is unclear if the actual stability of the computed structures containing the ptC would remain as expected or would rearrange to a more stable carbon skeleton, although new structures have been proposed and several attempts have been made to characterize them as stable compounds. The spiropentadiene dication system has been seen as a promising way to build ptC-containing neutral compounds, but little is known about the electronic nature of this system. In this work, we have done an investigation of key points on the $C_5H_4^{2+}$ potential energy surface and a study of the electronic nature by the atoms in molecules theory[10] (AIM). The AIM caculations also were performed in the neutral and monocationic C_5H_4 for comparison purposes.

Computational Details

The geometries of the species were optimized by using standard techniques.[11] Vibrational analysis of the optimized geometries of selected points on the potential energy surface was carried out to determine whether the resulting geometries are true minima or transition states by checking the existence of imaginary frequencies. Calculations were performed at the B3LYP/6-311++G** level[12] by using the Gaussian 98 package.[13] The electronic density was derived from the Kohn−Sham orbitals obtained at the B3LYP/6-311++G** level[14] for further AIM calculations. Critical points, Laplacian of charge density, delocalization, and localization indexes[15] were calculated by means of the AIM2000 software.[16] All energy differences correspond to enthalpy values at 298.15 K and 1 atm.

Results and Discussion

Scheme 1 shows the ring-opening and hydride-shift reactions affording other isomeric open chain species (**1**−**9**).

Figure 1 shows the optimized geometries for **1**−**9**, their corresponding bond lengths, and the relative enthalpies of ring-opening and hydride-shift reactions from the spiropentadiene dication. The spiropendiene dication, **1**, is confirmed as a planar-carbon-containing species. Besides **1**, the only minima found were **3**, **5**, and **9**. The structure **7** was found to rearrange directly to **9**. It was found that the most stable among the minima is **5**. The structures **1**, **3**, and **9** are 32.2, 24.4, and 6.3 kcal/mol higher in energy than **5**, respectively. The relative stability of **5** can be ascribed to the balance between charge−charge repulsion and electronic stability. Structure **10** was not found as a stable intermediate, leading to structure **9** after geometry optimization.

Figure 2 shows the pictorial view of the rearrangements shown in Scheme 1. The ring opening of **1** through transition state **2** affording **3** has a barrier of 2.3 kcal/mol. This value is compatible with the ring-opening process found to analogue structures.[7,8] Thus, the ring opening of **1** is quite favorable at ordinary temperatures. Structure **3** rearranges in a barrierless process through transition state **4**, yielding **5** in an exothermic process (−24.4 kcal/mol). Further ring opening in **5**, yielding acyclic intermediates, such as **9**, presents relatively high kinetic barriers (43.3 kcal/mol). This is probably due to the relative stability of the aromatic cyclopropenyl moiety, which tends to be preserved.

Figure 3 shows the bond lengths and interatomic distances (in Å) of neutral spiropentadiene, spiropentadiene monocation, and spiropentadiene dication. The bond length between the central carbon atom and the external carbon atom is nearly

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10.1021/jp074895e CCC: $40.75

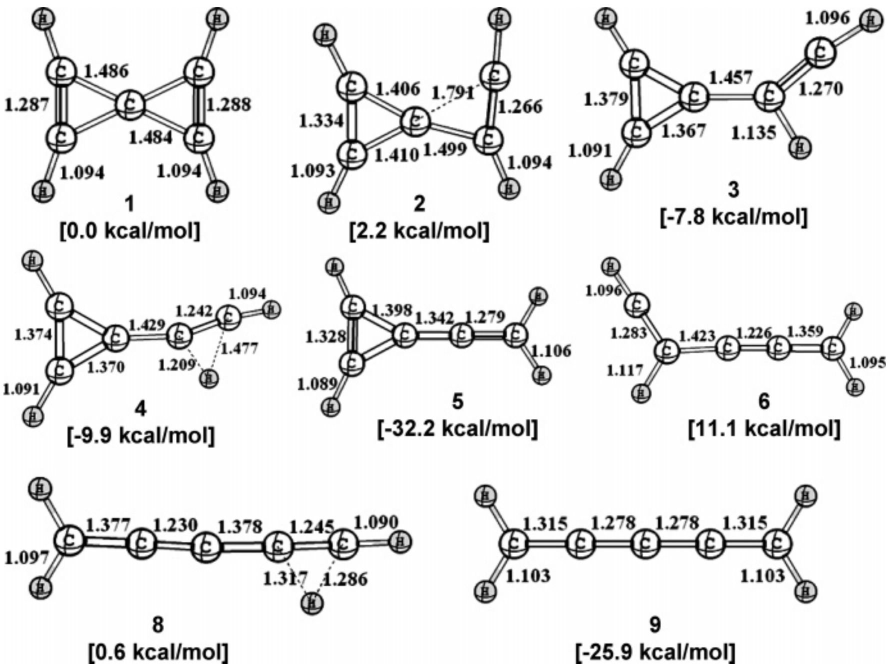
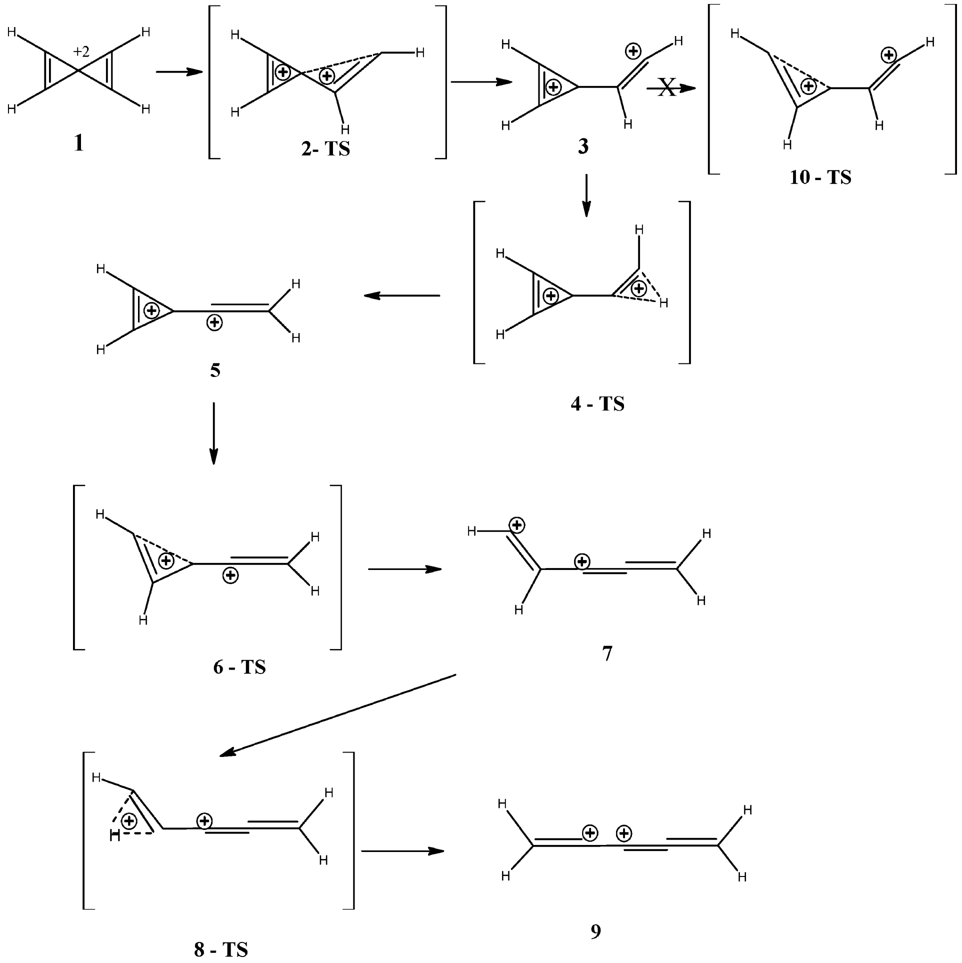


Figure 1. Relative enthalpies of ring-opening and hydride-shift reactions from spiropentadiene dication (in kcal/mol), optimized structures of **1**−**9**, and selected geometrical parameters (bond lengths given in Å).

SCHEME 1



constant in all spiropentadiene structures. However, the bond length between the external carbon atoms in each ethylenic group decreases from the neutral spiropentadiene to the spiropentadiene dication, and the bond length between each vicinal C−H atomic pair slightly increases from the neutral spiropentadiene to the spiropentadiene dication.

From Figure 3, one also can see that the interatomic distances, $C_{ext}-C_{ext}$ (from different ethylenic groups) and $C_{ext}-H$ (from

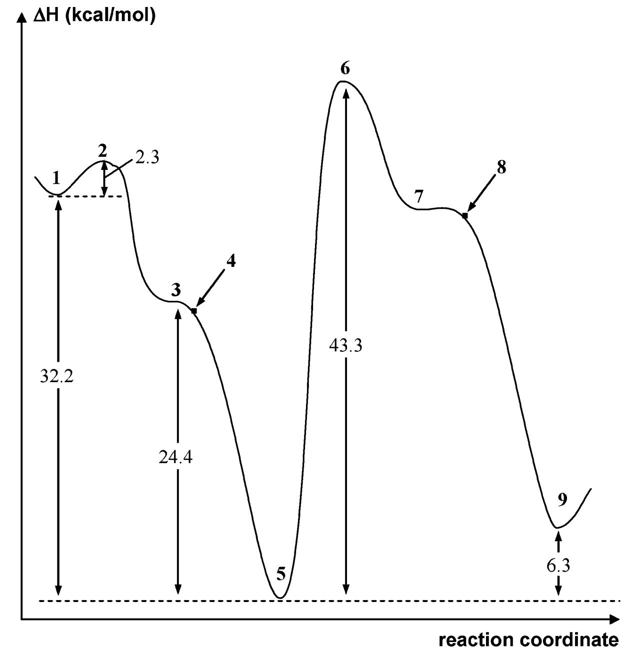
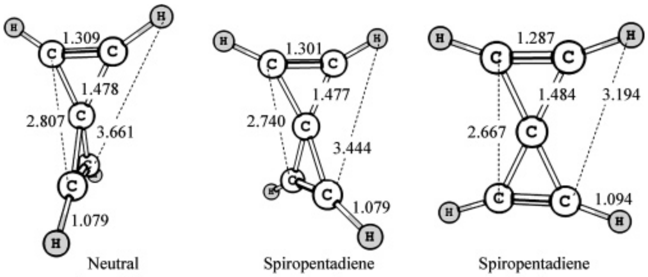


Figure 2. Pictorial representation of the potential energy surface for $C_5H_4^{2+}$.



Neutral spiropentadiene

Spiropentadiene monocation

Spiropentadiene dication

Figure 3. Bond lengths and interatomic distances (in Å) of neutral spiropentadiene, the spiropentadiene monocation, and the spiropentadiene dication.

different ethylenic groups), decrease from neutral spiropentadiene to spiropentadiene dication.

To investigate the electronic nature of the spiropentadiene moiety, AIM analysis was performed on the neutral spiropentadiene, its monocation, and its dication. The AIM theory is based on the analysis of the electronic density distribution, $\rho(r)$.[10] Much information can be obtained from the electronic density distribution analysis, such as the critical points related to bonds and rings and their respective eigenvalues and ellipticities. The delocalization index (DI) provides information about the number of electrons that are shared or exchanged between two atoms or basins,[15] which is originated from the integration of the Fermi hole density.

Figure 4 shows the molecular graph for the neutral, monocationic, and dication spiropentadiene. The DIs in neutral and dication spiropentadiene are also shown. The numbers 1−4 indicate the critical points. Critical point 2 is a ring critical point (RCP). The others are bond critical points (BCPs). For all studied spiropentadienes, the DIs involving the central carbon and the external carbons atoms are nearly 1.0, which means that one electron is shared between those atoms. It is interesting to note that the DIs of the $C_{ext}-C_{ext}$ bond in each external ethylenic moiety and the C−H bonds decrease from neutral spiropentadiene to the dication spiropentadiene, indicating reorganization in the electron density after removing two electrons of the spiropentadiene system mainly through the σ framework (Figure 4). Figure 4 shows the DI between the external carbon atoms of different ethylenic groups (DI = 0.06). This is an apparently small value. Then the spiropentadiene dication cannot be represented by a C^{+2} atom in the middle of a cyclobutadiene ring.

In the case of the dication spiropentadiene (Figure 4C), all four bonds between the ptC and the neighbor carbon atoms have DI = 1.02. Likewise, all four bonds involving the central carbon in the neutral spiropentadiene have DI = 1.01 (Figure 4A). For comparison purposes, the DI between any pair of carbon atoms in the cyclopropenyl cation is 1.437. This is an indication no participation of π electrons by aromatic delocalization in the ptC atom.

From the relation between bond order (n) and charge density in the BCP of a C−C bond (ρ_b), $n = \exp[A(\rho_b - B)]$ was plotted a ln n versus ρ_b graph from known values of bond order and charge density of BCPs from ethane, ethylene, acetylene, and benzene (Supporting Information). Then it was possible to obtain the bond orders of the $C_{ext}-C_{ext}$ bonds in the spiropentadiene systems. The bond order of the $C_{ext}-C_{ext}$ bond increases in the following order: neutral spiropentadiene ($n = 1.96$), spiropentadiene monocation ($n = 2.10$), and spiropentadiene dication ($n = 2.31$). The bond lengths of the $C_{ext}-C_{ext}$ bond in the spiropentadiene molecules follow the same order of decrease (Figure 3).

Table 1 shows atomic charge $q(\Omega)$, atomic volume $v(\Omega)$, atomic dipole moment $M_1(\Omega)$, the localization indexes (LIs), and electronic energy density $E_e(\Omega)$ of the external carbon atom, central carbon atom, and hydrogen atom in the neutral spiropentadiene, spiropentadiene dication, spiropentadiene monocation, and cyclopropenyl cation. The atomic charges of the hydrogen atoms increase from $+0.070e$ (neutral spiropentadiene) to $+0.365e$ (spiropentadiene dication). The atomic charges of the external carbon atoms also increase from neutral spiropentadiene ($-0.130e$) to the dication spiropentadiene ($+0.190e$) as indicated in Table 1. However, in the case of the central carbon atoms, the atomic charges become more negative from neutral spiropentadiene ($+0.210e$) to the dication spiropentadiene ($-0.164e$). This charge density flux from the ethylenic groups to the ptC atom also can be verified from the LIs of the ethylenic carbon atoms. This parameter represents the number of electrons that are localized in an atom, which does not represent the total number of electrons in an atomic basin or the electronic population, $N(\Omega)$. In fact, $N(\Omega)$ is obtained by the integration of the charge density within the atomic volume. This integration is equivalent to LI + $^1/_2$DI = $N(\Omega)$ only for a homoatomic dinuclear molecule.[17] As can be seen from Table 1, a higher LI in the central carbon atom occurs in a dication (Table 1). Besides, by analyzing $E_e(\Omega)$ in Table 1, one can see that the central carbon is more stabilized in the spiropentadiene dication than in the neutral system.

The removal of two electrons from the neutral spiropentadiene increases the atomic volume of the central carbon atom, because it becomes more negatively charged (Table 1). However, the atomic volumes of the hydrogen atoms and external carbon atoms decrease from the neutral spiropentadiene to the spiropentadiene dication, because they become more positively charged. In addition, the atomic dipole moments of the external carbon atoms increase from neutral spiropentadiene to the spiropentadiene dication because the atomic charge in the hydrogen atom becomes more positive from the neutral spiropentadiene to the spiropentadiene dication.

In the comparison of topological and electronic parameters of carbon atoms between the cyclopropenyl cation and the

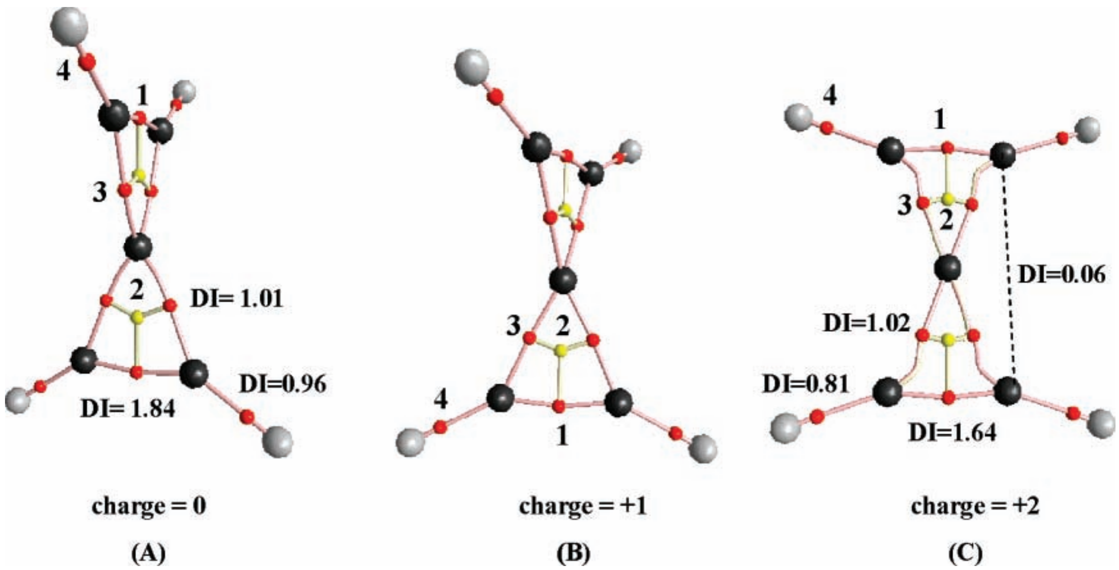


Figure 4. Molecular graphs of the (A) neutral spiropentadiene, (B) spiropentadiene monocation, and (C) spiropentadiene dication. The DIs for each pair of atoms in the neutral and dication spiropentadienes are included. The numbers denote the critical points.

TABLE 1: Atomic Charge $q(\Omega)$, Atomic Volume $v(\Omega)$, Atomic Dipole Moment $M_1(\Omega)$, the Localization Indexes (LIs), and Electronic Energy Density $E_e(\Omega)$ of the External Carbon Atom, Central Carbon Atom, and Hydrogen Atom of Neutral Spiropentadiene, the Spiropentadiene Dication, the Spiropentadiene Monocation, and the Cyclopropenyl Cation[a]

molecule	atom	$q(\Omega)$	$v(\Omega)$	$M_1(\Omega)$	LI[b]	$E_e(\Omega)$
neutral spiropentadiene	external carbons	−0.130	102.9	0.25	4.110	−38.1398
	central carbon	0.210	65.7	0	3.680	−37.8800
	hydrogens	0.070	48.4	0.15	0.383	−0.5835
spiropentadiene monocation	external carbons	0.045	94.4	0.34		−38.0764
	central carbon	0.048	70.8	0		−38.0076
	hydrogens	0.217	39.6	0.11		−0.5238
spiropentadiene dication	external carbons	0.190	88.2	0.46	3.940	−37.9995
	central carbon	−0.164	77.0	0	4.066	−38.1385
	hydrogens	0.365	31.8	0.10	0.192	−0.4497
cyclopropenyl cation	carbon	0.075	91.5	0.33	4.013	−38.0845

[a] Ω is the atomic basin. The atomic charge $q(\Omega)$, the atomic volume $v(\Omega)$, the atomic dipole moment $M_1(\Omega)$, and the electronic energy density $E_e(\Omega)$ are in au. [b] Localization index can only be calculated for closed shell molecules.

TABLE 2: Charge Density (ρ), the Laplacian of Charge Density ($\nabla^2\rho(r)$) (in au), the Ellipticity (ϵ) of the Critical Points of Spiropentadiene Systems and the Eigenvalues of the Hessian Matrix of the Charge Density of the Spiropentadiene Dication (in au)

		neutral			monocation			dication					
critical point (CP)	position of the CP	ρ	$\nabla^2\rho(r)$	ϵ	ρ	$\nabla^2\rho(r)$	ϵ	ρ	$\nabla^2\rho(r)$	ϵ	λ_1	λ_2	λ_3
1[b]	$C_{ext}-C_{ext}$ bond path[a]	0.342	−0.916	0.167	0.353	−1.000	0.121	0.369	−1.109	0.128	−0.722	−0.640	0.253
2[c]	RCP[d]	0.214	0.292		0.220	−0.024		0.224	0.200		−0.289	0.087	0.402
3[b]	$C_{ext}-C_{cent}$ bond path	0.244	−0.376	0.393	0.241	−0.308	0.560	0.230	−0.113	1.477	−0.327	−0.132	0.346
4[b]	$C_{ext}-H$ bond path[a]	0.278	−0.952	0.005	0.282	−1.020	0.007	0.275	−1.050	0.004	−0.832	−0.830	0.612

[a] These bonds involve vicinal atoms. [b] Critical points 1, 3, and 4 are (3,−1). [c] Critical point 2 is (3,+1) [d] RCP means ring critical point.

spiropentadiene dication from Table 1, one can see that the planarization of the central carbon in the spiropentadiene dication probably has no contribution from π electrons because these parameters in the spiropentadiene dication are different from those in cyclopropenyl cation. Thus, the bonding scheme in the spiropentadiene dication is qualitatively different from that of the cyclopropenyl cation; i.e., the spiropentadiene dication is not the merging of two cyclopropenyl moieties.

The charge density flux also can be followed by the bond path angle. The bond path angle of each three-membered ring in the neutral spiropentadiene (88.1°) is approximately similar to that from cyclopropane (77.1°) and that from the cyclopropenyl cation (78.4°). Nevertheless, in the dication spiropentadiene, it is only 45.0°. This decrease in the bond path angle of the three-membered rings when going from neutral spiropentadiene to the dication is an indicative of accumulation of electron density inside the three-membered rings of the dication molecule, similarly to what happens in three-center two-electron (3c2e) bonds.

Table 2 depicts the charge density (ρ), the Laplacian of charge density ($\nabla^2\rho(r)$), and the ellipticity (ϵ) of the critical points of spiropentadiene systems and the eigenvalues of the Hessian matrix of the charge density of the spiropentadiene dication related to the critical points 1−4. Critical point 2 is a RCP. The others are BCPs. Each critical point is identical in each spiropentadiene system (Figure 5). For example, BCP 1 is a critical point in the bond between vicinal external carbons. BCP 3 is a critical point in a bond involving one external carbon and the central carbon atom. BCP 4 is the critical point in the bond between an external carbon and its vicinal hydrogen atom

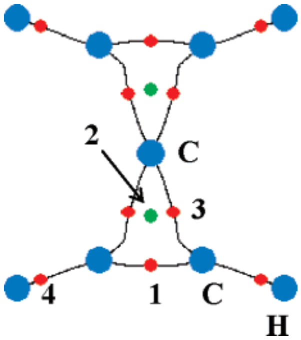


Figure 5. Molecular graph of the charge density of the spiropentadiene dication and its critical points 1−4.

for every type of spiropentadiene. As can be seen in Table 2, the charge density of BCP 1 increases continuously from the neutral to the dication system, while the opposite trend is observed for BCP 3. The charge density in BCP 4 is nearly invariant in these systems. The charge density of RCP 2 increases when going from neutral to the dication spiropentadiene. Even after removing one or two electrons from the spiropentadiene moiety, the electron density in each ring center increases as the charge densities in the external carbon and hydrogen atoms decrease (Table 2).

Another important analysis from the AIM theory is the Laplacian of the charge density, $\nabla^2\rho(r)$. It is defined as the sum of the three principal curvatures of the function at each point of space. The density is locally concentrated in those regions where $\nabla^2\rho(r) < 0$ when $\rho(r)$ is a local maximum. Likewise, the density is locally depleted in those regions where $\nabla^2\rho(r) > 0$ when $\rho(r)$ is a local minimum. Table 2 shows that the $\nabla^2\rho(r)$ of BCP 1 becomes more negative (more locally concentrated) from the neutral to the mono- and to the dication of spiropentadiene. This tendency indicates that the bond increases its covalent nature. However, $\nabla^2\rho(r)$ of BCP 3 becomes less negative (less locally concetrated) from the neutral spiropentadiene to the spiropentadiene dication, indicating that the central carbon atom has a decreasing covalent interaction with the carbon atoms of both ethylene groups from the neutral to the dication molecule.

The ellipticity (ϵ) in a BCP is derived from the relationship between the λ_1 and λ_2 eigenvalues of the Hessian of electron density. Its increase is a measure of how the electron density distribution is distorted from the axial symmetry of the bond. As ϵ approaches zero, the bond tends to be single or triple, i.e., completely symmetrical to the interatomic axis. By analyzing ϵ on BCP 4 (Figure 5), it is clear that its corresponding bond has almost no change in nature in the three molecules and it resembles a single bond in all cases. The ellipticity of BCP 1 on the dication is 23% smaller than that from the neutral compound. The DI in the $C_{ext}-C_{ext}$ bond is smaller in the dication parent (Figure 4). The charge density of BCP 1 is higher in the dication, and $\nabla^2\rho(r)$ of BCP 1 in the dication is more negative than the other BCP 1's. Then, there is a higher charge accumulation in the region around BCP 1; however, there is no relation between the increase of charge density in BCP 1 and the decrease of the DI of this bond. They are independent parameters. The ϵ on BCP 3 shows that removing two electrons from the spiropentadiene system makes the ptC bonds to the ethylene groups completely distorted from the bond axis as happens in 3c2e bonds.[17] As discussed above, the Laplacian of BCP 3 has a decreasing covalent tendency, but its corresponding bond has an increasing ellipticity when going from neutral to dication spiropentadiene (Table 1). In addition, the ptC−C_{ext} bond has an invariant DI and only a 5% reduction in the charge density of BCP 3 from the neutral to the dication species (Table 2).

In carbonium ions, the structural change is associated with ellipticity values much higher than unit. In some cases, the $|\lambda_1|/\lambda_3$ relationship has a high value in molecules close to degeneracy.[18] The ellipticities of all BCPs of all spiropentadiene systems are not high. The evaluation of the $|\lambda_1|/\lambda_3$ relationship for BCP 3 from the neutral to the dication spiropentadiene molecules yields the respective values: 1.197, 1.142, 0.945. In the AIM theory, the three eigenvalues of the Hessian matrix of a BCP may be used as a valuable tool for evaluation of structure fluctuations. If any eigenvalue of the Hessian matrix is zero, then it indicates the proximity of a structural change, such as in a rearrangement.[19] For the spiropentadiene dication, λ_1, λ_2, and λ_3 for all BCPs are not zero (Table 2), which is consistent with a stable compound, i.e., a molecule that is not under structural changes.

Table 3 shows the position, in Cartesian coordinates, and the values of $\nabla^2\rho(r)$ of the (3,−3) critical points from the valence shell charge concentration (VSCC) graph of the spiropentadiene dication. In this VSCC graph, the Euler equation ($V - E + F = 2$) has been satisfied.[20] The origin of the Cartesian coordinates coincides with the coordinates of the ptC carbon atom. The dication spiropentadiene has 16 (3,−3) critical points. Each group of four (3,−3) CPs are in each quadrant of the plane that passes through all of its atoms, and they have the same values of $\nabla^2\rho(r)$. The (3,−3) critical points 1 and 2 are located in the region between the ptC atom and each C_{ext} atom. The (3,−3) critical point 3 is located in the region between each C_{ext} atom and its corresponding vicinal H atom. The (3,−3) critical point 4 is located in the region between each atomic pair $C_{ext}-C_{ext}$. From the coordinate positions, one can see that (3,−3) CP 1 is closer to the ptC atom than (3,−3) CP 2 and that the former has a higher negative value. Then the charge density is more locally concentrated in the (3,−3) CP closer to the ptC.

Figure 6 shows the contour maps of the Laplacian distribution of the electronic charge density for the spiropentadiene mol-

TABLE 3: Position (in Cartesian Coordinates) and the Values of the Laplacian of the Charge Density of the (3,−3) Critical Points from the Laplacian Molecular Graph of the Spiropentadiene Dication

(3,−3) critical point from the Laplacian molecular graph[a]	region where the (3,−3) critical point is located	Cartesian coordinates of the (3,−3) critical points[b]			
		x	y	z	$\nabla^2\rho(r)$
1	between ptC and C_{ext}	0.72	0.63	0.00	−0.692
2	between ptC and C_{ext}	1.05	1.49	0.00	−0.369
3	between C_{ext} and H	2.12	2.81	0.00	−1.416
4	between C_{ext} and C_{ext}	0.27	2.76	0.00	−1.239

[a] The dication spiropentadiene has 12 (3,−3) critical points. Each group of three (3,−3) CPs are in each quadrant of the plane that passes through all of its atoms, and they have the same values of the Laplacian. [b] The origin of the Cartesian coordinates coincides with the coordinates of the ptC carbon atom.

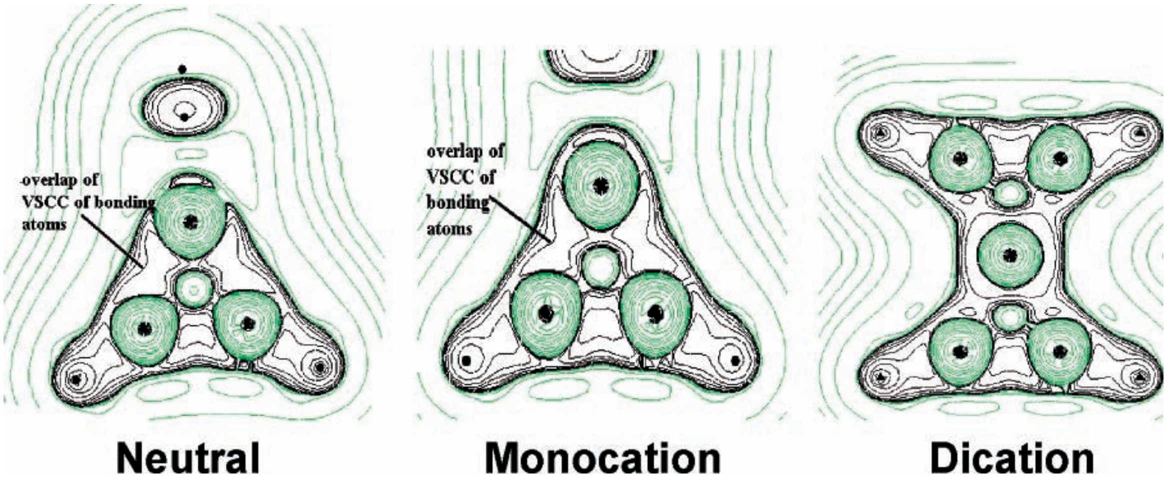


Figure 6. Contour maps of the Laplacian distribution of the electronic charge density for the spiropentadiene molecules in the plane that contains, at least, two external carbon atoms and the ptC atom. The green curves are related to charge depletion, while the black lines are charge concentration.

ecules in the plane that contains all atoms. As can be seen the neutral and monocation molecules have overlapping charge concentrations between all neighbor atoms. It means that there is an overlap of the respective valence shell charge concentration for every pair of connected atoms in neutral and monocation molecules (Figure 6). Overlap of VSCC means a fusion of distinct Laplacian surfaces into one where there is charge accumulation. However, in the dication molecule, there is no overlap of VSCC between the ptC atom and the neighboring carbon atoms (Figure 6). The lack of overlap of VSCC between the ptC atom and the neighbor carbon atoms indicates a reducing interaction between the ptC and the other carbon atoms.

On the basis of the comparison of the bond lengths and bond orders of the $C_{ext}-C_{ext}$ bond between the spiropentadiene dication and neutral spiropentadiene, one can deduce that the π electrons do not participate in the planarization of the ptC atom because the $C_{ext}-C_{ext}$ bond has more double bond character in the spiropentadiene dication than in the neutral spiropentadiene. In addition, the atomic parameters of carbon atoms (atomic charge, atomic volume, atomic dipole moment, and LI) are very different by comparing the spiropentadiene dication and the cyclopropenyl cation. The DI between external carbon atoms of different ethylenic groups and the difference between bond lengths of C=C in cyclobutadiene and the $C_{ext}-C_{ext}$ bond in spiropentadiene dication indicate that the spiropentadiene dication is not a C^{+2} atom in the middle of a cyclobutadiene ring.

Conclusions

The AIM theory shows that the ptC from the spiropentadiene dication is mainly stabilized by σ electrons and this atom has a negative charge. The bonds to the ptC atom have less covalent character than the central carbon from neutral spiropentadiene. The total positive charge is spread along the structure skeleton. The analysis of the potential energy surface shows that the dication spiropentadiene has a 2.3 kcal/mol activation barrier for ring opening, making it a possible base structure for synthesizable ptC compounds. The geometrical parameters and the results of the AIM theory indirectly indicate that the π electrons do not participate in the planarization of the ptC in the spiropentadiene dication and the spiropentadiene dication is not a C^{+2} atom in the middle of a cyclobutadiene ring.

Acknowledgment. The authors thank CNPq, CAPES, and FAPERJ for financial support and Gabriel Merino for his helpful comments.

Supporting Information Available: Atoms in molecules theory, computed energy values of compounds 1−9, *Z* matrices of optimized structures, total energies, and geometry coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For a recent review, see: Keese, R. *Chem. Rev.* **2006**, *106*, 4787.

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