If one were to embark on an assessment of the history of modern chemistry, the second half of the nineteenth century would clearly stand out as a period in which several predictions of fundamental significance in structural chemistry, some of them with far reaching implications in almost the whole of chemistry, were made by chemists with exceptional intuitive skills. This period of rapid development for the structural theory of organic chemistry witnessed the laying of the key foundations of modern structural chemistry. The first milestone on the way to modern organic chemistry was laid in 1858, when Kekule and Couper independently proposed that carbon is tetravalent. Shortly thereafter, Crum Brown proposed carbon-carbon double bonds for ethylene, and Erlenmeyer proposed a carbon-carbon triple bond for acetylene. In 1865 Kekule suggested that carbon chains could form rings. It was in 1874 that van't Hoff and Le Bel independently put forward the idea of tetrahedral geometry around a tetracoordinate carbon. This was a remarkable prediction indeed considering the fact that it was made long before reliable structural tools became available to chemists. This remarkable hypothesis paved the way for a profound understanding of the structural properties of organic molecules long before their model was confirmed by experimental techniques such as electron and X-ray diffraction studies.

Nature appears strict in its adherence to tetrahedral coordination of tetracoordinate carbons. It took almost a hundred years for arguably the most important alternative geometry, namely planar tetracoordination, to be more seriously considered as a structural possibility for carbon compounds. It was Roald Hoffmann who first formulated the basic model for hypothetical planar methane. Following this work, the tempo of efforts in this direction mounted and there have been more rational attempts to

*In the present thesis, the word 'tetrahedral' is used in a broader sense to cover near tetrahedral non-planar shapes which arise when the four groups around carbon are different.
realize planar tetracoordinate carbon.\textsuperscript{4,5,6} When Hoffmann put forth his views on alternatives to tetrahedral geometry, the synthesis of anti-van't Hoff compounds was not the main focus of the work, but merely the potential occurrence of this geometry in transition states. The results of this investigation provided the impetus for further theoretical and preparative studies.

Chemists have always been fascinated with the possibility, howsoever remote it be, that compounds might be found or can be synthesized in which a tetracoordinate carbon either is planar or can undergo planar inversion with a sufficiently low barrier to permit experimental detection. One can trace several reasons for the unceasing interest in this kind of structures. The bonding in this type of molecules is extremely interesting and the study of planar tetracoordinate carbon can reveal the limits of classical theory to explain the structure and bonding in such systems\textsuperscript{7,8}. Another factor which makes this an attractive subject of research is the presumption that deviation from classical structures would cause interesting changes in physical and chemical properties. The stereomutation of tetrahedral molecules through a planar transition state also would be of considerable interest from a stereochemical point of view.\textsuperscript{9}

The present thesis is a written account of the theoretical investigations carried out by the author to identify systems which would prefer planarity around tetracoordinate carbons. This chapter gives a brief review of the literature on the experimental as well as theoretical work on planar tetracoordinate carbon. The second chapter is a general introduction to ab initio molecular orbital theory, the methodology adopted for the present work. The third chapter of the thesis presents the results of the present theoretical work, which is essentially a computational search involving novel strategies towards planar tetracoordinate carbon.

In order to find out the methods by which one can stabilize a planar conformation around a tetracoordinate centre, one has to answer the following question:

\textit{Why planar methane is inherently unstable?}

Hoffmann proposed that the stability of tetrahedral methane over the planar form can be accounted for by examining the electronic structures of both these conformations (Fig. 1.1).\textsuperscript{3} He constructed the molecular orbitals of the $T_d$ and $D_{4h}$
conformations of methane by combining the atomic orbitals on carbon with combinations of hydrogen atomic orbitals of the right symmetry. In the tetrahedral form, there are four bonding combinations of the central atom valence s and p orbitals with the hydrogen s orbitals. Thus in the Td conformation of methane, all the eight valence electrons are in bonding orbitals. As presented in Fig. 1.1, the planar

![Diagram of atomic orbitals for methane](image)

**Figure 1.1**: Bonding in the Td and D4h forms of CH₄
conformation of methane is an electron deficient system in the molecular plane, where only six electrons are available to make four C-H bonds. A pure p orbital, which is centered on the carbon and orthogonal to the molecular plane, remains non-bonding, with a lone pair of electrons. This is the electronic basis of the instability of planar tetracoordinate carbon.

A close examination of the molecular orbitals of the planar methane shows that its frontier molecular orbitals are closely spaced in comparison to the spacing between them in the $T_d$ form. This should favour promoting one of the electrons of the HOMO of $a_{2u}$ symmetry to the LUMO of $b_{1g}$ symmetry and make the closed shell electronic state $^1A_{1g}$ and the open shell electronic states compete each other. Fig 1.2 shows the possible electronic states of planar methane.$^{10}$

![Figure 1.2 Possible Electronic States of Planar Methane](image)

Durmaz, Murral and Pedlay used an approximate ab initio method with minimal basis set of Slater Type Orbitals (STO's) to demonstrate that the lowest square planar triplet state is 179.9 kcal/mol higher in energy than the tetrahedral structure and is 73.7 kcal/mol lower than the square planar closed-shell singlet.$^{11}$ This was apparently the first suggestion that the lowest energy state in square planar arrangement might be open-shell. Krogh-Jespersen et al. carried out ab initio calculations on a series of molecules which are valence isoelectronic with methane.$^7$ They predicted that the closed-shell singlets are lower in energy than the lowest triplet states and, when the central carbon atom is replaced by a more electropositive element (e.g. Si), the HOMO ($a_{2u}$) and LUMO ($b_{1g}$) do switch their order.

Crans and Synder have done MNDO and PRDDO-GVB calculations and they got the open shell singlet as the most stable state for planar methane.$^{12}$ In 1993 Gordon and Schmidt carried out MCSCF calculations on planar methane and proved the closed shell singlet state to be lower than the $^1B_{2u}$ state by 4.6 kcal/mol and the $T_d$ structure to be 158.8 kcal mol$^{-1}$ below the closed-shell state $^1A_{1g}$ of $D_{4h}$ symmetry.$^{13}$
At all levels of theory, the energy required to access planar methane is calculated to be much larger than the energy required to break a C-H bond. Ab initio methods, irrespective of the basis set used, always gave four imaginary frequencies for D$_{4h}$ methane.$^{13}$ It is thus established by means of theoretical methods that the square planar methane does not correspond to either a minimum or a transition state for the inversion of methane.

1.2 Potential Energy Surface of Methane

In analysing the PES of methane, one may obtain a deeper insight into the relative stabilities of nonclassical steroisomers of methane and their role in the process involving the interconversion of methane enantiomers. However, even for such a simple molecule as methane, the complete calculation of the PES, which is a hypersurface within a ten-dimensional space, is practically impossible. The ensuing computational difficulties are enormous. Because of this, the analysis of the PES, instead of performing a complete calculation, may be confined to studying its separate portions.$^{10}$ We are mostly interested in finding out the position of the D$_{4h}$ conformation of methane on the potential energy surface of inversion.

Hoffmann proposed that the transformation of tetrahedral methane to planar conformation is either through a twisting path (T$_d$-D$_2$-D$_{4h}$) or through a squashing (T$_d$-D$_{2d}$-D$_{4h}$) path(Fig. 1.3).$^3$ An analysis of potential energy surface of methane for topomerization of methanotetrahedron also shows that the D$_{4h}$ conformation is not a saddle point, but is rather located at a flattened hill-top and cannot therefore be regarded as a transient structure.

\[
\text{Squashing Path} \quad (T_d\rightarrow D_{2d}\rightarrow D_{4h}) \quad \begin{array}{c}
\begin{array}{c}
\text{H}
\end{array}
\end{array} \quad \xrightarrow[\text{Squashing Path}]{(T_d\rightarrow D_{2d}\rightarrow D_{4h})} \quad \begin{array}{c}
\begin{array}{c}
\text{H}
\end{array}
\end{array}
\]

\[
\text{Twisting Path} \quad (T_d\rightarrow D_{2}\rightarrow D_{4h}) \quad \begin{array}{c}
\begin{array}{c}
\text{H}
\end{array}
\end{array} \quad \xrightarrow[\text{Twisting Path}]{(T_d\rightarrow D_{2}\rightarrow D_{4h})} \quad \begin{array}{c}
\begin{array}{c}
\text{H}
\end{array}
\end{array}
\]

Figure 1.3: Possible distortion modes of tetrahedral methane to planar form
Gordon and Schmidt revisited the question "Does methane invert through square planar conformation?" in 1993. For getting the answer they have traced each and every imaginary frequency of the square planar geometry at MCSCF/TVZ++G (dp) level of theory to find out the actual transition state for inversion of methane.

Gordon's study reveals that for the open shell \( ^1B_{2u} \) state, there are two imaginary frequencies, following both of which ultimately leads to the \( T_d \) global minimum. Since the state has higher energy than the closed state \( ^1A_g \), the analysis of imaginary frequencies of the \( ^1B_{2u} \) state are not relevant. For the \( ^1A_g \) state, the largest imaginary frequency leads to the tetrahedral state. The other nondegenerate imaginary mode leads to a \( C_4v \) structure, which has three imaginary frequencies. One of these, at 974i, leads to \( T_d \) global minimum, and the other two imaginary frequencies are a degenerate pair which distort the molecule into \( C_s \) symmetry. A small distortion along the direction indicated by this mode, followed by full geometry optimization, leads to the \( T_d \) structure. With three imaginary frequencies, this is a rather high energy pathway and not a true transition state leading the planar form to a tetrahedral one.

![Diagram of methane structures](image)

**Figure 1.4: Structures starting from \( D_{4h} \ ^1A_g \) (Number of imaginary frequencies given in parenthesis)**

Distortions along either of the pair of degenerate in-plane imaginary modes of the \( ^1A_g \) square planar geometry leads to a \( C_{2v} \) structure having three imaginary modes. Frequency at 3544i cm\(^{-1}\) corresponds to inversion motion to tetrahedral minimum. An imaginary mode at 981i cm\(^{-1}\) leads to the \( C_{4v} \) structure.
discussed in the last paragraph. The third imaginary frequency (1257i cm\(^{-1}\)) is an in-plane distortion; optimization via a distortion into \(C_5\) symmetry in the direction suggested by this mode leads to a new \(C_{2v}\) structure with two pairs of equivalent C-H bonds. The pair of hydrogens that are somewhat stretched from the usual C-H bond lengths are separated by a distance which is only about 0.15Å longer than the equilibrium H-H distance in \(H_2\).

The \(C_{2v}\) structure has two more imaginary frequencies, one at 2688i \(\text{cm}^{-1}\) is towards \(T_d\), and the other at 937i \(\text{cm}^{-1}\) leads to a distorted version of \(C_{4v}\) structure, optimization of which gave an unusual \(C_5\) structure. All four hydrogens of this structure are in the same hemisphere, and two hydrogens are separated by a distance of 0.847Å. The C-H distance for these two hydrogens is now 1.316Å. The structure has one imaginary frequency. Intrinsic Reaction Coordinate (IRC) calculation showed that this leads to a \(T_d\) minimum\(^{14}\).

To summarize, based on MCSCF calculations Gordon and Schmidt have established that the true transition state for the interconversion of the two tetrahedral structures of methane has a distorted \(C_5\) structure, which is quite different both geometrically and energetically from the previously presumed \(D_{4h}\) structure.

### 1.3 Stabilisation of Planar Tetracoordinate Carbon

On examination of the electronic structure of planar methane, Hoffmann\(^3\) concluded the following points. In the planar form, (1) All C-H bonds are weaker than in tetrahedral methane. (2) Since the three-centre bonding uses only hydrogen electrons there is considerable charge transfer from H to C. (3) The planar carbon atom possesses a pure 2p lone pair perpendicular to the molecular plane. (4) The transformation of tetrahedral to planar methane is a symmetry allowed process for both the twisting (\(T_d-D_2-D_{4h}\)) and the squashing (\(T_d-D_{2d}-D_{4h}\)) pathways.

Accounting for the above facts, Hoffmann proposed the following methods to stabilize planar tetracoordinate carbon. One strategy to construct anti-van't Hoff arrangements would be to force the tetracoordinate carbon to adopt planar form by extreme angular distortions by incorporation into a strained polycyclic environment. The effectiveness of this approach has been tried out both computationally and experimentally.
A different strategy is based on a qualitative analysis of the electronic structure of planar methane. It is apparent from the Fig. 1.1 that the molecular plane of \( \text{D}_{4h} \) methane is electron deficient and the \( \pi \) plane is electron rich. Therefore, the unfavourable electronic structure of planar tetracoordinate carbon can be stabilised by using appropriate substituents which can increase the electron density in the sigma plane and reduce that in the \( \pi \) electron system. The latter can be achieved by delocalisation into suitable, empty \( p \) orbitals of substituents or by incorporation into a conjugated \( \pi \) system. Additionally, incorporation into small rings can direct a compound to a planar geometry since the ideal bond angles are reduced for the transition from tetrahedral to planar coordination.

We have had a glimpse of the factors that destabilize a planar tetracoordinate carbon. There has been a lot of examples from the literature of the efforts towards stabilizing planar tetracoordinate carbon. A review of the literature is given next.

### 1.3.1 Stabilization of Planar Tetracoordinate Carbon Based on Strain Concepts

A simple, brute force approach to achieve otherwise unfavourable geometries would be to thrust upon the system the constraints of a rigid molecular framework\(^{15}\). To achieve planarity at a tetracoordinate carbon the idea of fusing the central carbon atom to an annulene perimeter can be in principle fruitful. Hoffmann et al.\(^3\) and later Keese\(^{16}\) proposed that structures 1.1-1.5 are possible candidates for planar tetracoordinate carbon. Their idea was that the planar framework of the annulene would induce steric constraints to central carbon atom forcing it to adopt a planar structure. Additionally, the \( \pi \) system might stabilize the lone pair electron density through extensive delocalisation.

```
1.1
```

```
1.2
```

```
1.3
```
But calculations proved that the planar conformations of the above structures have higher energy than the corresponding non-planar conformations.

Fenestranes (e.g. 1.6) are another class of compounds which are proposed as possible candidates for planar tetracoordinate carbon. This family of compounds also have considerable strain around the central carbon atom. The strain energy of these systems are dependent highly upon whether the rings are cis or trans fused. Planarising distortions at the central tetracoordinate carbon are due to the opening of opposite bond angles. Keese and coworkers found that for achieving planar geometry around a central carbon atom, the greatest possible number of trans-linkages of the rings are necessary. It would involve concomitant increase in the strain energy of these systems considerably. Although fenestrane systems have been prepared with notable distortions from tetrahedral geometry, these systems are far away from planar geometry around the central carbon. Computations also proved that fenestrane systems have very large strain energies.

Paddlanes are another class of polycyclic hydrocarbons suggested to be attractive synthetic targets for realization of planar tetracoordinate carbon. However both semiempirical and ab initio calculations indicate that pyramidal rather than planar geometries at the bridgehead carbon are preferred. Furthermore, paddlane systems 1.7 and 1.8 were calculated to be highly strained and unstable thermodynamically.
The Bowlane 1.9, which has the bridgehead of [1.1.1.1] paddlane replaced by an eight membered ring, is also proposed as a possible candidate for planar tetracoordinate carbon.\textsuperscript{19} MM2 calculations showed that structure 1.9 with \( C_{4v} \) symmetry has a strain energy which is not so excessive.\textsuperscript{22} Ab-initio calculations suggest that the \( C_{4v} \) structure 1.9 is a transition state connecting two equivalent \( C_{2v} \) (1.10) minima.\textsuperscript{22} In the minimum \( C_{2v} \) structure the opposite bond angles of the quaternary bridgehead carbons are 141.8° and 170.9°, which are not far from the 180° for planar structure. The strain energy calculated for these molecules are somewhat high, but comparable to those of strained molecules which have already been synthesised. Hence, bowlane is judged to be a prospective candidate for the realization of nearly planar tetracoordinate carbon.

Recently Radom et al. explored computationally a new class of neutral saturated hydrocarbons, the alkaplanes, which contain a potential planar tetracoordinate carbon.\textsuperscript{23} Extending bowlane principle to higher symmetry, hexaplane and octaplane were constructed by capping a planar \( C(C)_4 \) arrangement with cycloalkanes. The \( S_4 \) symmetric octaplane 1.11, which is a local minimum at the HF/6-31G* level, has a C-C-C angle of 168.8 degree at the tetracoordinate carbon. This deviates only slightly from the ideal 180° value for planarity. Strain energies per carbon atom calculated at correlated levels for such systems are not larger than those for known strained hydrocarbons.
1.3.2. Stabilization of Planar Tetracoordinate Carbon Based on Bonding Principles

We have already seen that a substituent which donates sigma electrons and accepts π electrons can stabilize the planar structure preferentially. Calculations also proved that electropositive groups are suitable substituents for reducing the energy difference between planar and tetrahedral structures, since they can increase the electron density in the sigma framework. π acceptors conjugate with the nonbonding carbon lone pair can delocalize the electron density and thereby preferential stabilization of planar form is possible.

The effect of a single substituent on planar-tetrahedral energy difference is substantial. Electropositive groups like -BH₂, -BeH, -Li, etc. are effective in lowering the difference. The cyano group, a good π acceptor is not favourable for the stabilization of planar tetracoordinate carbon since it is a good sigma acceptor at the same time. Calculations proved that electronegative substituents -F, -OH, -NH₂ etc. destabilise the planar conformation of tetracoordinate carbon because the lone pair of electrons present on the substituents further increase the electron density of the π system.

Second row substituents show the same trend as the first row elements in stabilizing planar tetracoordinate carbon. However calculations revealed that sodium is not as stabilizing as lithium, and chlorine is not as destabilizing as fluorine. Planar CH₃Na is destabilized by unfavourable electrostatic repulsions between the positively charged sodiums and the neighbouring hydrogens. The unfavourable C(π) lone pair interactions are reduced in planar chloromethane due to the more diffuse chlorine 3p lone pair and long C-Cl bond.

Comparisons of the all-planar conformation and conformations in which the hydrogens of the substituents lie in a plane perpendicular to the molecular
plane allow an assessment of the relative importance of $\sigma$ vs. $\pi$ effect with substituents like $-\text{BH}_2$, $-\text{NH}_2$, $-\text{Cl}_2^+$ etc. Delocalization of the carbon lone pair into the boron $p$ orbital is precluded in perpendicular $\text{CH}_3\text{BH}_2$ (1.13b), which is reflected in an increase in the energy by 26 kcal mol$^{-1}$ (RHF/4-31G). This difference is a measure of the $\pi$ interaction. In perpendicular forms only $\sigma$ effect is operative along with a modest amount of hyperconjugation. Similarly, rotation of $-\text{NH}_2$ can eliminate the unfavourable $\text{C}(\pi)-\text{N}$ (lone pair) effect and, therefore, the planar distortion energy gets lowered by 16 kcal mol$^{-1}$ (RHF/4-31G).

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{B} \\
\text{H} & \quad \text{H} \\
\text{1.13a} & \quad \text{H} \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{B} \\
\text{H} & \quad \text{H} \\
\text{1.13b} & \quad \text{H} \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{N} \\
\text{H} & \quad \text{H} \\
\text{1.14a} & \quad \text{H} \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{N} \\
\text{H} & \quad \text{H} \\
\text{1.14b} & \quad \text{H} \quad \text{H}
\end{align*}
\]

If one substituent lowers the distortion energy substantially, then two or more such substituents should do better. A second substituent can lower the planar - tetrahedral energy difference further. Analogous to the monosubstituted methanes, electronegativity effects in $\text{CH}_2\text{X}_2$ systems are quite important. In $\text{CH}_2(\text{BeH})_2$ the planar tetrahedral energy difference is reduced to 23.4 kcal mol$^{-1}$ compared with 47.5 kcal mol$^{-1}$ for the monosubstituted compound $\text{CH}_3\text{BeH}$ at Becke3LYP/6-311+G* level of theory. For the disubstituted molecule $\text{CH}_2(\text{BH}_2)_2$, the planar tetrahedral energy difference is calculated to be lower than that of the monosubstituted species. Replacing the $-\text{BH}_2$ by the more electropositive $-\text{AlH}_2$ leads to a further stabilization of the planar form. In addition, the steric repulsions between the hydrogens of adjacent $-\text{BH}_2$ groups in the cis-planar are less significant with $-\text{AlH}_2$ substituent.

Early computations have indicated that the planar and "tetrahedral" $C_2\text{v}$ structures of dilithiomethane, both singlets and triplets, are very close in energy. Calculations done with the inclusion of configuration interactions proved that the planar form is about 8.3 kcal/mol more stable than the "tetrahedral" singlet, which is the global minimum. Calculations at all levels of theory gave the planar cis
form of CH₂Li₂ to be more stable than the planar trans form. In the cis form the π orbital on lithium atoms and the lone pair electron density on the central carbon get delocalized and a "homoaromatic cyclopropenium" type molecular system is formed.

When coming to tri- or tetra-substitutions, the degree of preferential stabilization of planar forms get decreased, since a part of the stabilization energy obtained by electronic means is lost by steric repulsion between substituents. The third lithium atom in CHLi₃ reduces the planar - tetrahedral difference further, but only modestly. It is found that the introduction of one more lithium actually increases the planar - tetrahedral energy difference.

The planar geometry becomes more favourable on going from CH₃BeH to C(BeH)₄. However, the lowering of the planar-tetrahedral energy difference by the third and fourth BeH substituents is only modest compared to the first two substitutions. Multiple BH₂ substitution results in interligand repulsions in the coplanar conformation; unfavourable steric interaction between hydrogen atoms raise the energy of planar form and preclude the stabilizing π delocalizations. The different planar forms of C(BH₂)₄ are shown below. The energy ordering is in the order 1.15a>1.15c>1.15b. Planar forms of CH(BH₂)₃ and C(BH₂)₄ are multi-order saddle points lacking significant stability.

Minimal basis set ab initio calculations suggested that the most stable configuration of CF₂Li₂ is the cis-planar C₂ᵥ form rather than the "tetrahedral" one. But a study of the potential energy surface (at HF/4-31G level) of singlet CF₂Li₂ revealed that the planar form is not a minima. Three minima were located (1.16b-d). The most stable isomer is found to be a lithium-bridged C₂ᵥ structure 1.16b, which does not contain a planar tetracoordinate carbon.
Calculations by Schleyer and Boldyrev showed that *cis*- \( \text{CSi}_2\text{Al}_2 \) and *trans*-\( \text{CSi}_2\text{Al}_2 \) are molecules having stable planar tetracoordinate carbons.\(^{28}\) Recently Boldyrev and Simons have done calculations on \( \text{CSi}_2\text{Al}_2 \), \( \text{CSi}_2\text{Ga}_2 \) and \( \text{CGe}_2\text{Al}_2 \). They found that *cis* \( \text{CSi}_2\text{Al}_2 \) and *trans* \( \text{CSi}_2\text{Al}_2 \) planar structures have one imaginary frequency and distortion along this mode leads to slightly pyramidal local minima. But *cis* - and *trans* \( \text{CSi}_2\text{Ga}_2 \) and *cis* and *trans* \( \text{CGe}_2\text{Al}_2 \) are true minima in their planar geometries, and, their corresponding "tetrahedral" structures lie 25-28 kcal mol\(^{-1}\) higher in energy and they have one imaginary frequency each.\(^{29}\)

### 1.3.3. Stabilization of Planar Tetracoordinate Carbon by Introduction of Small Ring Systems

Since planar tetracoordinate carbon can be stabilized, both electronically by appropriate substituents, and by strain effects, small rings with electropositive substituents should favour exceptional geometries.\(^{2}\) Both angle strain and repulsive interactions between substituents, steric as well as electrostatic, can be reduced. For cyclopropane, it is found that the energy difference between the planar and "tetrahedral" forms is about 25 kcal mol\(^{-1}\) less than that for methane.\(^{22}\) 1,1-Dilithiocyclopropane is calculated to have a planar form which is more stable than the "tetrahedral" form. The planar structure 1.17 has no imaginary frequency at Becke3LYP/6-311+G* level.

![Diagram](image)

1.17

Diboracyclopropane is reported to have a planar \( \text{C}_{2\nu} \) form having less energy than the twist \( \text{C}_{2\nu} \) analog.\(^{30}\) The stability of the planar form 1.18a can be attributed to the aromaticity of the planar form, with the two carbon \( \pi \) electrons
delocalized over three centers, which is impossible in the "tetrahedral" form 1.18b. Force calculations proved that the CB₂H₄ global minimum energy structure does not possess a planar tetracoordinate carbon. The hydrogen bridged isomer 1.18c with a three centre B-H-B bond was found to be 33.3 kcal mol⁻¹ more stable than the planar C₂ᵥ form 1.18a.

Schleyer and coworkers have done density functional calculations on 2,3-diboraspipropentane structures, and, they have reported that the planar form 1.19 has lower energy than all other isomers they have studied. Frequency calculations at the same level of theory gave no imaginary frequency for this planar structure. The stability of planar 2-3 diboraspipropentane results from the small C-Cᵈspiro-C angle and aromatic delocalization. This conformer has been computed to be 7.9 kcal mol⁻¹ lower in energy than the distorted "tetrahedral" form at Becke3LYP/6-311+G* level.

The planar geometry of 3,3-dilithio-2-diboracyclopropane(1.20a) was calculated to be more stable than tetrahedral geometry 1.20b. The stabilization of planar form 1.20a is due to delocalization of carbon π lone pair over the three centres in the BBC ring. A long Li-Li distance decreases unfavourable electrostatic interactions between the positively charged lithium atoms. Additional LiB and Li...BH interactions further stabilize planar form 1.20a. Calculations of the harmonic vibrational frequencies proved that the planar conformation is an energy minimum.
We have already seen the effect of lithium substitution on the planar-tetrahedral energy difference, especially when two lithium atoms are attached to the same carbon atom. The "in plane" geometry of the unsolvated phenyllithium dimer 1.21a with a planar tetracoordinate carbon was computed to be more stable than the perpendicular dimer 1.21b.\(^{32,33}\) However, solvation of lithium reverses this preference; X-ray structure of \([\text{C}_6\text{H}_5\text{Li} \cdot \text{TMEDA}]_2\) as well as MNDO calculations with a model solvent indicate 1.21b, the perpendicular form, to be favoured. The effectiveness of oxygen-lithium chelation in stabilizing planar tetracoordinate geometries was verified by MNDO calculations on 1.22. Calculations predicted that the planar form 1.22 would be more stable than the "tetrahedral" analog. The X-ray structure of the methoxy derivative 1.23, which was synthesized later, shows a tetramer comprising two planar tetracoordinate carbon dimer units.
Unsolvated dimeric cyclopropenyllithium 1.24 was computed to prefer an "in plane" geometry with planar tetracoordinate R^1R^2CLi_2 carbons. However, as with the phenyl lithium dimer 1.21a, lithium solvation favours the perpendicular geometry for 1.24. Lithiated cyclopropanes bearing heteroatoms in appropriate vinylic Cβ substituents are good candidates for the realization of planar tetracoordinate carbon. Schleyer et al. proved that substituted cyclopropanes 1.24a and 1.24b in solvated form (exist as dimer) possess planar tetracoordinate carbon.

There are a number of examples in transition metal organometallic chemistry for molecules with stable anti-van't Hoff structures. The first molecule with a planar tetracoordinate carbon atom was synthesized (structure 1.25) by F. A. Cotton et al. in 1977, and in 1979 Keese established the presence of planar tetracoordinate carbon in this compound. Structurally related dizirconocene complex, 1.26, was synthesized by Butchwald et al. Planar tetracoordination of these type of complexes arises from formation of a σ-multicenter bond between the carbon atom of the aryl anion and the two metal centres. In addition, anchoring groups at the ortho-positions of the aromatic moieties fixate planar configuration. A recent theoretical study of both 1.25 and 1.26 indicated that the planar tetracoordinate carbons in the bridging phenyl groups should be described as a phenyl anion with a sigma lone pair pointing towards the center of the metal-metal axis. These lone pairs are stabilized by delocalization into metal d orbitals with predominantly metal - metal bonding character.
In 1989 Chisholm et al. characterised 1.27, in which an allene group bridges two tungsten atoms. Both metal atoms and the three carbon atoms of the bridging ligand lie almost perfectly in one plane. Complexes 1.28a-c and 1.29, described by Cotton et al., are analogous systems with heteroatoms in the bridging unit. Comparable structures are formed in the dipalladium complexes 1.30 and 1.31 with bridging carbon and disulphide or allenyl units.

Planar coordination geometry at tetravalent carbon can also exist in 1,3-diyne ligands that bridge two metals. Complex 1.32, characterized by Tuban et al. have two planar tetracoordinate carbons. Further examples of this type of complexes have been characterised by Evans et al. (Structure 1.33) and Rosenthal et al. (Structure...
The Complex 1.35, with a nickel complex fragment coordinating to two ring atoms of titanacyclocumulene, has a pair of planar tetracoordinate carbon atoms. The anti-van't Hoff structures are also observed in 1.36 and 1.37, in which two metal centers formally coordinate side-on to a dimetallated acetylene moiety. Both these molecules comprise two planar tetracoordinate carbon atoms each.

The rhenium complex 1.38, a tetrametalla[3,3,3,3] fenestrane, also exhibits an almost planar geometry at the central carbon atom. Structure 1.39 also exhibits a planar conformation around the central carbon atom, which is stabilized by three metal centers (one tungsten and two rhenium) around the carbon.
The class of complexes of the type 1.40, characterised by Evans et al. are examples of anti-van't Hoff/Le Bel compounds in which a hydrogen atom is bound to the planar tetracoordinate carbon centre. The bonding features are most readily understood as multicentred bonds between the sp² carbon atom of the N-alkylformimidoyl ligand and the two metals; the planar structure is fixed by the additional metal-nitrogen bond (Structure 1.41).²⁹

A class of dimetallic compounds in which planar tetracoordinate carbon in a simple olefinic bonding is stabilised by the combined electron donating abilities of a main group and a transition metal to become the global minimum of the system was reported by Erker et al.⁵⁰ In compound 1.42 the main group metal can either be aluminium, gallium, or even boron. Prompted by the experimental work, Gleiter et al. made a theoretical model based on ethylene. Their calculations showed that planar arrangement is mainly stabilized by sigma interactions between C₁ and the strong sigma-acceptor zirconium.⁵⁰α
$X = \text{Cl, H, Me}$

1.42