Towards Design of the Smallest Planar Tetracoordinate Carbon and Boron Systems

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Abstract: A series of cyclic hydrocarbons analogs where a carbon displays unusual planar tetracoordinate structure is proposed, employing hybrid density functional theory calculations using B3LYP functional and 6-311+G** basis set. Various strategies were employed to design the neutral planar tetracoordinate hydrocarbon analogs. The same strategy is employed for designing the planar tetracoordinate boron systems. The simplest neutral planar tetracoordinate hydrocarbons were proposed and the effect of substitution on their stability has been assessed. The aromatic stabilization is gauged with nucleus independent chemical shift calculations. The activation barriers for the ring opening reaction, the highest occupied molecular orbital and lowest unoccupied molecular orbitals gap and singlet-triplet energy difference were estimated to gauge the plausibility experimental realization.

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Key words: planar tetracoordinate carbon; boron; aromatic stabilization; ring-opening barrier; nucleus independent chemical shift

Introduction

Fundamental paradigms such as chirality and stereoisomerism in chemistry and biology rests on the rule that a tetracoordinate carbon prefers to have its ligand in a tetrahedral arrangement.[1,2] A closer examination reveals that EH_4 (where E = C, Si, B^-, Al^-, N^+, P^+) type molecules with eight valence electrons prefer a tetrahedral arrangement over the corresponding planar one, and this has become one of the most powerful structural principle in chemistry for more than a century.[3,4] Obviously, stereomutation of tetrahedral compounds are of paramount chemical interest, and this racemization of the chiral molecules is precluded because of the inaccessibility of the putative planar transition structure. Although, most of our understanding in chemistry is based on qualitative rules and concepts, exceptions to the established concepts continue to be a part of excitement and enthusiasm in research, which eventually defines the boundaries for a given concept. Once the boundary for an established concept is clearly established it becomes easier to effectively employ these concepts.

As the planarity leads to the destruction of stereo differentiation for the tetracoordinate systems, the relative stability of the planar system in comparison to the tetrahedral arrangement has become a fundamentally interesting point. About 35 years ago Hoffmann et al., have set-off the quest to understand the reasons for the natural preference for tetrahedral structure and in this circumstances one can reverse it.[3] This is soon followed by an elegant and exhaustive attempt by Schleyer and co-workers and this group continue to explore the problem ever since.[4–7] Two distinct approaches, namely the electronic stabilization and brute-force structural constraints, were employed by a degree of success to get access to the unusual planar tetracoordinate structures.[8] The strategy to adopt extreme angular distortions by incorporation into a strained polycyclic environment has been pursued both experimentally and computationally.[9] The successful attempts which provided good results along the electronic stabilization protocols, are those based on organometallic analogs. Several elegant and well-designed attempts lead to realization of a good number of planar tetra coordinated carbon containing molecules in organometallic chemistry. Earlier well-designed computational strategies involved the incorporation of Li, B, Al and other electron deficient substituents.[5,6,10,11] Thus, the quest to understand the basis for the preference for tetrahedral arrangement over the planar one is on.[12–19] The earlier computational and experimental observations of encountering a planar tetracoordinate arrangement of carbon are largely by chance rather than by design. The efforts have lead to computational design of planar penta, hexa, hepta, octacoordinate carbon, with hypercoordinate boron, silicon, as well as phosphorous.[13] Also, there is interest in designing molecules with multiple planar tetracoordinate carbon centers.[14]

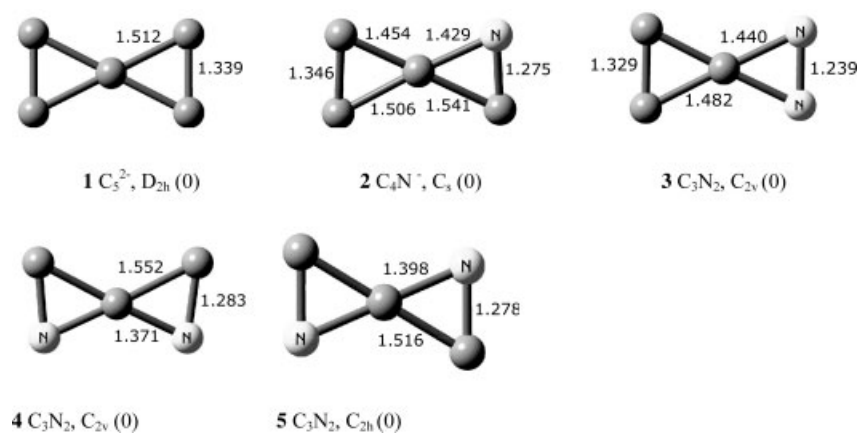*Correspondence to:* G. N. Sastry; e-mail: gnsastry@iict.res.in

Figure 1. Geometries of $C_{5-m}N_m^{m-2}$ systems at B3LYP/6-311+G** level of theory.

However, in hydrocarbons and the main group element chemistry the advances are rather limited, until about a few years ago. First, Merino et al.[15,16] have identified the smallest unit $C(C)_4$ unit in C_5^{2-} which contain the planar tetracoordinate carbon (ptC). Then in a preliminary report, we have put forward the smallest neutral planar tetracoordinate hydrocarbons.[17] Later Pancharatna et al. have elegantly extended the systems reported by Merino et al. to show that the preference for the ptC will be prevailed even in extended systems.[18] This is followed by excellent design of planar tetracoordinate hydrocarbons by the Perez et al.[12] Esteves et al.[19] and Minyaev et al.[20] All these studies have one common objective that the central carbon is engaged in a strong π-delocalization network and thus impart aromatic stabilization to the system. When the aromatic stabilization of the extended π-network involving carbon with the tetracoordination overtakes the traditional tetrahedral arrangement, the molecules begin to display the unique preference for the planar geometry. We have also shown that similar strategy can give access to even systems where there are multiple ptC centers in the molecule.[14] Now it has been left to the computational chemists and experimentalists to design and access the unusual structures. Thus, the last couple of years have witnessed excellent progress towards the design of the neutral ptC containing organic molecules.[21]

In this paper, we address the issue of design of molecules with ptCs and its other isoelectronic heteroatom analogs, broadly confining to organic molecules. Our quest is to identify the simplest molecule, which exhibits ptC. What are possible strategies to achieve the 'unusual' geometry? Thirdly, how to optimize the skeletons obtained with other substituents? Is it possible to extrapolate the strategy to other eight valence electron count systems? From theoretical point of view it is fascinating to design molecules, which are most stable in the unusual planar geometry compared to the traditional tetrahedral structures. However, computational design of such structures and characterizing them as the minima on the potential energy surface is only the first step. The crucial aspect lies in the experimental viability, which depends on their stability and resistance to rearrange to more stable products. Therefore, we have also examined the stability of the compounds as given by energy differences between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMO), singlet-triplet energy differences and the aromatic stabilization gauged by nucleus independent chemical shift (NICS) values. Importantly, the ring opening barriers and the reaction exothermicity of the ring opening for the susceptible ring opening pathways.

Methodology

All the calculations are done using Gaussian 03 suite of programs.[22] The structures of all the molecules considered in this study were optimized at B3LYP level[23] using 6-31G* and 6-

Table 1. NICS (1) Values (in ppm), HOMO–LUMO Energy Gaps (in eVs), Singlet Triplet Energy Gaps, Transition State Ring Opening Barriers (TS-1, TS-2), Reaction Energies (ΔE_R), and Relative Energies (ΔE) of $C_{5-m}N_m^{m-2}$ Obtained at B3LYP/6-311+G** Level of Theory.

Structure	NICS (1)	Δ_{H-L}	Δ_{S-T}	TS-1	TS-2	ΔE_R	ΔE
1 C_5^{2-}	−17.2	2.95	209.89	14.6	a	−190.5	–
2 C_4N^-	−18.9; −14.9	4.95	320.81	11.5	38.0	−143.6	–
3 C_3N_2	−18.4; −13.6	3.80	225.35	48.7	2.5	−123.36	166.08
4 C_3N_2	−16.2	5.85	355.39	29.7	0.8	−205.4	0.0
5 C_3N_2	−16.6	5.65	339.02	47.9	1.8	−227.7	22.50

All the energies are given in kJ/mol. a – only one ring opening TS is possible.
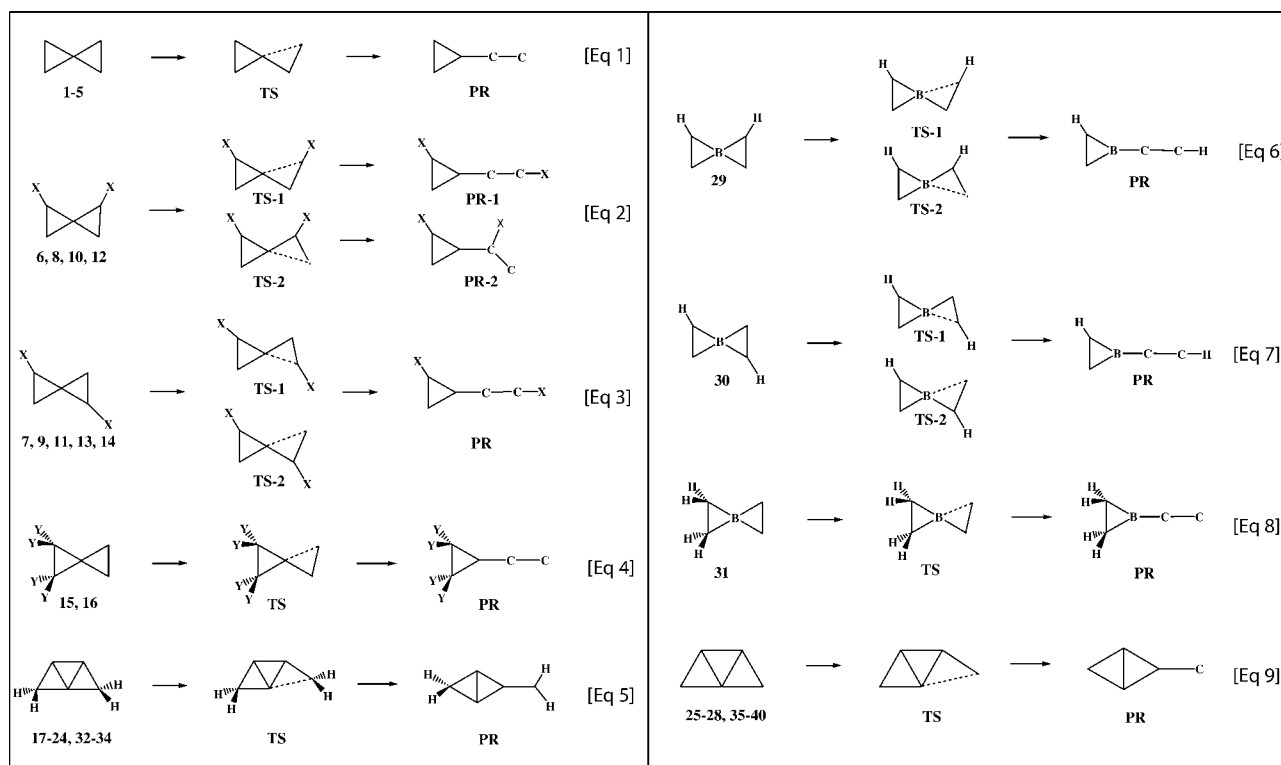
Scheme 1. The schematic representation of the ring opening barriers of planar tetracoordinate compounds (X = —H, —Me, —CMe$_3$, —F, —Cl; Y = —H, —CH3) considered in the present study. **TS** and **PR** correspond to transition state and the product, respectively. The structures, with same skeleton (with different substituents) are represented with the same equation. In case of eqs. (3), (6), and (7) product corresponding to TS-2 is collapsing to same product of TS-1. Incase of methyl and *t*-butyl substituted compounds (12–14) we could not locate the transition state and the corresponding product.

311+G** basis sets. The frequency calculations were also carried out on the optimized geometries at both the basis sets to estimate the dependency of basis set on the geometries and nature of stationary points. Both levels yield virtually identical results indicating less sensitivity as a function of basis set. The NICS values,[24] the frontier orbital energies, and the singlet-triplet vertical energy differences were also estimated. Extensive efforts were put to obtain all possible ring opening transition states to ensure the kinetic stability of the designed structures. The bond order analysis was carried out using Gamess program.[25] The TS-1 and TS-2 nomenclatures were used to describe the transition states for the two most probable ring-opening pathways. (Intrinsic reactions coordinate) IRC calculations were done in most cases to ensure that they connect to the systems with the ptC.

Results and Discussion

The simplest conceivable molecular entity to have a planar tetracoordinate system should have a minimum of five atoms. Earlier studies reveal that C_5^{2-} and CM_4^{2-} (M = Al) display the required structural features,[15] albeit the corresponding electrically neutral systems do not have planar equilibrium geometries. As we focus on the hydrocarbons, we choose to build the molecules starting from a bicyclic C_5 moiety. Let us analyze two different protocols to achieve molecules with electro-neutrality starting from the spiro-bicyclic C_5 skeleton; (a) employing the Schleyer's charge compensation strategy[25] to obtain electronically equivalent to C_5^{2-} (b) to examine the effect of substitution on the C_5 skeleton. Importantly, planarity in these systems is because of their intrinsic electronic structure and not due to the brute-force structural constraints.

$C_{5-m}N_m^{m-2}$ Systems

Structures **2–5** were generated based on the charge compensation strategy of obtaining the structures with ptCs with minimal number of atoms (Fig. 1). The conceived carbon-nitrogen systems are the smallest in the series. Interestingly, all the four possible structures were computed to be minima on their respective potential energy surfaces. The corresponding phosphorous analogs were tried and as they do not correspond to minima on the potential energy surface, they were not considered further. The NICS values presented in Table1 indicate that the nitrogen analogs also have high negative values, indicating their aromatic stability comparable to that of the parent system **1**. The HOMO-
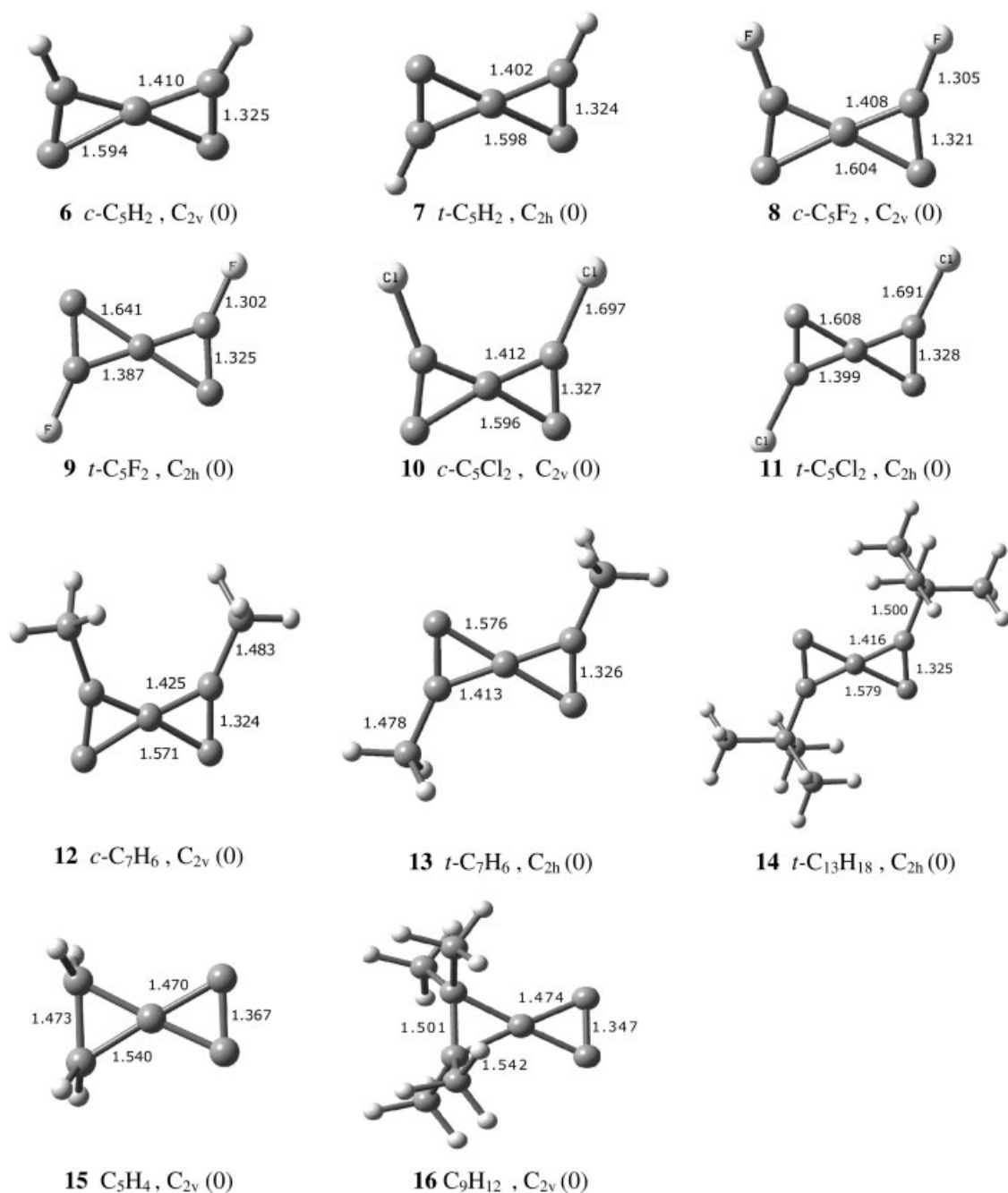
Figure 2. Geometries C_5X_2 (X = —H, —F, —Cl, —CH$_3$, —C(CH$_3$)$_3$) and C_5R_4 (R = —H, —CH3) type systems at B3LYP/6-311+G** level of theory.

LUMO energy differences and the singlet-triplet gaps are in fact much higher than the parent system. However, one of the ring opening barriers for all the three C_3N_2 systems are too low to detect them experimentally. The structures **4** and **5**, where the two nitrogen atoms are placed on different rings are more stable than **3** where both the nitrogen atoms are in the same three membered rings. The corresponding ring opening pathways are depicted as in eq. (1) of Scheme 1.

C$_5$X$_2$ (X = —H, —Me, —CMe$_3$, —F, or —Cl), C$_5$H$_4$, and C$_5$Me$_4$ Systems

Obviously, the central challenge is to produce a neutral hydrocarbon C(C)$_4$ moiety where the central carbon display planar tetracoordination. The strategy is to put substituents on the spiropentadiene core and examine the possibility of hitting at the elusive species (Fig. 2). While placing two hydrogens on one of the

Table 2. NICS (1) Values (in ppm), HOMO–LUMO Energy Gaps (in eVs), Singlet Triplet Energy Gaps, Transition State Ring Opening Barriers (TS-1, TS-2), Reaction Energies (ΔE_R) and Relative Energies (ΔE) of C_5X_2 [X= [—]H, [—]F, [—]Cl, [—]CH$_3$, [—]C(CH$_3$)$_3$], and C_5R_4 (R = [s—]H, [—]CH$_3$) Type Systems Obtained at B3LYP/6-311+G** Level of Theory.

Structure	NICS (1)	Δ_{H-L}	Δ_{S-T}	TS-1	TS-2	ΔE_R	ΔE
6 c-C$_5$H$_2$	−16.6	5.65	339.02	47.0	5.7	−201.3, 4.9	0.00
7 t-C$_5$H$_2$	−15.3	5.96	367.20	57.1	21.0	−183.0	−18.23
8 c-C$_5$F$_2$	−13.2	5.45	361.19	30.1	46.2	−197.4, 1.7	0.00
9 t-C$_5$F$_2$	−13.7	5.09	361.81	37.5	60.5	−182.9	−14.47
10 c-C$_5$Cl$_2$	−14.0	5.08	325.23	28.8	27.4	−211.09, 0.3	0.00
11 t-C$_5$Cl$_2$	−14.4	4.98	309.30	35.1	42.6	−195.90	−15.19
12 c-C$_7$H$_6$	−15.4	5.89	369.78	29.9	d	−211.1	0.00
13 t-C$_7$H$_6$	−15.9	5.80	378.15	36.7	d	−183.6	−27.72
14 t-C$_{13}$H$_{18}$	−15.9	5.80	373.85	38.8	d	−182.9	
15 C$_5$H$_4$	−19.0	4.80	288.40	8.6	a	−132.5	
16 C$_9$H$_{12}$	−19.7	5.05	311.59	23.1	a	−112.6	

All the energies are given in kJ/mol. a – only one ring opening TS is possible. d – the ring-opening barrier could not be located.

three membered rings does not yield a viable structure, **6** and **7**, where hydrogen each is placed on the 2 three membered rings are located as minima on their potential energy surfaces. Thus, as has been claimed by our earlier study, **6** and **7** represent the smallest neutral hydrocarbons displaying the unusual planar tetracoordination. Further, we examined the effect of halo substitution (X = F, Cl) to assess whether this will aid retention/ enhancement of this novel preference or loss of it. Encouragingly, all the halo substituted systems are minima on their potential energy surfaces, and all of them retain the aromatic character (Table 2). In all cases the trans disposition of the substituents, **7**, **9**, and **11** gave higher stability to the molecular systems. Further, we have also examined the methyl and t-butyl trans-substituted systems, **13** and **14**, which again emerged as the minimum. It has been observed that among all the substitutions considered, the fluoro substituted isomers, **8** and **9**, appeared to be most stable with regard to the ring opening pathways [eqs. (2), (3) of Scheme 1]. The halo substitution, in general appears to enhance the barrier for ring opening.

We also have obtained another isomer **15** and its per-methyl substituted analog **16**, which display the ptC arrangement. Actually, we stumbled on this geometry when we are systematically exploring the benzene isomers.[26] The present study indicate that per-methyl substitution on the earlier reported structure **15**, significantly enhances the ring opening barrier. Equation 4 given in Scheme 1 represents the ring opening pathways of the **15** and **16** structures.

Interestingly, this substitution also leads to an increase in the aromatic stability of the other ring, as gauged by the NICS value, besides increase in the HOMO-LUMO and singlet-triplet energy differences. Thus, the substitution by bulkier and electron donating groups seem to stabilize the novel structural preference observed in **16**, and experimental efforts in this direction should be rewarding.

Tricyclic and Boron Systems

As has been reported in our preliminary communication,[17] when C$_5$H$_4$ was subjected to addition and removal of upto two electrons, the structures undergo skeletal distortions toward a fused

tricyclic systems similar to those in Figure 3. While the traditional tetrahedral arrangement is preferred in the anionic counterparts, the mono and dications retained the novel preference for the planar geometry; however, they isomerise to the fused tricyclic geometry. Then we realized that it is important to consider the fused tricyclic skeleton for this electronic arrangement, and considered the corresponding mono and di boron substitutions to achieve neutrality. As known from the earlier studies that the addition of small three membered rings to the molecular system, enhances the stability of the planar tetracroodinate geometry around carbon.[17a] This approach lead to identification of about six structures, when we tried the putative boron substituted devoid of hydrogen. Four of the isomers **25–28** emerged as minima. Table 3 reveals that both the mono substituted isomers **19** and **20** have comparable energies, with the former being slightly more stable. Interestingly, all the molecules considered further are aromatic and an interesting feature in this class of compounds is that most of them have high barriers for the plausible ring opening pathways [eqs. (5) and (9) of Scheme 1]. While, the diboron-substituted analogs **21–24** appear to be viable candidates that bare carbon boron clusters **25–28** does not appear to be suitable candidates for the following reasons. Firstly, they have very small HOMO-LUMO and singlet-triplet gaps. Also, some of the rings have positive NICS values indicating that they are antiaromatic and the ground state of structure **26** is not singlet.

Planar Tetracoordinate Boron

Having realized that the strategies embodied in the aforementioned sections have successfully generated the novel structural preference for the planar tetracoordination over the tetrahedral arrangement for the tetracoordinated main group elements, we ventured to test whether it is possible to access the boron analogs. Following this, we have generated about 15 structures, **29–40** (Fig. 4), which are obtained in designing the molecules planar tetracoordinate boron (ptB). All the considered structures are minima and all of them have a planar tetracoordination. Among the structures considered **35**, **37**, and one of the rings in **40** have
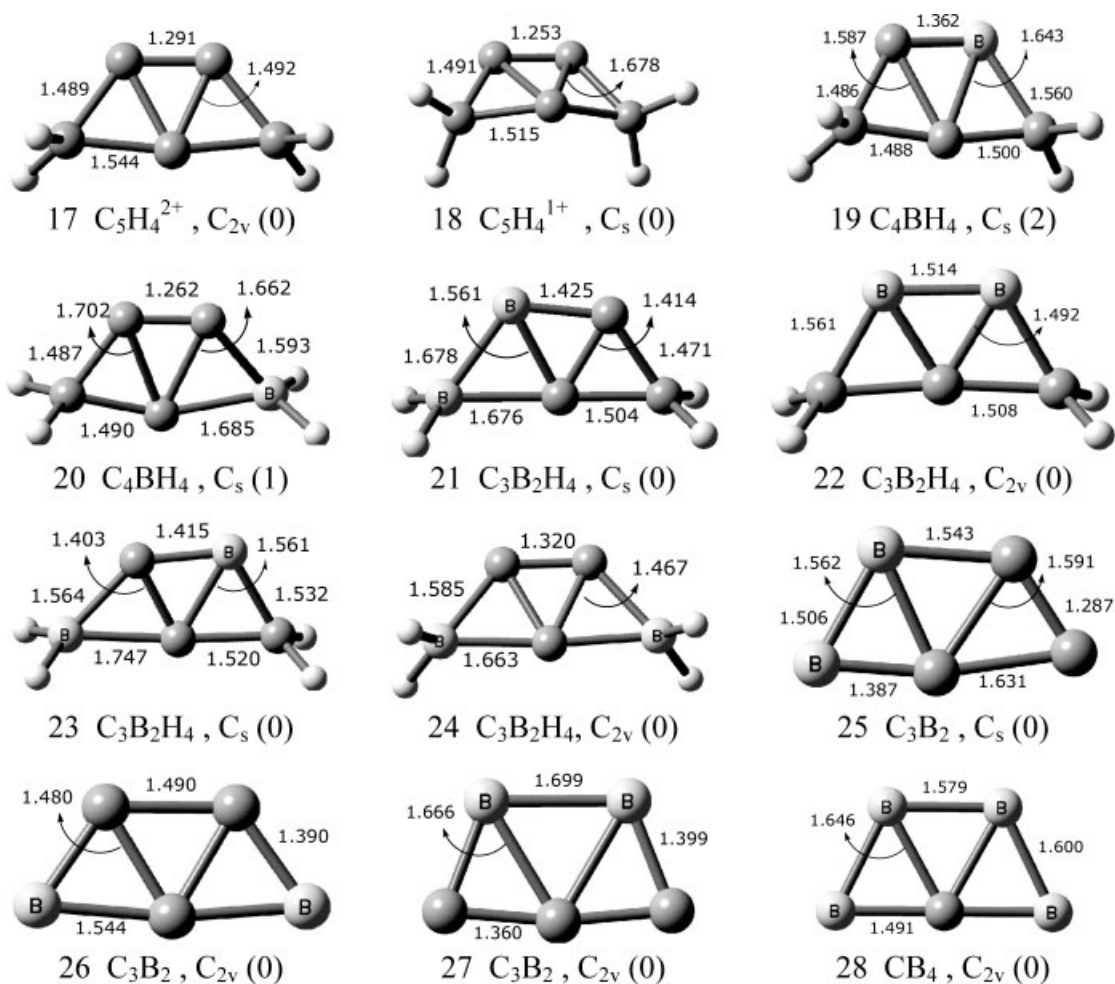
Figure 3. Geometries of tricyclic systems at B3LYP/6-311+G** level of theory.

Table 3. NICS (1) Values (in ppm), HOMO–LUMO Energy Gaps (in eVs), Singlet Triplet Energy Gaps, Transition State Ring Opening Barriers (TS-1, TS-2), Reaction Energies (ΔE_R), and Relative Energies (ΔE) of Tricyclic Systems Obtained at B3LYP/6-311+G** Level of Theory.

Structure	NICS (1)	Δ_{H-L}	Δ_{S-T}	TS-1	TS-2	ΔE_R	ΔE
17 $C_5H_4{}^{2+}$	−12.5	6.27	452.06	17.8	a	−71.6	
18 $C_5H_4{}^{1+}$	−16.6	3.78	c	54.6	a	−82.6	
19 C_4BH_4	−12.7	2.47	c	–b–	b	b	0.00
20 C_4BH_4	−11.9	3.35	c	–b–	b	b	3.52
21 $C_3B_2H_4$	−18.3	5.80	409.14	93.5	10.8	86.2; −35.9	0.00
22 $C_3B_2H_4$	−19.8	5.81	339.80	124.9	a	110.9	−60.76
23 $C_3B_2H_4$	−19.4	6.14	376.08	71.4	d	−31.4	−56.13
24 $C_3B_2H_4$	−18.5	5.96	422.25	7.5	a	−24.9	−5.52
25 C_3B_2	−11.2; 2.1; −5.1	2.47	111.77	84.1	9.5	72.36	0.00
26 C_3B_2	11.2; −9.2	1.89	−54.08	21.6	a	47.68	126.13
27 C_3B_2	5.7; −6.6	2.75	120.16	201.0	a	211.7	−72.52
28 CB_4	−15.0	2.17	30.98	127.6	a	107.1	

All the energies are given in kJ/mol. a – only one ring opening TS is possible. b – not minimum in the potential energy surface. c – represents corresponding doublet. d – the ring-opening barrier could not be located.
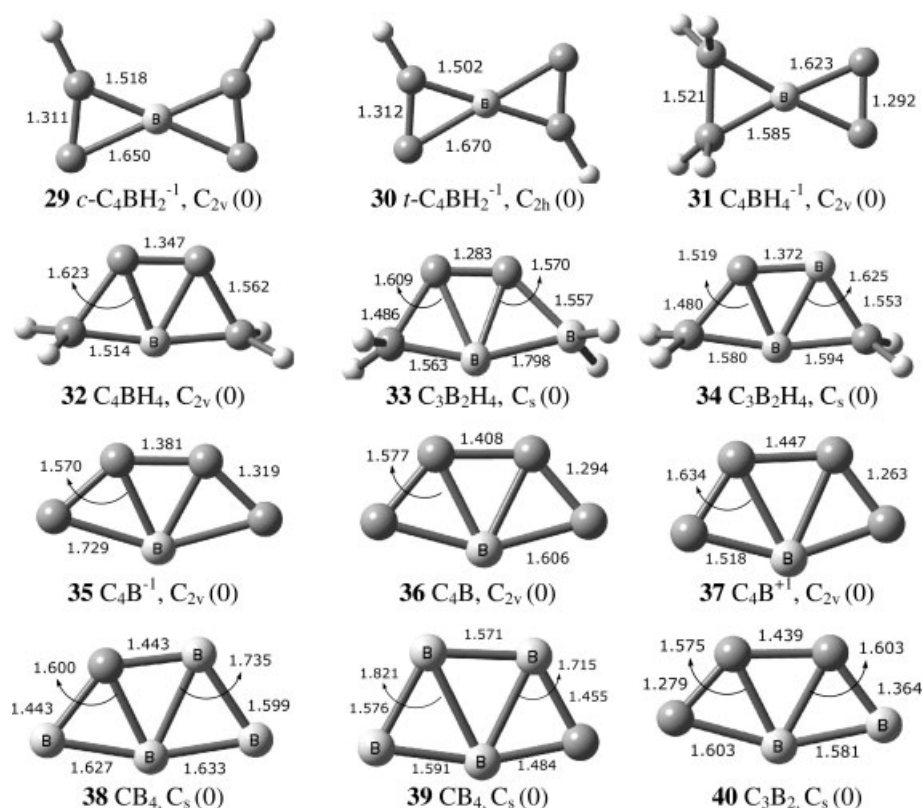
Figure 4. At B3LYP/6-311+G** level optimized geometries of planar tetra coordinate boron.

positive NICS values, indicating their antiaromatic character (Table 4). This is also reflected in the corresponding low values of HOMO-LUMO and singlet-triplet gaps. While all rings in 39, CB_4 isomer have a high negative NICS value, it does not seem to be stable as the ground state for this particular structure is a triplet. One encouraging thing about the boron compounds, which exhibit planar tetracoordination is that the ring opening does not seem to be a factor to preclude their experimental verification, which is perhaps the most important factor in the carbon analogs. The ring opening pathways are shown in Scheme 1

Table 4. NICS (1) Values (in ppm), HOMO–LUMO Energy Gaps (in eVs), Singlet Triplet Energy Gaps, Transition State Ring Opening Barriers (TS-1, TS-2), Reaction Energies (ΔE_R), and Relative Energies (ΔE) of Planar Tetra Coordinate Boron Systems Obtained at B3LYP/6-311+G** Level of theory.

Structure	NICS (1)	Δ_{H-L}	Δ_{S-T}	TS-1	TS-2	ΔE_R	ΔE
29 c-$C_4BH_2^{-1}$	−16.7	3.62	265.55	72.9	87.6	−97.4	0.00
30 t-$C_4BH_2^{-1}$	−16.6	3.93	267.33	81.5	96.4	−86.5	2.59
31 $C_4BH_4^{-1}$	−8.3; −18.7	4.16	373.02	5.3	a	−91.24	0.00
32 C_4BH_4	−15.5	3.34	c	97.1	a	−82.6	51.52
33 $C_3B_2H_4$	−17.6	5.95	378.76	180.4	17.8	−97.5; 16.0	0.00
34 $C_3B_2H_4$	−19.3	5.69	345.05	203.5	127.0	201.4; 103.9	−11.41
35 C_4B^{-1}	3.6	3.97	204.16	31.6	a	e	0.00
36 C_4B	−1.8	4.17	c	d	d	e	65.97
37 C_4B^{+1}	13.1	3.62	151.84	113.5	a	109.2	286.69
38 CB_4	−13.8, −16.5	2.02	2.97	36.7	55.2	120.3	0.00
39 CB_4	−11.2; −16.2; -10.5	1.87	−3.11	23.1	102.5	138.9	−4.32
40 C_3B_2	−6.9; 2.1; −11.0	2.70	84.01	63.2	153.2	e	

All the energies are given kJ/mol. a − only one ring opening TS is possible. c − represents corresponding doublet. d − the ring-opening barrier could not be located. e – product could not be obtained.

Table 5. NBO Charges on the Central Planar Atom, Bond Orders, and Total Bond Orders (TBO) of the Considered Planar Tetra Coordinate Systems at B3LYP/6-31G* Level of Theory.

Structure	Charge	Bond Order				TBO
		1	2	3	4	
1 C_5^{2-}	−0.261	1.089				4.356
2 C_4N^-	−0.113	1.206	1.065	0.929	0.879	4.079
3 C_3N_2	0.034	1.097	0.771	–	–	3.736
4 C_3N_2	0.147	1.075	0.794	–	–	3.738
5 C_3N_2	0.117	1.021	0.851	–	–	3.756
6 c-C_5H_2	−0.111	1.141	0.781	–	–	3.844
7 t-C_5H_2	−0.105	1.132	0.798	–	–	3.860
8 c-C_5F_2	−0.176	1.074	0.758	–	–	3.664
9 t-C_5F_2	−0.163	1.092	0.729	–	–	3.640
10 c-C_5Cl_2	−0.093	1.092	0.779	–	–	3.742
11 t-C_5Cl_2	−0.085	1.079	0.791	–	–	3.740
12 c-C_7H_6	−0.088	1.097	0.830	–	–	3.854
13 t-C_7H_6	−0.078	1.073	0.853	–	–	3.852
14 t-$C_{13}H_{18}$	−0.057	1.042	0.848	–	–	3.780
15 C_5H_4	−0.130	1.143	0.830	–	–	3.946
16 C9H12	−0.122	1.161	0.738	–	–	3.798
17 $C_5H_4^{+2}$	0.458	0.804	0.797	–	–	3.202
18 $C_5H_4^{+1}$	0.586	0.963	0.364	–	–	2.654
19 C_4BH_4	0.363	0.981	0.970	0.652	0.496	3.099
20 C_4BH_4	0.468	0.940	0.758	0.520	0.481	2.699
21 $C_3B_2H_4$	−0.093	1.154	0.875	0.767	0.731	2.373
22 $C_3B_2H_4$	−0.294	0.945	0.924	–	–	3.738
23 $C_3B_2H_4$	−0.073	1.184	0.875	0.757	0.676	3.492
24 $C_3B_2H_4$	0.007	0.923	0.707	–	–	3.272
25 C_3B_2	−0.378	1.668	0.833	0.739	0.532	3.772
26 C_3B_2	−0.211	0.950	0.860	–	–	3.620
27 C_3B_2	−0.075	1.465	0.536	–	–	4.002
28 CB_4	−0.991	1.155	0.720	–	–	3.750
29 c-$C_4BH_2^{-1}$	0.293	1.006	0.989	–	–	3.990
30 t-$C_4BH_2^{-1}$	0.297	1.012	1.009	–	–	4.042
31 $C_4BH_4^{-1}$	0.428	1.217	0.844	–	–	4.122
32 C_4BH_4	0.356	1.030	0.661	–	–	3.382
33 $C_3B_2H_4$	0.658	0.934	0.782	0.724	0.654	3.094
34 $C_3B_2H_4$	0.594	0.962	0.939	0.891	0.641	3.433
35 C_4B^{-1}	0.479	0.887	0.678	–	–	3.130
36 C_4B	0.517	1.017	0.646	–	–	3.326
37 C_4B^+	0.946	1.127	0.555	–	–	3.364
38 CB_4	−0.089	1.182	1.213	0.806	0.564	3.765
39 CB_4	−0.030	1.402	1.303	0.592	0.546	3.843
40 C_3B_2	0.523	1.257	1.035	0.677	0.624	3.593

cules, finding out conditions in which a molecular system defies the traditional bonding principles of tetrahedral tetracoordinate geometry and adopts a planar geometry is interesting in its own right. It has to be noticed that all the systems considered here prefer the unusual planar tetracoordination compared to the conventional tetrahedral geometry. We have examined the natural charges on the central carbon to see whether there is any unusually high localization of the charge. The near normal charge distribution indicate that most of the bonding is due to strong covalent linkages and not only dominated by the electrostatic forces. Secondly, the bond order of all the four bonds emanating from the central carbon were computed, Table 5. Total bond order is obtained by summing up all the four bond orders of the bonds forming the tetracoordination. The values indicate that all the four bonds are very strong and close to the bond order of unity. This analysis unambiguously clarify that the four bonds are fairly strong in most cases and the central carbon is engaged in a pure covalent linkages despite possessing the unusual feature of planar tetracoordination.

Conclusions

The current study unfolds the designing of the electronically stabilized neutral hydrocarbons where one carbon atom exhibits an unusual planar tretracoordination. The unconventional preference for the planarity is driven by the electron delocalization of these systems. These molecules and several other related ones are examples, which defy conventional Van't Hoff–Lebel structural principles. The strategy employed here is not only restricted to carbon but can be extrapolated to boron. Most molecules reported have a high HOMO-LUMO and singlet triplet energy differences, besides the three membered rings are highly aromatic in nature. The present proposes; (a) the smallest neutral ptC containing hydrocarbon in **6** and **7**, (b) the smallest electroneutal hetero organic compounds with ptC in **3**, **4**, and **5**, (c) while the main bottleneck is the stability of the compounds towards ring opening and those compounds, which show higher barriers for ring opening, such as t-C_5F_2, c-C_5F_2, t-C_5Cl_2, and $C_3B_2H_4$ provide interesting targets for prospective experimental efforts. While the experimental realization of these systems does provide challenges in terms of their kinetic stability, it is only a question of time before the experimentalist start producing one after the other of these fascinating molecules.

Acknowledgments

[eqs. (5)–(9)]. A perusal of Tables 3 and 4 indicate that the ring opening reaction energies in this class of compounds are only slightly exothermic and some time they are even endothermic. The reasons for stabilizing the ptC by the electron deficient early transition metal fragments are also similar to those responsible for stabilizing these organoborane systems.

The Charge and Bond Strength of ptC

While, the principle goal is to encourage the prospective experimentalists to go after these potentially interesting class of mole-

References

1. Van'tHoff, J. H. Arch Neerl Sci Exactes Nat 1874, 9, 445.
2. Lebel, J. A. Bull Soc Chim Fr 1874, 22, 337.
3. (a) Hoffmann, R.; Alder, R. W.; Wilcox, C. F. J Am Chem Soc 1970, 92, 4992; (b) Hoffmann, R. Pure Appl Chem 1971, 28, 181.

4. (a) 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; (b) Krogh–Jespersen, M. B.; Chandrasekhar. J.; Wurthwein, E.-U.; Collins, J. B.; Schleyer, P. v. R. J Am Chem Soc 1979, 102, 2263.

5. (a) Krogh–Jespersen, K.; Cremer, D.; Poppinger, D. J.; Pople, A.; Schleyer, P. v. R.; Chandrasekhar, J. J Am Chem Soc 1979, 101, 4843; (b) Wurthwein, E.-U.; Schleyer, P. v. R. Angew Chem Int Ed 1979, 18, 553; (c) Sorger, K.; Schleyer, P. v. R. J Mol Struct (THEOCHEM) 1995, 338, 317.

6. (a) Wang, Z. X.; Manojkumar, T. K.; Wannere, C.; Schleyer, P. v. R. Org Lett 2001, 3, 1249; (b) Wang, Z. X.; Schleyer, P. v. R. J Am Chem Soc 2001, 123, 994.

7. Erhard, S.; Frenking, G.; Chen, Z.; Schleyer. P. v. R. Angew Chem Int Ed 2005, 44, 1078.

8. (a) Rottger, D.; Erker, G. Angew Chem Int Ed Engl 1997, 36, 812; (b) Siebert, W.; Guanale, A. Chem Soc Rev 1999, 28, 367; (c) Choukroun, R.; Cassoux, R. Acc Chem Res 1999, 32, 494.

9. (a) Radom, L.; Rasmussen, D. R. Pure Appl Chem 1998, 70, 1977; (b) McGrath, M. P.; Radom, L. J Am Chem Soc 1993, 115, 3320; (c) Rasmussen, D. R.; Radom, L. Angew Chem Int Ed 1999, 38, 2876.

10. Sahin, Y.; Praesang, C.; Hofmann, M.; Subramanian, G.; Geiseler, G.; Massa, W.; Berndet, A. Angew Chem Int Ed 2003, 42, 671.

11. (a) Li, X.; Zhang, H.-F.; Wang, L S.; Geske, G. D.; Boldyrev, A. I. Angew Chem Int Ed 2000, 39, 3630; (b) Wang, L.-S.; Boldyrev, A. I.; Li, X.; Simons, J. J Am Chem Soc 2000, 122, 7681; (c) Zhai, H.-J.; Wang, L.-S.; Alexandrova, A. N.; Boldyrev, A. I. J Chem Phys 2002, 117, 7917.

12. Perez, N.; Heine, T.; Barthel, R.; Seifert, G.; Vela, A.; Mendez-Rojas, M. A.; Merino, G. Org Lett 2005, 7, 1509.

13. (a) Li, Si.-D.; Ren, G.-M.; Miao, C. Q.; Jin, Z.-H. Angew Chem Int Ed 2004, 43, 1371; (b) Li, Si.-D.; Ren, G.-M.; Miao, C.-Q. J Phys Chem A 2005, 109, 259.

14. Priyakumar, U. D.; Sastry, G. N. Tetrahedron Lett 2004, 45, 1515.

15. Merino, G.; Mendez-Rojas, M. A.; Vela, A. J Am Chem Soc 2003, 125, 6026.

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

17. (a) Priyakumar, U. D.; Reddy, A. S.; Sastry, G. N. Tetrahedron Lett 2004, 45, 2495; (b) Priyakumar, U. D.; Sastry, G. N. Indian J Chem 2004, 43, 455.

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

19. Esteves, P. M.; Ferreira, B. P. N.; Correa, R. J. J Am Chem Soc 2005, 127, 8680.

20. (a) Minyaev, R. M.; Gribanova, T. N.; Minkin, V. I.; Starikov, A. G.; Hoffmann, R. J Org Chem 2005, 70, 6693; (b) Minkin, V. I.; Minyaev, R. M.; Hoffmann, R. Usp Khim 2002, 71, 989.

21. Merino, G.; Mendez-Rojas, M. A.; Vela, A.; Heine, T. J Comput Chem 2006.

22. 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.; Baboul, A. G.; 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.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head–Gordon, M.; Replogle, E. S.; Pople, J. A.Gaussian 03; Gaussian: Pittsburgh, PA, 2001.

23. (a) Becke, A. D. J Chem Phys 1993, 98, 5648; (b) Lee, C. T.; Yang, W. T.; Parr, R. G. Phys Rev B 1988, 37, 785.

24. Schleyer, P. V.; Maerker, C.; Dransfeld, A.; Jiao, H. J.; Hommes, N. J Am Chem Soc 1996, 118, 6317.

25. Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. J Comput Chem 1993, 14, 1347.

26. Dinadayalane, T. C.; Priyakumar, U. D.; Sastry, G. N. J Phys Chem A 2004, 108, 11433.