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The design of molecules containing planar tetracoordinate carbon[☆]

U. Deva Priyakumar,[*] A. Srinivas Reddy and G. Narahari Sastry[*]

Molecular Modelling Group, Organic Chemical Sciences, Indian Institute of Chemical Technology, Hyderabad 500 007, India

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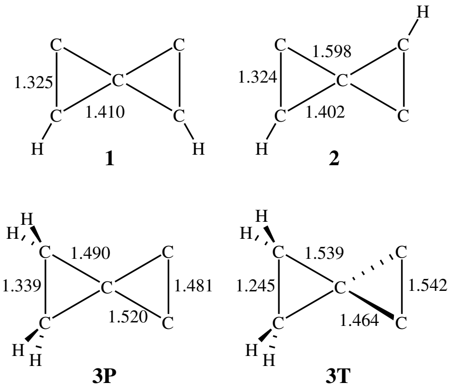
Abstract—A novel preference for planar tetracoordination was observed over the conventional tetrahedral arrangement in a new series of C_5H_2, C_5H_4, $C_5H_4^{1+/2+}$ and related compounds. The stability of these molecules is assessed with the ring-opening barriers, HOMO–LUMO gap, singlet–triplet energy differences and nucleus independent chemical shift values.

The tetrahedral arrangement of saturated carbon centres is a fundamental paradigm in chemistry and provides the third dimension in chemical thinking. About three decades ago, Hoffmann's group explored the possibility of stabilizing planar tetracoordinate carbon (ptC).[1] The quest to enhance the stability of planar tetracoordinate carbon over the corresponding tetrahedral counterpart has continued unabated over the last few decades.[2,3] Elegant and well conceived theoretical and experimental designs were employed to achieve the ptC through electronic stabilization as well as brute force structural constraints.[3–7] Previously reported electronically stabilized compounds are usually charged, heteroorganic or organometallic.[3,5–8] The remarkable preference of a planar over the tetrahedral structure manifested in the C_3H_2 unit failed to enthuse further efforts as the planar structure is not a minimum.[9] Recently, the preference of a planar arrangement for the central carbon atom of C_5^{2-} was reported.[8] Pure hydrocarbon or carbon skeletons showing an unprecedented structural preference for ptC is interesting, however a neutral hydrocarbon stabilized exclusively by electronic interactions is elusive.



1 2 3P 3T

Figure 1. The principal geometric parameters obtained at the B3LYP/6-311+G** level.

We have explored the prospects of designing the smallest neutral hydrocarbon bearing a ptC by considering the spiro-C_5 unit as a prototype. Our systematic studies lead to three minima, **1**, **2** and **3** (Fig. 1). These molecules represent the smallest neutral electronically stabilized hydrocarbons. Identification of the tetrahedral structure for **1** and **2** was not successful. The planar form of **3** is 69.7 kJ/mol more stable than its tetrahedral counterpart.[†] B3LYP/6-311+G** optimizations and frequency calculations were performed on all the compounds considered in the present study. All calculations were performed using the Gaussian 98 program package.[10] Nucleus independent chemical shift (NICS)[11] calculations have been employed to estimate the aromatic nature and the HOMO–LUMO and singlet–triplet energy differences were computed to assess the structural stability (Table 1). Interestingly, the NICS values indicate that while the planar structure is aromatic, the

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[*] Corresponding authors. Tel.: +91-40-27160123x2621; fax: +91-40-27160512; e-mail: gnsastry@iict.res.in

[†] A total of around 10 structures were considered; only **1**, **2** and **3P** were found to be minima.

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Table 1. The activation energy barriers ($\Delta E^{\ddagger}$) and reaction energies (ΔE_r) for the ring-opening reactions, number of imaginary frequencies (N_{Img}), NICS(1) values, HOMO–LUMO energy gaps ($\Delta_{\mathrm{H-L}}$) and singlet–triplet energy differences ($\Delta E_{\mathrm{s-t}}$) obtained at the B3LYP/6-311+G** level

Structure	N_{Img}	$\Delta E^{\ddagger}$ (kJ/mol)	ΔE_r (kJ/mol)	NICS(1) (ppm)	$\Delta_{\mathrm{H-L}}$ (eV)	$\Delta E_{\mathrm{s-t}}$ (kJ/mol)
1[a]	0	47.0	−201.3	−15.3	5.96	367.2
		5.7				
2[a]	0	57.1	−183.0	−15.5	5.93	376.9
		21.0				
3P	0	8.6	−132.5	−19.0	4.80	288.4
3T	2	[b]	[b]	11.5	2.83	70.9
4	0	54.6	−141.9	−12.5	[c]	[c]
5	0	17.8	−71.6	−16.6	6.27	452.1
6	0	97.1	−82.6	−15.5	[c]	[c]
7	1	[b]	[b]	−11.9	[c]	[c]
8	2	[b]	[b]	−12.7	[c]	[c]
9	0	7.5	−24.9	−18.5	5.96	422.2
10	0	71.4[d]	−31.4	−19.4	6.14	376.1
11[a]	0	93.5	86.2	−18.3	5.80	409.1
		10.8	−35.9			
12[a]	0	180.4	−97.5	−17.6	5.95	378.8
		17.8	16.0			
13[a]	0	203.5	201.4	−19.3	5.69	345.0
		127.0	103.9			
14[a]	0	124.9	110.9	−19.8	5.81	339.8

[a] The two entries for the activation barriers and reaction energies correspond to the two modes of ring opening (see Scheme 1).

[b] Not a minimum on the potential energy surface.

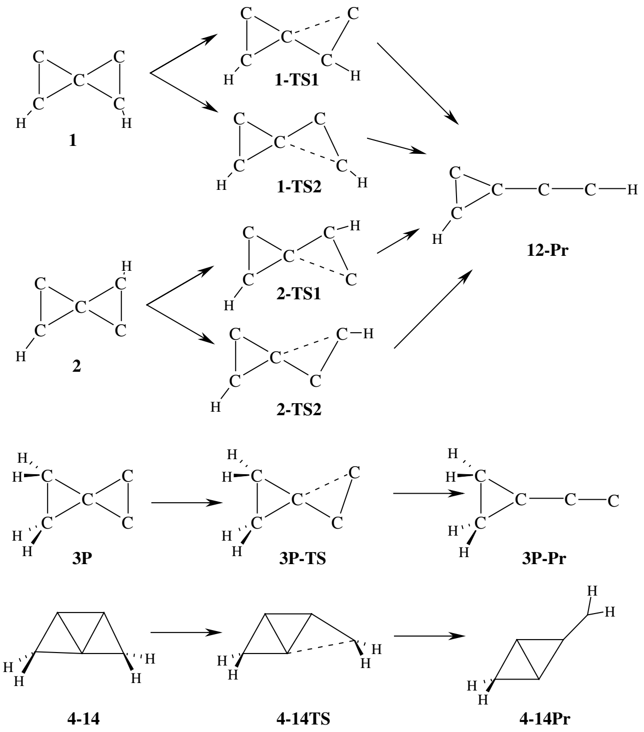
[c] Correspond to doublet states.

[d] Transition state for the other ring opening could not be located.

tetrahedral counterpart is anti-aromatic. Obviously, the three-membered rings in the C_5 skeletons are strained. However, the strain is not exclusive to the planar arrangement and in any case does not enforce planarity. Therefore, the planar structural preference for the current series may be traced exclusively to electronic factors.

Computationally designing novel structures and characterizing them as minima on the potential energy surface is not an end in itself. Synthetic viability depends on the depth of the valley and resistance towards the rearrangements to more stable isomers. Table 1 indicates that the NICS values of the planar structures are very negative indicating high aromaticity. Furthermore the substantial HOMO–LUMO and singlet–triplet energy differences indicate the fairly good structural stability of **1**–**3**.

Discouragingly, the ring-opening activation energies are not high enough, especially for **1** and **3**, indicating the instability towards ring opening. The schematic diagram of the ring-opening reactions is depicted in Scheme 1.[‡] The same lacuna has also been observed in the C_5^{2-} structure. Plagued with low activation energies for the ring-opening rearrangement, we explored the design of compounds devoid of such a problem. Firstly, the C_5H_4 structure **3** was subjected to addition and removal of up to two electrons. Structures **1** and **2** show skeletal distortions losing the ptC arrangement upon either addition or removal of electrons. The mono and dianionic forms of **3** revert to the conventional structural preference, namely the tetrahedral form, which is more stable than the planar one. The mono and dications, **4** and **5**, retain the novel preference for the planar arrangement.



Scheme 1. The schematic representation of the ring-opening reactions considered in the present study. **TS** and **Pr** correspond to transition state and the product, respectively. The ring-opening pathways are common in structures with 'B' for **6**–**14**. Thus, no special mention is made for C or B in the ring-opening pathway for **4**–**14**.

[‡] The recently proposed C_5^{2-} moiety was also found to have a very low barrier (14.6 kJ/mol) for the ring opening and the exothermicity of the reaction is 190.3 kJ/mol.

However, the cationic species displayed a connectivity of tricyclic structures shown in **4** and **5**, which are about 120.2 and 417.8 kJ/mol more stable than the bicyclic arrangement possessing the **3**-type connectivity. While the dication **5** is perfectly planar, the monocation **4** is not a minimum. A pyramidal structure (not tetrahedral) is a minimum and is about 19 kJ/mol more stable than the planar one. Interestingly, the charged isomers have higher barriers for activation compared to the neutral counterpart.

Encouraged by this novel structural preference of the cationic species, Schleyer's charge-compensation strategy[5a] was employed to obtain the neutral analogues of **4** and **5**. This resulted in three isomers for **4** (**6**–**8**) and six for **5** (**9**–**14**) (Fig. 2). The planar forms of all these compounds were computed to be minima, except **7** and **8**, which are a transition state and a second-order saddle point, respectively. For all the minimum energy structures, we have located the ring-opening transition states and characterized them through intrinsic reaction coordinate (IRC) calculations. Isomers **6**, **13** and **14** were found to have high barriers and the reactions are highly endothermic for **13** and **14** indicating that these compounds are viable species for experimental observation.

All the planar forms exhibit quantitative negative NICS values indicating high aromaticity in this class of compounds. Similarly, the planar molecules have substantial HOMO–LUMO and singlet–triplet energy gaps. An examination of the frontier orbital shapes indicates a high delocalization of the ptC's lone pair, through the donation of the electrons to the empty π-orbital of the adjacent bare C–C unit. The stabilization of the lone pair on the carbon of ptC, resulted not only in the widening of the HOMO–LUMO gap but also resulted in high aromatic stabilization. Thus, the designed series of compounds are driven by the high aromatic stabilization of the three-membered ring.

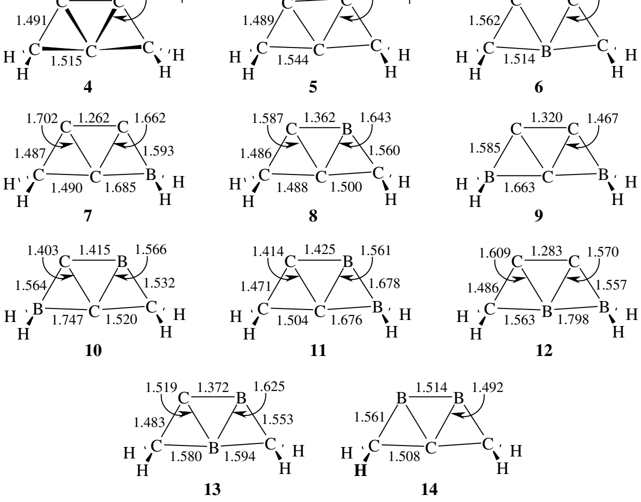


Figure 2. The principal geometric parameters obtained at the B3LYP/6-311+G** level.

In summary, the present study reports the computational design of the, hitherto unknown, smallest neutral ptC containing hydrocarbons (**1**, **2** and **3**), which are minima on their potential energy surfaces. The remarkable preference of these compounds for the planar arrangement is due to aromatic stabilization. Systematic exploratory studies have led to a new series of compounds exhibiting a novel preference for planar tetracoordination. A charge-compensation strategy has yielded a series of potential ptC-containing molecules as well as those with planar tetracoordinate borons, **6**, **12** and **13**. These structures are highly stable both kinetically and thermodynamically and we anticipate that the present study will trigger experimental efforts in this direction. The current strategy of stabilizing the planar tetracoordinate compounds seems to be a general one and can be extended to other heteroaromatic main group elements.[12]

Acknowledgements

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