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Stabilization of Planar Tetracoordinate Carbon[1a]

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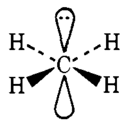
Abstract: The energies of planar vs. tetrahedral geometries of tetracoordinate organic molecules have been surveyed by ab initio molecular orbital calculations. Because of their π acceptor and σ donor character, electropositive substituents, especially lithium, are particularly effective in stabilizing the planar arrangements selectively. Multiple substitution by such metals and by three-membered rings provides further stabilization, and 1,1-dilithiocyclopropane (XVII) and 3,3-dilithiocyclopropene (XVIII), inter alia, are actually calculated (RHF/STO-3G theory) to be more stable planar than tetrahedral.

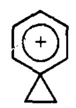
van't Hoff and LeBel's proposal that tetracoordinate carbon prefers tetrahedral geometry[2] celebrated its centenary in 1974.[3] No fundamental exception, e.g., an organic compound in which all four substituents lie in a plane, is known. It is not difficult to understand why this should be so. Singlet planar methane is sp^2 hybridized with a lone pair of electrons in the remaining p orbital (I).[4] Consequently, only six electrons instead of eight are involved in bonding. Numerous theoretical calculations[5] at different levels of sophistication have been applied to this problem and are summarized in Table I. The best available ab initio quantum mechanical calculations indicate D_{4h} singlet planar methane should be about 150 kcal/mol less stable than the tetrahedral form.[6] Since the bond dissociation energy of the C-H bond is only 104 kcal/mol[7] D_{4h} planar methane would not be expected to exist under any circumstances. Figure 1 shows the molecular orbitals of planar methane.[40]

Nevertheless, chemists have long been fascinated with the possibility that compounds might be found in which a carbon either is planar or can undergo planar inversion with a sufficiently low barrier to permit experimental detection. The possibility that the stereomutation of cyclopropane might proceed via the twisting of one of the methylene groups through the carbon plane was considered[8a] but has been rejected.[8b] MINDO/2 calculations suggest that the phenonium ion (II) may have a low barrier to planar inversion, but this process has not been detected experimentally.[9] *trans*-Fenestrane (III),[6a,10] [2.2.2.2]paddlane (IV),[11] and aromatic molecules such as V[4b] have been suggested as possibilities having planar carbons, but none of these have yet been synthesized.

III and IV represent the traditional "brute-force" approach to problems of this type; such systems will be highly strained if not prohibitively so. Instead of contriving against nature, it might be better to find ways preferentially to stabilize planar over tetrahedral geometries.



I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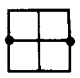
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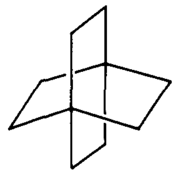
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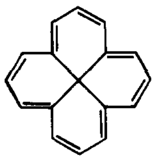
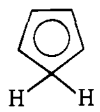

V



VI

Previous investigations (Table II),[4,12] particularly that of Hoffmann, Alder, and Wilcox,[4b] have revealed how this might be done. For example, extended Hückel calculations (EHT) showed that the energy required to distort cyclopentadiene would be much reduced by the aromatic 6 π-electron character of the planar form (VI). σ-Donating electropositive substituents such as $-SiH_3$, $-BH_2$, and lithium should be effective in reducing the planar-tetrahedral energy difference.[4b] Since the "natural" angle in planar carbon derivatives is 90° instead of 109.5°, the introduction of small rings also should help to stabilize the planar forms since both angle strain and repulsive steric interactions between substituents would be reduced.[9] This effect, along with π delocalization, contributes to the very low distortion energy (19[12a] or 22[12b] kcal/mol) calculated by MINDO/2 for the *planar* phenonium ion (II). Another approach often previously proposed[4] is simply to remove two electrons thereby giving a six valence electron species. Unfortunately, CH_4^{2+}, although calculated to prefer planarity strongly, is unstable toward dissociation into CH_3^+ and H^+.[13]

Planar tetracoordinate carbon is a difficult problem to attack

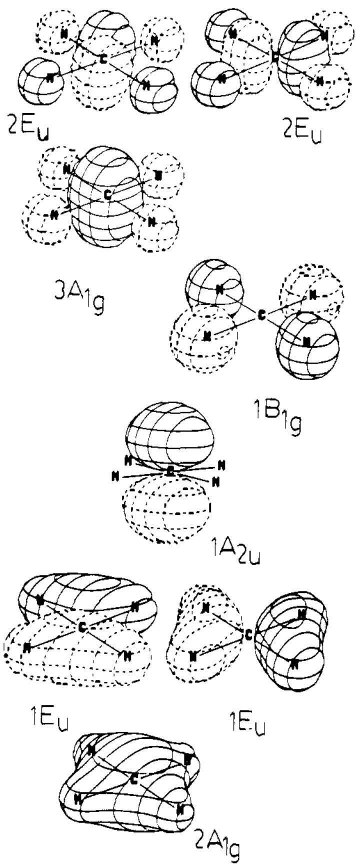


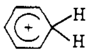
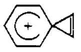
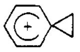
Figure 1. Valence molecular orbitals of planar methane (D_{4h}) arranged in order of increasing energy. The lower four are occupied in the singlet.

Table I. Calculated Energy Difference for Planar (D_{4h}) vs. Tetrahedral (T_d) Singlet Methane Using Several Molecular Orbital Methods (kcal/mol)

ΔE	Method or basis set	Ref
127	EHT	4b
187	CNDO	4b
95	PNDO	5b
120	MINDO/3	*a*
250	Minimal STO	5a, d
240	RHF/STO-3G	5c, 6b
168	RHF/4-31G	5c, 6b
165	RHF/6-31G	6b
171	RHF/6-31G*	6b, *b*
166	RHF/6-31G**	6b, *b*
160	Double ζ with polarization	6a
157	RMP2/6-31G**	*b*
150	RHF/6-31G** with CI	6b

[a] E. D. Jemmis, unpublished. [b] This work.

Table II. Semiempirical Calculations of Planar–Tetrahedral Energy Differences (kcal/mol)

Molecule	Method	ΔE
	EHT	97[a]
	EHT	97[b]
$C(CN)_4$	EHT	79[b]
	EHT	67[b]
$C(SiH_3)_4$	EHT	67[b]
$C(BH_2)_4$	EHT	42[b]
	EHT	25[b]
	MINDO/2	19[c]
		22[d]

[a] Reference 9. [b] Reference 4b. [c] Reference 12a. [d] Reference 12b.

experimentally but it is easy computationally. Our approach has been to explore systematically by ab initio calculations the planar-tetrahedral energy difference in a variety of molecules. This has culminated in the discovery of relatively simple derivatives of methane that are indicated to prefer planar over tetrahedral geometries.

Computational Method

Several levels of sophistication were employed to determine the planar-tetrahedral energy differences. Most of the work was carried out using Hartree-Fock theory. For singlet states the spin-restricted form (RHF)[15a] involving doubly occupied molecular orbitals was used but triplet states were handled by the spin-unrestricted version.[15b] Initially the minimal STO-3G basis set[14] was used in conjunction with standard geometries.[16] Geometry optimization at the RHF/STO-3G level (or UHF/STO-3G for triplets) was then carried out, according to procedures described previously,[17] on the smaller molecules and on those which were indicated to have small planar distortion energies. Calculated structures are given in Table III. Single calculations at the split valence RHF/4-31G or UHF/4-31G levels[18] were then performed on the STO-3G minimized geometries. Total energies at these three levels are reported in Table IV. As can be seen from Tables V-VII, both geometry optimization and extension of the basis set uniformly reduce the energy differences. This arises since the "standard" models are appropriate for tetrahedral geometries but less so for planar structures largely because of significant π bonding or π antibonding between the substituent and the planar carbon atom; geometry optimization thus tends to lower the energy of the planar forms to a greater extent than the tetrahedral. Furthermore, since the planar carbon atoms have both σ and π bonds, they should benefit more from the increased flexibility of the split valence basis set than do the tetrahedral geometries.

To confirm the reliability of these results, more rigorous studies were made in two cases. Methane has been treated most extensively. Reoptimization of the structure using the RHF/6-31G*[19] level (which contains d-type polarization functions on carbon) yields a value for the barrier to planarity (171 kcal/mol) in close agreement with the RHF/4-31G result (168 kcal/mol) and a closely similar bond length.[20] Further extension of the basis set to include p functions on hydrogen (RHF/6-31G**) yields a value of 166 kcal/mol for the inversion barrier. Similarly a single calculation was performed at the RHF/6-31G* level for CH_2Li_2 at the STO-3G geometry.[20] The RHF/6-31G* barrier to inversion of 8 kcal/mol differs by only 2 kcal from the RHF/4-31G value, 10 kcal. A final check of the calculated structures was made by carrying out a partial geometry optimization of methyllithium (both C_{3v} and C_{2v}) using the extended RHF/4-31G level. This was done to ensure that the minimal STO-3G basis does not overestimate the role of the lithium 2p functions. Reoptimization of the C_{3v} structure resulted in an improvement in the RHF/4-31G total energy (−45.959 86 au) of only 0.2 kcal/mol while the C-Li distance shortened 0.02 Å (2.008 to 1.990 Å) and the ∠HCLi angle changed 1.2° (112.6 to 111.4°). Reoptimization of the planar form gave a modestly larger lowering of 4.0 kcal/mol in the total energy (−46.898 30 au, RHF/4-31G) but a larger change in r(C-Li) (from 1.727 to 1.899 Å); ∠HCLi widens only slightly from 64.5 to 64.8°.

Similarly, RHF/4-31G reoptimization of tetrahedral CH_2Li_2 resulted in an improvement in the total energy (−53.77521 au) of only 0.4 kcal/mol and changes in the C-Li distance (1.924 to 1.966 Å) and LiCLi angle (119.8 to 115.0°) of 0.042 Å and 4.8°, respectively. Reoptimization of the planar form gave an energy decrease of 2.7 kcal/mol (−53.76231 au, RHF/4-31G), and an increase in the bond length (1.744 to 1.838 Å) of 0.094 Å and in the LiCLi angle (97.8 to 98.9°) of 1.1°. Based on these results, it seems that the 4-31G values listed in Tables V-VII are upper limits lying only a few kilocalories above the Hartree-Fock result.

The effect of electron correlation on the methane inversion barrier also was examined using restricted Møller-Plesset second-order perturbation theory[21] applied to the 6-31G** wave function (this is designated RMP2/6-31G**). This method showed that inclusion of correlation energy led to a further lowering in the planar inversion barrier by 9 kcal/mol, from 166 to 157 kcal/mol (Table I).

An additional question is whether the electronic configuration depicted in I is truly the ground state. To test this the pair of electrons in the p orbital of planar methane was removed and placed in the electron deficient σ system (b_{1g} orbital). This results in an increase in the energy by 88 kcal (RHF/6-31G*) and abnormally long bond lengths of 1.237 Å. This result might not have been expected. Isoelectronic BH_4^- and valence isoelectronic SiH_4 prefer a vacant p orbital in their singlet planar ground states.[22] The highest occupied b_{1g} orbital is then of d symmetry. The problem of whether the ground states are singlet or triplet is considered below.

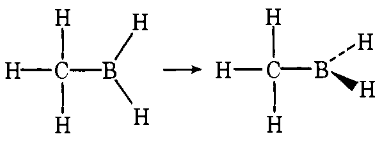
Results and Discussion

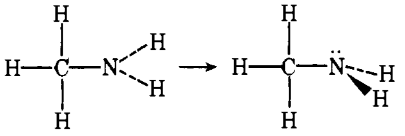
Three effects should lower the planar distortion energy. Planar tetracoordinate carbon should be stabilized preferentially (1) by delocalizing the lone pair by π conjugation,[4b] (2) by providing more electron density to carbon by σ donation,[4b] and (3) by enforced reduction of the angle around the planar carbon atom by means of small rings.

Monosubstituted Methanes

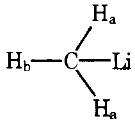
Consider first the effect of a single substituent (Table V). Because of lone pair repulsion and high electronegativity, fluorine raises the planar-tetrahedral energy difference. On the other hand, the electropositive substituents, BH_2, BeH, and especially Li, lower the energy difference dramatically due to the simultaneous operation of σ-donating and π-accepting effects. Interestingly, the cyano group, a good π acceptor but also a good σ acceptor, is not particularly favorable.

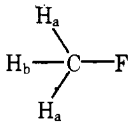
Comparisons of all planar (e.g., VIIa) and perpendicular (e.g., VIIb) forms allow an assessment of the relative importance of σ vs. π effects with substituents such as BH_2, CH_2^+, and NH_2. Delocalization of the carbon lone pair into the boron p orbital is precluded in perpendicular CH_3BH_2 (VIIb) resulting in an increase in the energy of the planar form by 26 kcal/mol (RHF/4-31G). This is a measure of the π effect. If BH_2 is replaced by isoelectronic CH_2^+ the effect is even more dramatic, 115 kcal/mol (RHF/STO-3G). In the perpendicular forms (e.g., VIIb) only the σ effect should be operative (along with a modest amount of hyperconjugation), and the reduction of the planar-tetrahedral difference is 36 kcal/mol for a BH_2 substituent. Evidently the σ and π effects are of comparable significance in the influence of BH_2 on the planar-tetrahedral energy difference. Similarly, rotation of NH_2 in CH_3NH_2 (VIIIa,b) can eliminate the unfavorable C_π-N (lone pair) effect thereby lowering the planar distortion energy by 16 kcal/mol (RHF/4-31G).


VIIa VIIb


VIIIa VIIIb

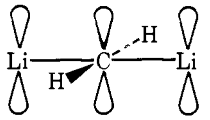
The calculated geometries (Table III) provide further insight into the electronic structure of the planar arrangements. Electropositive substituents which stabilize the planar form appear to be bridging a planar carbanion. Thus, in CH_3Li (IX) $\angle H_aCH_b$ is 115°, nearly the ideal 120° value. Destabilizing ligands such as fluorine (X) produce an opposite distortion ($\angle H_aCH_b$ is 63.3° in X); in these cases, H_b assumes the role of bridging ligand. Overlap populations indicate significant bonding between Li and H_a in IX and between H_a and H_b in X.

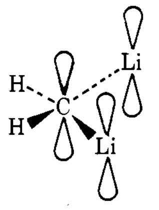

IX


X

Polysubstituted Methanes

If one substituent lowers the distortion energy substantially, then two or more such substituents should be better. Although one does not normally think of disubstituted methanes as having cis and trans forms, this, of course, is possible if planar structures are adopted.[23] As illustrated in Table VI, if the substituents in question are metals, the cis planar isomers appear to be about 30 kcal/mol more stable than the trans. The electronic structure of *trans*-CH_2Li_2, with two π electrons in a linear three-center orbital (XI), is reminiscent of the allyl cation. The cis form, XII, is even better; the two π electrons are delocalized in a cyclic arrangement, isoconjugate with the cyclopropenium ion (XIII). XII is "homoaromatic" in the sense that a π bond but not a σ bond exists between the two lithium atoms (cf. Figure 2). This is revealed by the Li···Li Mulliken overlap populations which are repulsive (−0.12) for the σ electrons, but bonding (+0.18) for the π. The 97.7° Li-C-Li bond angle in XII also indicates a balance between the attractive π and the repulsive σ Li···Li effects. The C-Li bond lengths in CH_2Li_2 decrease going from the tetrahedral[2] (1.924 Å) to the trans planar (1.807 Å) to the cis planar (1.744 Å) arrangements.


XI


XII


XIII

The third lithium atom in $CHLi_3$ produces a further, but modest, lowering of the tetrahedral-planar energy difference. The RHF/STO-3G minimized structure of the planar form reveals an even larger widening of the LiCLi angle to 101.7°. Because of geometric constraints, simultaneous angle enlargement of all LiCLi angles from 90° is impossible in planar CLi_4. Evidently steric (repulsive σ) effects dominate whatever further favorable influences are produced by substitution of the fourth lithium atom, and the planar-tetrahedral energy

Table III. Calculated Geometries (RHF/STO-3G) of Tetrahedral[2] and Planar Structures[a]

Molecule	Symmetry and structure	Optimized parameter
CH_3F (X)	C_{2v} planar	$r(\mathrm{C-H_a}) = 1.124$ $r(\mathrm{C-H_b}) = 1.136$ $r(\mathrm{C-F}) = 1.403$ $\angle \mathrm{H_aCF} = 116.7$
CH_3OH (OH in plane)	C_s	$r(\mathrm{C-O}) = 1.473$ $r(\mathrm{O-H}) = 0.995$ $r(\mathrm{C-H_a\ cis}) = 1.118$ $r(\mathrm{C-H_a\ trans}) = 1,107$ $r(\mathrm{C-H_b}) = 1.136$ $\angle \mathrm{COH} = 101.1$ $\angle \mathrm{OCH_a}$ cis = 117,6 $\angle \mathrm{OCH_a}$ trans = 113.0 $\angle \mathrm{OCH_b} = 180,0$ (ass.)
CH_3OH (OH perpendicular)	C_s	$r(\mathrm{C-O}) = 1.602$ $r(\mathrm{O-H}) = 0.996$ $r(\mathrm{C-H_a}) = 1.117$ $r(\mathrm{C-H_b}) = 1.143$ $\angle \mathrm{COH} = 84.9$ $\angle \mathrm{OCH_a} = 86.6$ $\angle \mathrm{OCH_b} = 180.0$ (ass.)
CH_3NH_2 (VIIIa)	C_s	$r(\mathrm{C-N}) = 1,513$ $r(\mathrm{C-H_a}) = 1.104$ $r(\mathrm{C-H_b}) = 1.131$ $r(\mathrm{N-H}) = 1.044$ $\angle \mathrm{NCH_a} = 112,0$ $\angle \mathrm{HNC} = 104.7$ $\angle \mathrm{HNH} = 101.7$
CH_3NH_2 (VIIIb)	C_s	$r(\mathrm{C-N}) = 1.438$ $r(\mathrm{C-H_a\ cis}) = 1.135$ $r(\mathrm{C-H_a\ trans}) = 1.113$ $r(\mathrm{N-H}) = 1.036$ $\angle \mathrm{NCH_a}$ cis = 120.1 $\angle \mathrm{NCH_a}$ trans = 116.0 $\angle \mathrm{HNC} = 104.7$ $\angle \mathrm{HNH} = 105,2$
CH_3CH_3	C_s	$r(\mathrm{C-C}) = 1.507$ $r(\mathrm{C-H_a}) = 1.106$ $r(\mathrm{C-H_b}) = 1.130$ $r(\mathrm{C-H}) = 1.091^b$ $\angle \mathrm{H_aCC} = 113.9$ $\angle \mathrm{HCC} = 112.2^b$
CH_3BH_2 (VIIa)	C_{2v} planar	$r(\mathrm{C-H_a}) = 1.073$ $r(\mathrm{C-H}) = 1.070$ $r(\mathrm{C-B}) = 1.511$ $r(\mathrm{B-H}) = 1.157$ $\angle \mathrm{H_aCB} = 77.3$ $\angle \mathrm{CBH} = 120.9$
CH_3BH_2 (VIIb)	C_{2v} planar	$r(\mathrm{C-H_a}) = 1.156$ $r(\mathrm{C-H_b}) = 1.051$ $r(\mathrm{C-B}) = 1.612$ $r(\mathrm{B-H}) = 1.166$ $\angle \mathrm{H_aCB} = 58.5$ $\angle \mathrm{CBH} = 120.4$
CH_3BeH	C_{2v} planar	$r(\mathrm{C-H_a}) = 1.113$ $r(\mathrm{C-H_b}) = 1.064$ $r(\mathrm{C-B}) = 1.543$ $r(\mathrm{Be-H}) = 1.280$ $\angle \mathrm{HCBe} = 66.29$
CH_3Li (IX)	C_{2v} planar	$r(\mathrm{C-H_a}) = 1.090$ $r(\mathrm{C-H_b}) = 1.068$ $r(\mathrm{C-Li}) = 1.727$ $\angle \mathrm{HCLi} = 64.49$
CH_3CN	C_{3v}	$r(\mathrm{C-H}) = 1.088$ $r(\mathrm{C-C}) = 1.489$ $r(\mathrm{C{\equiv}N}) = 1.154$ $\angle \mathrm{HCC} = 109.93$
CH_3CN	C_{2v} planar	$r(\mathrm{C-H_a}) = 1.119$ $r(\mathrm{C-H_b}) = 1.130$ $r(\mathrm{C-C}) = 1.382$ $r(\mathrm{C{\equiv}N}) = 1.164$ $\angle \mathrm{H_aCC} = 114.68$
CH_3Na	C_{3v}	$r(\mathrm{C-Na}) = 2.087$ $r(\mathrm{C-H}) = 1.092$ $\angle \mathrm{HCNa} = 114.3$
CH_3Na	C_{2v} planar	$r(\mathrm{C-Na}) = 2.131$ $r(\mathrm{C-H_a}) = 1.076$ $r(\mathrm{C-H_b}) = 1.053$ $\angle \mathrm{H_aCNa} = 62.3$
$CH_3CH_2^+$	C_{2v}	$r(\mathrm{C-C}) = 1.318$ $r(\mathrm{C-H_a}) = 1.114$ $r(\mathrm{C-H_b}) = 1.184$ $r(\mathrm{C^+-H}) = 1.094$ $\angle \mathrm{H_aCC} = 113.4$ $\angle \mathrm{CC^+H} = 121.3$
$CH_3CH_2^+$ (CH_2 perpendicular)	C_{2v}	$r(\mathrm{C-C}) = 1.420$ $r(\mathrm{C-H_a}) = 1.120$ $r(\mathrm{C-H_b}) = 1.144$ $r(\mathrm{C^+-H}) = 1.128$ $\angle \mathrm{C^+CH_a} = 110.6$ $\angle \mathrm{HC^+C} = 124.0$
$CH_2(BeH)_2$	C_{2v} tetrahedral	$r(\mathrm{C-Be}) = 1.666$ $r(\mathrm{C-H}) = 1.088$ $r(\mathrm{Be-H}) = 1.290$ $\angle \mathrm{HCH} = 107.0$ $\angle \mathrm{BeCBe} = 113.9$ $\angle \mathrm{CBeH} = 180,0$
$CH_2(BeH)_2$	C_{2v} planar	$r(\mathrm{C-Be})\ 1.557$ $r(\mathrm{C-H}) = 1.097$ $r(\mathrm{Be-H}) = 1.284$ $\angle \mathrm{HCH} = 105.3$ $\angle \mathrm{BeCBe} = 86.4$ $\angle \mathrm{BeBeH} = 140.1$
$CH_2(BeH)_2$	D_{2h}	$r(\mathrm{C-Be}) = 1.580$ $r(\mathrm{C-H}) = 1,286$ $r(\mathrm{Be-H}) = 1.290$
$HC(BeH)_3$	C_{3v}	$r(\mathrm{C-Be}) = 1.644$ $r(\mathrm{C-H}) = 1.093$ $\angle \mathrm{HCBe} = 108,7$
$HC(BeH)_3$	C_{2v}	$r(\mathrm{C-Be_a}) = 1,616$ $r(\mathrm{C-Be_b}) = 1.546$ $r(\mathrm{C-H}) = 1.102$ $\angle \mathrm{HCBe} = 89.5$
$C(BeH)_4$	D_{4h}	$r(\mathrm{C-Be}) = 1.622$
$C(BeH)_4$	T_d	$r(\mathrm{C-Be}) = 1.630$
cis-CH_2Li_2 (XII)	C_{2v} planar singlet	$r(\mathrm{C-Li}) = 1.744$ $r(\mathrm{C-H}) = 1.110$ $\angle \mathrm{HCH} = 101.4$ $\angle \mathrm{LiCLi} = 97.7$
trans-CH_2Li_2 (XI)	D_{2h} planar singlet	$r(\mathrm{C-Li}) = 1.807$ $r(\mathrm{C-H}) = 1.073$
CH_2Li_2	C_{2v} tetrahedral singlet	$r(\mathrm{C-H}) = 1.091$ $r(\mathrm{C-Li}) = 1.923$ $\angle \mathrm{HCH} = 106.7$ $\angle \mathrm{LiCLi} = 119.8$
CH_2Li_2 (XXIa)[b]	C_{2v} tetrahedral triplet	$r(\mathrm{C-H}) = 1.091$ $r(\mathrm{C-Li}) = 2.050$ $\angle \mathrm{HCH} = 105.2$ $\angle \mathrm{LiCLi} = 68.5$
cis-CH_2Li_2 (XXIb)[b]	C_{2v} planar triplet	$r(\mathrm{C-H}) = 1.098$ $r(\mathrm{C-Li}) = 1.999$ $\angle \mathrm{HCH} = 101.9$ $\angle \mathrm{LiCLi} = 68.9$
$CHLi_3$	C_{3v}	$r(\mathrm{C-H}) = 1,107$ $r(\mathrm{C-Li}) = 1.872$ $\angle \mathrm{HCLi} = 104.8$
$CHLi_3$	C_{2v} planar	$r(\mathrm{C-H}) = 1.135$ $r(\mathrm{C-Li_a}) = 1.846$ $r(\mathrm{C-Li_b}) = 1.748$ $\angle \mathrm{LiCH} = 78.42$
CLi_4	D_{4h}	$r(\mathrm{C-Li}) = 1.905$
CLi_4	T_d	$r(\mathrm{C-Li}) = 1.859$
CH_2Na_2	C_{2v} tetrahedral	$r(\mathrm{C-Na}) = 2.050$ $r(\mathrm{C-H}) = 1.09$ $\angle \mathrm{NaCNa} = 123.0$ $\angle \mathrm{HCH} = 109.47$
cis-CH_2Na_2	C_{2v} planar	$r(\mathrm{C-Na}) = 1.946$ $r(\mathrm{C-H}) = 1.099$ $\angle \mathrm{N_aCN_a} = 92.9$ $\angle \mathrm{HCH} = 103.2$

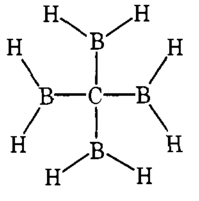
Table III (*Continued*)

Molecule	Symmetry and structure	Optimized parameter
trans-CH_2Na_2	D_{2h}	r(C–Na) = 2.012 r(C–H) = 1.036
cis-CLi_2F_2	C_{2v} planar	r(C–F) = 1.401 r(C–Li) = 1.695 ∠FCF = 99.50 ∠LiCLi = 117.1
CLi_2F_2	C_{2v} tetrahedral	r(C–F) = 1.380 r(C–Li) = 2.118 ∠FCF = 105.4 ∠LiCLi = 114.6
Cyclopropene	C_{2v} planar	$r(C_1–C_3)$ = 1.693 $r(C_3H)$ = 1.058 $\angle C_1C_3C_2$ = 43.0 $\angle HC_3H$ = 124.4
Cyclopropane	C_{2v} planar	$r(C_1–C_2)$ = 1.542 $r(C_1–H)$ = 1.063 $\angle C_2C_1C_3$ = 54.4 $\angle HC_1H$ = 110.8
Lithiocyclopropane	C_s	$r(C_1–Li)$ = 1.702 $r(C_1–C_2)$ = 1.496 $r(C_1–C_3) = r(C_1–C_2)$ (ass.) $r(C_1–H)$ = 1.068 $\angle C_2C_1C_3$ = 60.9 ∠LiCH = 70.6 ∠CCLi = 93.3
Lithiocyclopropane	C_s tetrahedral	$r(C_1–Li)$ = 1.961 $r(C_1–C_2)$ = 1.513 $r(C_1–H)$ = 1.084 $\angle C_2C_1C_3$ = 59.0 ∠LiCH = 117.8 $\angle LiC_1C_2$ = 123.9
Diboracyclopropane (XV)	C_{2v} planar	r(C–B) = 1.514 r(C–H) = 1.085 ∠HCH = 101.3 ∠BCB = 57.5
Diboracyclopropane (XV)	C_{2v} tetrahedral	r(C–B) = 1.540 r(C–H) = 1.082 ∠HCH = 110.53 ∠BCB = 63.1
2,3,4,5-Tetraboraspiropentane (XVI)	C_{2v} planar	r(C–B) = 1.527 ∠BCB = 60.2
2,3,4,5-Tetraboraspiropentane (XVI)	C_{2v} tetrahedral	r(C–B) = 1.531 ∠BCB = 61.2
3,3-Dilithiocyclopropene	C_{2v} tetrahedral	$r(C_3–Li)$ = 2.092 $r(C_3–C_1)$ = 1.498 ∠LiCLi = 102.6 $\angle C_1C_3C_2$ = 50.8
1,1-Dilithiocyclopropane (XVIIc)	C_{2v} planar	r(C–Li) = 1.733 $r(C_1–C_2)$ = 1.530 ∠LiCLi = 100.02 $\angle C_2C_1C_3$ = 58.0
1,1-Dilithiocyclopropane (XVIIa)	C_{2v} tetrahedral	r(C–Li) = 1.952 r(C–C) = 1.526 ∠LiCLi = 106.5 ∠CCC = 58.6
3,3-Dilithio-1,2-diboracyclopropane (XIX)	C_{2v} planar	r(C–Li) = 1.802 r(C–B) = 1.485 ∠LiCLi = 129.5 ∠BCB = 62.3
3,3-Dilithio-1,2-diboracyclopropane (XIX)	C_{2v} tetrahedral	r(C–Li) = 1.831 r(C–B) = 1.510 ∠LiCLi = 123.7 ∠BCB = 61.3

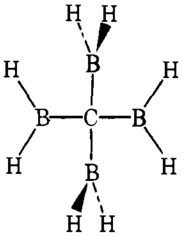
[a] Bond lengths in ångströms, angles in degrees. See structures IX and X for specification of atoms. Unlisted parameters have standard values (ref 16). Exocyclic hydrogens lie in the plane perpendicular to and bisecting the ring angle. [b] Local C_{3v} symmetry assumed for the tetrahedral methyl group which has dihedral angle H_aCCH of 90°. [c] UHF/STO-3G geometries for triplet states.

difference increases somewhat. This repulsive σ effect is less significant with BeH substituents, and a steady decrease in the planar-tetrahedral energy differences is noted in going from CH_3BeH (Table V) to $C(BeH)_4$ (Table VI).

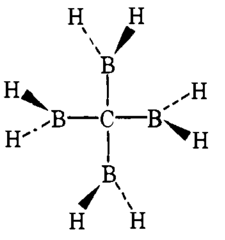
The repulsive σ effect is revealed more dramatically in the case of $C(BH_2)_4$. The planar D_{4h} structure, XIVa, lies 54 kcal/mol higher in energy than the D_{2h} structure XIVb. This is attributed to relief of the unfavorable interactions between hydrogen atoms. Alternatively, a "propeller" type distortion to the D_4 structure XIVc results in an energy intermediate between those of XIVa and XIVb. Evidently, a large amount of the favorable π delocalization must be sacrificed in order to overcome the unfavorable interligand steric effects.



XIVa



XIVb



XIVc

Some second-row substituents, Na and Cl, were examined as well (Tables V, VI, and VIII). These elements demonstrated the same trends as were observed for the first-row substituents in that sodium lowered the inversion barrier in CH_3Na and CH_2Na_2 while Cl raised the barrier of CH_2LiCl relative to that of CH_3Li. However, sodium had a much smaller stabilizing effect than lithium presumably because of the diffuseness of its 3p orbitals. For the same reason, chlorine is not as destabilizing as fluorine since the unfavorable C_π–X (lone pair) (X

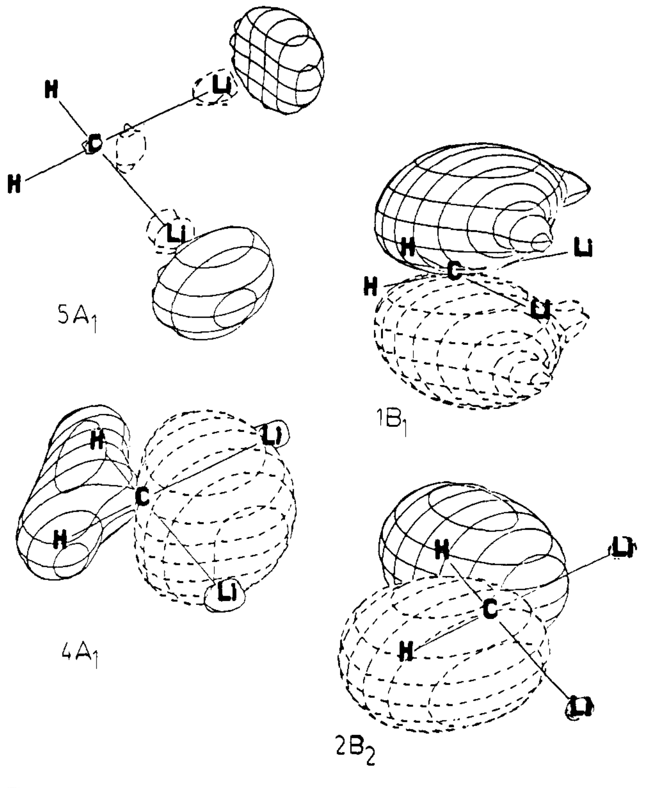
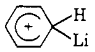
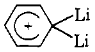
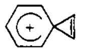
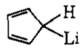
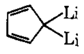


Figure 2. Four molecular orbitals of cis-planar CH_2Li_2 (C_{2v}). The HOMO ($1b_1$) of the singlet shows the three-center, two-electron "homoaromatic" π bonding. The $5a_1$ MO is the LUMO in the singlet, but the HOMO in the triplet. Because of the diffuseness of the p orbitals on lithium, a contour of 0.06 au was employed.

Table IV. Total Energies (au) of Molecules in Tetrahedral[2] and Planar Arrangements

			STO-3G optimized geometry			
	RHF/STO-3G Standard geometry[a]		RHF/STO-3G		RHF/4-31G	
Molecule	Tetrahedral	Planar	Tetrahedral	Planar	Tetrahedral	Planar
CH_4 (I)	−39.726 86	−39.344 30	−39.726 86	−39,344 41	−40,139 76	−39,871 47
CH_3F (X)	−137.168 36[d]	−136,699 47	−137.169 06[c]	−136.747 31	−138,856 86[c]	−138.514 99
CH_3OH (OH planar)	−113.545 02[d]	−113,087 19	−113.545 98[c]	−113.126 43	−114,865 25[c]	−114.534 29
CH_3OH (OH perpendicular)		−113.107 74		−113.148 61		−114.546 03
CH_3NH_2 (VIIIA)	−94.030 43[d]	−93.581 69	−94.032 86[c]	− 92.619 96	−95,064 98[c]	− 94.748 87
CH_3NH_2 (VIIIB)		−93.600 24		− 93.637 55		− 94.774 74
CH_3CH_3	−78.306 18[d]	−77.909 53	−78.306 18[c]	−77.921 26	−79,115 82[c]	−78.837 69
CH_3BH_2 (VIIA)	−64.666 50	−64.407 08	−64,667 69[e]	−64.421 52	−65,347 72	−65.179 65
CH_3BH_2 (VIIB)		−64.328 26		−64.381 03		−65,138 08
CH_3BeH	−54.152 24	−53.929 26	−54.153 22[f]	−53.993 63	−54,733 49	−54.607 91
CH_3Li (IX)	−46.419 99	−46.247 88	−46.421 59[f]	−46.338 05	−46.959 62	−46.891 92
CH_3CN	−130.270 79	−129.902 23	−130.271 56	−129.925 61	−131,727 12	−131.475 02
CH_3Na	−198.937 38	−198.732 98	−198,940 68	−198.819 00	*i*	*i*
$CH_3CH_2^+$ (CH_2 planar)	−77.405 21	−77,204 26	−77.408 06	−77.239 45	−78,194 96	−77,076 34
$CH_3CH_2^+$ (CH_2 perpendicular)		−77.021 29		−77.053 93		−77.925 46
cis-$CH_2(BeH)_2$	−68.592 16	−68.476 71	−68.592 99	−68.503 75	−69.338 31	−69.266 91
trans-$CH_2(BeH)_2$		−68.431 08		−68.442 52		−69.226 69
$CH(BeH)_3$	−83.050 72	−82.973 85	−83.053 18	−82.988 52		
$C(BeH)_4$	−97.526 43	*b*	−97.531 98	−97.480 43		
cis-CH_2Li_2 (XII)	−53.131 15	−53.074 59	−53.134 07	−53.107 51	−53,774 54	−53.758 05
trans-CH_2Li_2 (XI)		−53.030 64		−53.048 69		−53,698 81
cis-CH_2Li_2 triplet (XXI)			−53.152 50	−53.137 66	−53.799 94	−53.795 31
$CHLi_3$	*b*	*b*	−59.885 90	−59.870 21	−60.608 65[o]	−60.596 82[o]
CLi_4	*b*	*b*	−66.666 68	−66.631 93	−67,465 13[o]	−67,438 90[o]
cis-CH_2Na_2	−358.061 10	−357.958 14	−358.063 77	−357.978 44	*i*	*i*
trans-CH_2Na_2		−357.883 18		−357.891 73	*i*	*i*
cis-$CHLi_2CN$	−143.704 51	−143.651 63				
trans-$CHLi_2CN$		−143.603 93				
cis-CLi_2F_2 (XX)	−248.032 79	−248.020 57	−248.058 01	−248.077 75	*b*	*b*
Cyclopropene	−114.393 25	−114.035 26	−114.401 16[g]	−114.088 35	−115,641 68[g]	−115.401 58
Cyclopropane	−115.660 37	−115,344 76	−155,666 16[g]	−115.363 47	−116.883 50[g]	−116.659 23
Lithiocyclopropane	−122.356 56	−122.204 65	−122.364 59	−122.261 31	−123.698 98	−123.616 38
Diboracyclopropane (XV)	−88.342 75	−88.260 18	−88.344 33	−88.289 85	−89.312 84	−89.281 81
2,3,4,5-Tetraboraspiropentane (XVI)	−137.020 04	−136,993 13	−137.032 13	−137.015 75	−138.551 82	−138.541 38
1,1-Dilithiocyclopropane pane (XVII)	−129.057 43	−129,037 51	−129,059 86	−129.071 26	*b*	*b*
3,3-Dilithiocyclopropene (XVIII)	−127.764 27	−127.777 52	−127.797 27	−127.812 11		
3,3-Dilithio-1,2-diboracyclopropane (XIX)	−101.876 82	−101.885 66	−101.888 69	−101.909 87	−103.061 93	−103.089 43
Cyclopentadiene (VI)	−190.446 53[j]	−190.145 93[j]				
Phenonium ion (II)	−304.231 42[k]	−304.096 58[k]				
$C(BH_2)_4$ (XIVA)	−139.497 19	−139,277 62				
$C(BH_2)_4$ (XIVB)		−139.364 17				
$C(BH_2)_4$ (XIVC)		−139.323 89[n]				
Spiropentane	−191.592 20	−191.326 40				
CH_2LiF	−143.863 07	−143.644 17				
CH_2LiCl	−500.429 36	−500.222 77				
1-Lithio-1-fluorocyclopropane	−219.817 72	−219.601 92				
$C_6H_7^+$	−228.253 16[h]	−228.034 99[h]				
	−235.063 00[k]	−234.988 86[k]				
	−242.162 80[k]	−241.828 62[k]				
	−302.963 09[l]	−302.860 70[l]				
	−197.044 75[j]	−197.168 61[m]				
	−203.877 03[j]	−203.902 88[m]				

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[a] See Table VII, footnote *a*. Parenthetical structural descriptions refer to orientations of substituents in the planar arrangements. [b] Convergence on the density matrix was not achieved. [c] W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, 11, 175 (1974). [d] W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, 92, 4796 (1970). [e] J. D. Dill, P. v. R. Schleyer, and J. A. Pople, *ibid.*, 97, 3402 (1975). [f] J. D. Dill, J. A. Pople, and P. v. R. Schleyer, to be published. [g] W. A. Lathan, L. Radom, P. C. Hariharan, W. J. Hehre, and J. A. Pople, *Top. Curr. Chem.*, 40, 1 (1973). [h] W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, 94, 6901 (1972). [i] 44-31G basis set not yet available for Na. [j] Experimental geometry for cyclopentadiene ring (L. H. Sharpen and V. W. Laurie, *J. Chem. Phys.*, 43, 2765 (1965)). [k] Ring geometries from W. J. Hehre, *J. Am. Chem. Soc.*, 94, 5919 (1972), for planar structure, cyclopropyl fragment rotated 90°. [l] C_6H_5 fragment from footnote *k*, cyclopropyl fragment from footnote *g*. [m] H. Preuss and G. Diercksen, *Int. J. Quantum Chem.*, 1, 349 (1967). [n] Dihedral angle, $\varphi(H,B,C,C) = 35°$. [o] Convergence achieved using direct descent technique (R. Seeger and J. A. Pople, *J. Chem. Phys.*, in press).

Table V. Calculated Planar–Tetrahedral[2] Energy Differences (kcal/mol) for Monosubstituted Methanes (RHF)

	Basis set		
Molecule	STO-3G (standard geometry)[a]	STO-3G (STO-3G optimized geometry)	4-31G (STO-3G optimized geometry)
CH_4 (I)	240	240	168
CH_3F (X)	294	265	215
CH_3OH (OH planar)	287	263	208
CH_3OH (OH perpendicular)	274	249	200
CH_3NH_2 (VIIIa)	281	259	198
CH_3NH_2 (VIIIb)	269	248	182
CH_3CH_3	250	243	175
CH_3BH_2 (VIIa)	164	155	106
CH_3BH_2 (VIIb)	213	180	132
CH_3BeH	140	100	79
CH_3Li (IX)	108	52	42[b]
CH_3CN	231	217	158
CH_3Na	124	76	c
$CH_3CH_2^+$ (CH_2 coplanar)	128	106	74
$CH_3CH_2^+$ (CH_2 perpendicular)	243	222	169

[a] Reference 16. [b] UHF/4-31G optimized structures have a difference of 38 kcal (see text). [c] 44-31G basis set not yet available for Na.

Table VI. Calculated Planar–Tetrahedral[2] Energy Differences (kcal/mol) for Polysubstituted Methanes (RHF)

	Basis set		
Molecule	STO-3G (standard geometry)[a]	STO-3G (STO-3G optimized geometry)	4-31G (STO-3G optimized geometry)
cis-$CH_2(BeH)_2$	72	56	45
trans-$CH_2(BeH)_2$	101	94	70
$CH(BeH)_3$	48	41	
$C(BeH)_4$	c	32	
cis-CH_2Li_2 (XII)	35	17	10[b]
trans-CH_2Li_2 (XI)	63	54	47
$CHLi_3$	c	10	7
CLi_4	c	22	6
cis-CH_2Na_2	65	59	
trans-CH_2Na_2	112	108	
cis-$CHLi_2CN$	33		
trans-$CHLi_2CN$	63		
CLi_2F_2 (XX)	8	−25	c

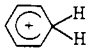
[a] Reference 16. [b] 8 kcal/mol both at 6-31G* (STO-3G geometries) and at 4-31G (4-31G geometries) (see text). [c] Convergence on the density matrix was not achieved.

Table VII. Calculated Planar–Tetrahedral[2] Energy Differences (kcal/mol) for Three-Membered Ring Compounds (RHF)

	Basis set		
Molecule	STO-3G (standard geometry)[a]	STO-3G (STO-3G optimized geometry)	4-31G (STO-3G optimized geometry)
Cyclopropene	225	196	151
Cyclopropane[c]	198	190	141
Lithiocyclopropane	95	65	52
Diboracyclopropane (XV)	52	34	20
2,3,4,5-Tetraboraspiropentane (XVI)	17	10	6
1,1-Dilithiocyclopropane (XVII)[c]	13	−7	b
3,3-Dilithiocyclopropene (XVIII)	−8	(−10)[d]	b
3,3-Dilithio-1,2-diboracyclopropane (XIX)	−6	−13	−17

[a] Reference 16; for planar molecules the standard bond angle is 90° except when a ring is present. In these cases the remaining substituents trisect the external angle. [b] Convergence on the density matrix was not achieved. [c] One carbon planar. [d] Incomplete optimization.

Table VIII. Calculated Planar–Tetrahedral[2] Energy Differences (RHF/STO-3G, kcal/mol) for Some Larger Systems at Standard Geometries

Molecule	Energy
Cyclopentadiene (VI)	189
Phenonium ion (II)	85
$C(BH_2)_4$ (XIVa)	84
$C(BH_2)_4$ (XIVb)	138
$C(BH_2)_4$ (XIVc)	113
Spiropentane[b]	167
CH_2LiF	137
CH_2LiCl	130
1-Lithio-1-fluorocyclopropane	135
	137
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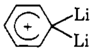
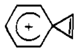
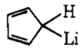
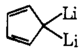
	21
	102
	77
	16

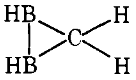
[a] See Table VII, footnote *a*, and Table III for the geometries of individual molecules. [b] Central carbon planar.

= F, Cl) interaction is not as bad for the more diffuse chlorine 3p lone pair.

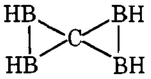
The high barriers to planarity of the carbenoids CH_2LiF and 1-lithio-1-fluorocyclopropane (Table VIII) support the recent findings of Hahnfield and Burton[24] on the stereochemical integrity of similar vinyl carbenoids. Contrary to an earlier report,[25] they found that these molecules did not isomerize in solution. Presumably, one possible mode of isomerization might have been a simple rotation of the LiCF group but this mechanism of rearrangement seems unlikely on the basis of our results.

Utilization of Small Rings

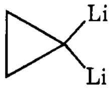
Three-membered rings overcome the steric problem. One can take advantage of such rings in two ways. The electropositive atoms can be incorporated into the ring structure, or they can be introduced as external substituents. Thus, XV meets the usual criteria for aromaticity in its planar arrangement, but the tetrahedral geometry is still preferred by 20 kcal/mol (RHF/4-31G). The same is true for XVI, a spiropentane analogue, but by only 6 kcal/mol (RHF/4-31G). 1,1-Dilithiocyclopropane (XVII) achieves our objective; the planar form is calculated even at the RHF/STO-3G level to be the energy minimum! 3,3-Dilithiocyclopropene (XVIII), the rather exotic compound XIX, and the bis-carbenoid CLi_2F_2 (XX) are even more favorable in their preference for planar geometries.



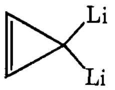
XV



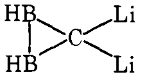
XVI



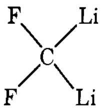
XVII



XVIII



XIX

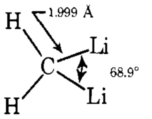


XX

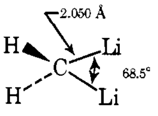
Triplet States

An obvious additional question, emphasized by Murrell,[5e] is the possibility of a triplet ground state. UHF/6-31G** calculations by Shavitt et al.[6b] indicate that triplet planar methane has an energy 2.5 kcal/mol lower than singlet planar methane. However, the problem of assessing triplet-singlet energy differences by single-determinant calculations is well known.[26] The stability of states of higher spin multiplicity is overestimated. For example, the stability of the triplet state of CH_2 is overestimated by 14 ± 6 kcal/mol[27] at the Hartree-Fock level. Therefore, it is not surprising that when configuration interaction is employed singlet methane becomes the more stable planar configuration by 4 kcal/mol.[6b] We have calculated the singlet-triplet difference for CH_2Li_2. The total energy of the planar triplet (UHF/4-31G) lies 23.4 kcal/mol below that of the planar singlet (RHF/4-31G). The tetrahedral triplet (UHF/4-31G) is only 15.9 kcal/mol below the tetrahedral singlet (RHF/4-31G). The planar distortion energy of the triplet is then only 2.9 kcal/mol (UHF/4-31G). In view of the overestimation of the stability of triplet methylene, it is difficult to assign the ground state configuration of CH_2Li_2 but the two states should be close in energy.

The structures of the two triplets, XXIa,b, show marked differences from the corresponding singlet geometries. For both triplets an electron is removed from a LiCLi orbital of π type (symmetry b_1) and placed in a Li···Li σ bonding orbital (symmetry a_1). This results in a marked reduction of the ∠LiCLi angles (to ca. 69° in both XXIa and XXIb); three-membered rings are formed. The C-Li bond lengthenings (Table III) reflect the removal of an electron from the π bonding orbital. The presence of low-lying triplet configurations may contribute to the tendency of polylithium compounds to associate,[28] but nothing is known about this at present.



XXIa

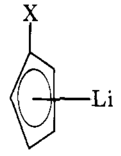


XXIb

Geometries of Lower Symmetry

There remains the problem of determining the most stable geometry. Orientations other than T_d and D_{4h} are certainly possible for methane as are corresponding structures for substituted methanes. Indeed, Shavitt's work[6b] indicates that a square-pyramidal (C_{4v}) geometry is preferred over square planar (D_{4h}) for methane suggesting that molecules such as *cis,cis,cis,cis*-fenestrane[10b] would undergo a similar distortion as do several known carboranes.[29] However, complete relaxation of all symmetry constraints would result in a prohibitive computational burden and was not generally pursued here. In two cases we did carry out a somewhat more complete search (at the RHF/STO-3G level) to probe the possibility that a structure intermediate between the "tetrahedral" C_{2v} and planar C_{2v} structures might be even lower in energy. For the case of CF_2Li_2, a form of C_2 symmetry, obtained by rotating the FCF plane in the cis planar form by 20° about the angle bisector, was found to lie 0.7 kcal/mol lower in energy than the planar structure. In contrast, a 5° rotation of the CLi_2 group in planar 1,1-dilithiocyclopropane (XVIIc) resulted in a higher energy.

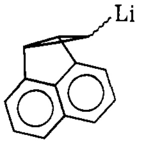
Two promising systems, 5-lithiocyclopentadiene and 5,5-dilithiocyclopentadiene (XXIIa and XXIIb), received no further attention since calculations at fixed geometries[30] showed that these molecules prefer the unrelated bridged structure XXIIa,b.



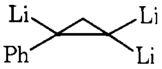
XXIIa, X = H
b, X = Li

Proposed Experimental Systems for Study

After a century of tetrahedral carbon, these results are startling and invite experimental verification. For molecules in which the tetrahedral structures are more stable, but the tetrahedral-planar energy difference is low, stereomutation should be observable.[31] Appropriately substituted phenonium ions are a possibility, but our ab initio results on II (Table VIII), although only with standard geometries, do not confirm the low MINDO/2 distortion energies[12,32] and preliminary experimental work failed to detect planar inversion.[9] A variety of alkyllithium compounds, including neohexyllithium[33] and the cyclopropyllithium derivative (XXIII),[34] are known to stereomutate in solution.[26] A dissociation-recombination mechanism involving ions or ion pairs has generally been assumed.[33] Electron donor solvents may well favor this mechanism, but we suggest that planar inversion should receive serious consideration as an alternative in nonpolar solvents especially since the distortion energy for methyllithium is calculated to be only 38 kcal/mol (RHF/4-31G optimized structures). Furthermore the structures we have calculated for planar alkyllithium compounds resemble trigonal carbanions bridged by lithium cations with significant bonding, not merely electrostatic attraction, between lithium and carbon as well as between lithium and the other adjacent atoms, especially hydrogen.[35] Stereomutation of alkyllithium derivatives may also occur in associated species, but we have not yet considered such possibilities computationally.



XXIII



XIV

Evidence for the existence of many di- and polylithium compounds, including CH_2Li_2,[36] CLi_4,[37] and the 1,1-dilithiocyclopropane derivative (XXIV),[38] has been reported,[26,39] but their structures are not known experimentally. Our results indicate that molecules of this type, at least as isolated species in the gas phase, are likely to be planar or to have low planar distortion energies. Although the experimental verification of these predictions may be complicated by the tendency of lithium compounds to be associated or to be solvated in electron-donor solvents,[26] efforts to overcome these problems should be rewarding.

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(2) *Exact* tetrahedral geometry (T_d symmetry) is seldom encountered, as it is possible only when all four substituents are the same. As deviations from 109.5° bond angles are generally small, "tetrahedral" is often employed as we do here in a loose sense to describe the preferred bonding arrangement in saturated organic molecules.

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