same conclusion—both **7** and **8** are unstable, gas-phase carbanions. However, when the inversion angles, $\theta$, at $C_\beta$ in **7** and **8** were maintained at their approximately tetrahedral 4-31G values, the $C_\beta$–$C_\alpha$ and the $C_\alpha$–F bond distances could be optimized (Table I). A rigid $C_\beta$ inversion barrier of 7.60 kcal/mol (relative to **8**) was calculated when all other geometric parameters were maintained constant (4-31G).

## Conclusion

Our theoretical considerations prompt us to generalize that *the rate of both syn and anti elimination will be increased by maximizing overlap of the developing carbanion at $C_\beta$ with the backside of the $C_\alpha$ leaving group.* Thus, the mechanism for syn elimination is in effect an E1cB process where expulsion of the leaving group occurs concomitantly with inversion at $C_\beta$. In a syn E2 (or E1cB) elimination, rehybridization at $C_\beta$ will occur until the best balance between orbital overlap at $C_\alpha$ and loss of counterion bonding between the developing carbanion and the departing hydrogen–base pair is attained. This suggestion is consistent with existing experimental data,[3] where E1cB-like transition states have been invoked for syn elimination, and provides a rational explanation for the failure to observe hydrogen–deuterium exchange in E1cB reactions. We also extend these concepts to include pyrolytic syn elimination (Cope) and $\alpha',\beta$ (ylide) elimination where intramolecular syn 1,2 elimination should also be enhanced by inversion of configuration at the carbanionic carbon.

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(7) Calculations employed the GAUSSIAN 70 series of programs[8] with standard STO-3G and 4-31G basis sets. The geometry of both conformers of ethyl fluoride was first optimized with an STO-3G basis set and then exhaustively minimized with a 4-31G basis set using 0.02 Å and 2° increments. The geometries of the ethyl fluoride carbanions were similarly optimized by STO-3G (0.01 Å and 1° increments) and then with a 4-31G basis set but excluding C–H bond distances. A similar procedure was used with the geometries of the hydride-induced elimination except that 0.1 Å and 5° increments were used.

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(9) The 4-31G total energies of $H^-$ and $H_2$ are −0.422 44 and −1.126 82 au, respectively. The STO-3G, 4-31G, and 6-31G total energies of $F^-$ are −97.613 32, −99.247 83, and −99.350 18 au, respectively. The fully optimized STO-3G and 4-31G total energies of ethylene are −77.073 92 and −77.922 15 au, respectively, while the 6-31G energy of the 4-31G optimized ethylene molecule is −78.004 42 au. The 6-31G total energies of the 4-31G optimized syn (**7**) and anti (**8**) ethyl fluoride anions are −177.320 88 and −177.329 06 au, respectively.

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(13) The 90° conformer has a minimum energy when the inversion angle $\theta$ was 62° (total energy −177.129 40 au). The planar carbanion ($C_\beta$) had a total energy of −177.118 32 au with all variables optimized including the C–F bond distance. The geometries used to calculate the rotational barrier were optimized in a similar fashion with the exception of the syn ($\theta$ = 0°) and anti ($\theta$ = 180°) conformers.

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# The Unusual Structures, Energies, and Bonding of Lithium-Substituted Allenes, Propynes, and Cyclopropenes

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**Abstract:** Propyne and allene undergo sequential hydrogen–lithium exchange experimentally to give $C_3H_3Li$ (two isomers), $C_3H_2Li_2$, $C_3HLi_3$, and $C_3Li_4$. Mono- and dilithiated cyclopropenes are also known. The structures and bonding of hypothetical isolated monomers with these compositions, investigated by ab initio molecular orbital methods, reveal remarkable features. While acetylide bonding, e.g., in propynyllithium (**1**), is the most favorable energetically, bridging lithiums are preferred over conventional placements. Allenyllithium (**11**), the simplest bridged molecule of this type, has a bent carbon skeleton ($\angle$CCC = 157.6°, STO-3G optimization) which better accommodates simultaneous Li bonding to C-1 and C-3. Even though Li is closest to C-2, bonding to that atom is indicated by the overlap populations to be negligible. The vinyl hydrogen of cyclopropene, with its enhanced acidity, exhibits a larger energy of replacement than that of ethylene. The methylene hydrogen behaves in the opposite way owing to the antiaromatic character of 3-cyclopropenyllithium (**5**). Examination of a number of structural possibilities indicated the most favorable forms, e.g., **17** for $C_3H_2Li_2$, with an acetylide and a bridging lithium. Two bridging lithiums in CLiC planes roughly at right angles are found in the lowest energy structures of $C_3HLi_3$ (**23**) and of $C_3Li_4$ (**36**), which in addition have one and two acetylide-type C–Li bonds, respectively. The orthogonal $\pi$ systems, each involved in bonding a bridging lithium, are responsible for this arrangement. Numerous other forms of these isomers were considered. With few exceptions, classical structures based on the corresponding hydrocarbons were much less stable than alternative arrangements in which the multicenter bonding capabilities of lithium could be better utilized. Another example is 1,2-dilithiocyclopropene, which prefers the doubly bridged (**4a**) over the classical (**4**) structure.

New theories of bonding evolve from a knowledge of structural characteristics of sets of related molecules. The development of the bonding principles governing boranes, by Lipscomb and others, has brought order to a field where every

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structure was once considered to be rule breaking.[2] Another group of electron-deficient molecules can be obtained by replacing one or more hydrogens of hydrocarbons by lithium.[3,4] Whatever the nature of the bonding in such organolithium compounds, ionic or covalent,[5,6] their structures are proving to be remarkable when compared with those of the hydrocarbons from which they are formally derived.[4,5] This is also true of the lithium derivatives of the $C_3H_4$ isomers, propyne, allene, and cyclopropene, the subject of the present investigation.

Experimentally, propyne can be lithiated sequentially, giving $C_3H_3Li$ (**1**), $C_3H_2Li_2$, $C_3HLi_3$, and $C_3Li_4$.[7,8] Spectroscopic evidence is available which characterizes these products as being allene-like or propyne-like, but no structural details of any of these compounds are known experimentally.[7,8] Allene behaves similarly, but with one important difference. An allenyl- (or propargyl-) lithium (**2**) is formed first, rather than **1**.[7,8] Cyclopropene, the third $C_3H_4$ isomer, is rather acidic; the high $^{13}C$-H vinyl coupling constant, 243 Hz, indicates very high s character.[9] Both mono- (**3**) and dilithiocyclopropene (**4**) can be prepared easily, but their geometries and energies are unknown.[10] The methylene hydrogens are less acidic; base-catalyzed exchange of these hydrogens occurs only when the vinylic positions are substituted.[11] 3-Lithio- (**5**) and 3,3-dilithiocyclopropenes (**6**) (or substituted analogues) are experimentally unknown. The anionically enhanced π-donor hyperconjugative character of C-Li bonds would be expected to destabilize **5** and **6** antiaromatically.[11] With **6**, another interesting feature emerges. Our published calculations suggest **7**, with a *planar* tetracoordinate carbon, to be more stable than the traditional "tetrahedral" form![5h]

$Li-C\equiv C-CH_3$

1, $C_{3v}$

$[HCCCH_2]Li$

2


3, $C_s$


4, $C_{2v}$


4a, $C_{2v}$


5 $C_s$


6 $C_{2v}$


7 $C_{2v}$

This paper presents the results of an ab initio study of various $C_3H_3Li$, $C_3H_2Li_2$, $C_3HLi_3$, and $C_3Li_4$ geometries. An attempt has been made to locate the local and absolute minima (isomers) on the potential energy surfaces. Since conventional bonding does not govern the structure of these molecules, the results obtained often seem surprising. This is shown by our calculated structures of $C_2Li_2$,[5a] $CH_2{=}CLi_2$,[5b] $C_4Li_4$,[5c] $C_3H_5Li$ (**8**),[5d] $C_3Li_4$,[5e] $(CH_2Li_2)_2$,[5f] etc.[5] Such calculations refer to isolated, hypothetically motion-free molecules. In condensed phases, lithium compounds tend to be associated and to be solvated. The reader should keep these differences in mind while evaluating the results we report.

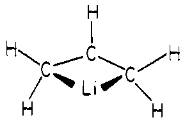
## Calculational Methods

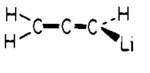
Single-determinant self-consistent field molecular orbital (SCF-MO) theory within the restricted Hartree-Fock formalism[12] was used throughout. Consequently, the designation "RHF" is taken to be understood. The minimal STO-3G basis with the standard exponents[13] was employed for all geometry optimizations. Single-point calculations using the split-valence 4-31G (5-21G for lithium) basis[14] were carried out on these optimized structures to check the relative energies. Complete mapping of the potential energy surface, even though desirable, is not yet practical. In the absence of such a systematic approach, we hope that the diversity of symmetries selected for each species includes the most stable geometry. Previous experience also provided a guide.[4,5] All calculations were carried out using the GAUSSIAN 70 series of programs;[15] a single precision Telefunken TR440 version written by Dr. H.-U. Wagner was used at Erlangen. An SCF damping routine, written by Dr. D. Poppinger, overcame convergence problems.

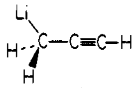
## Results

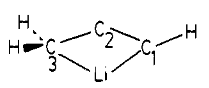
**$C_3H_3Li$.** All possible conventional monolithiated structures, **1**, **3**, **5**, **9**, and **10**, were constructed from their hydrocarbon parents, propyne, allene, and cyclopropene, using standard geometries.[16] The STO-3G energies are presented in Table I. As expected, the acetylide structure, **1**, is found to be the most stable form. The acetylenic hydrogen is acidic, and can readily be replaced by a metal. The Li-C(sp) bond length is the shortest found.[6,17]

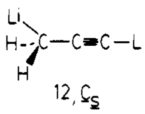
Geometry optimization of the other isomers within each specified symmetry led in some cases to substantial reductions in energy (Table I) and changes in structure (Table II). Optimization of allenyllithium (**9**) leads to a bent structure, **11**, in which the CCC unit no longer is linear. Li bridges the carbon skeleton, and the $CCH_2$ group becomes nonplanar, increasing C-Li bonding. The electronic structure of **11** is similar to that of allyllithium (**8**),[5d] where Li is bonded mainly through the interaction with nonbonding π orbitals (see Discussion). According to the STO-3G Mulliken population analysis, the negative charge in **11** is mainly centered on the two end carbons ($C_1$ = −0.13, $C_3$ = −0.19). The central carbon is nearly neutral with a charge of −0.028. The $C_1$-$C_2$ bond length, 1.264 Å, is shorter than that in allene (1.288 Å at STO-3G)[18] while $C_2$-$C_3$ is somewhat longer (1.356 Å). The standard geometry propargyl structure, **10**, also gives the same bridged form, **11**,

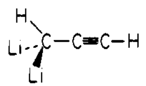

8, $C_s$

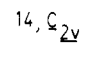

9, $C_s$


10, $C_s$


11, $C_s$


12, $C_s$


13, $C_s$


14, $C_{2v}$

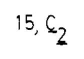

15, $C_2$

**Table I.** Calculated Total and Relative Energies of Lithium-Substituted Propynes, Allenes, and Cyclopropenes[a]

| structure | point group | STO-3G standard geometry | STO-3G opt geometry | rel energy (STO-3G opt geom) | 4-31G/5-21G STO-3G opt geometry total energy | 4-31G/5-21G STO-3G opt geometry rel energy |
|---|---|---|---|---|---|---|
| $C_3H_3Li$ | | | | | | |
| **1** | $C_{3v}$ | −121.205 15 | −121.206 47 | 0.0 | −122.568 59 | 0.0 |
| **9** | $C_s$ | −121.147 63 | | | | |
| **10** | $C_s$ | −121.151 80 | | | | |
| **11** | $C_s$ | | −121.187 58 | 11.7 | −122.548 30 | 12.7 |
| **3** | $C_s$ | −121.129 69 | −121.141 94 | 40.5 | −122.494 54 | 46.5 |
| **5** | $C_s$ | −121.072 23 | −121.092 51 | 71.5 | −122.451 48 | 73.5 |
| $C_3H_2Li_2$ | | | | | | |
| **12** | $C_s$ | −127.899 92 | | | | |
| **14** | $C_{2v}$ | −127.884 66 | | | | |
| **15** | $C_2$ | −127.873 07 | | | | |
| **16** | $C_{2v}$ | | −127.911 64 | 26.7 | −129.359 92 | 25.9 |
| **17** | $C_s$ | | −127.954 18 | 0.0 | −129.401 21 | 0.0 |
| **18** | $C_{2v}$ | | −127.940 96 | 8.3 | −129.388 13 | 8.2 |
| **19** | $C_2$ | | −127.934 11 | 12.6 | −129.380 68 | 12.9 |
| **20** | $C_{2v}$ | −127.884 69 | −127.893 10 | 38.3 | −129.377 09 | 15.1 |
| **4** | $C_{2v}$ | | −127.872 55 | 51.2 | −129.327 58 | 46.2 |
| **4a** | $C_{2v}$ | | −127.887 99 | 41.5 | −129.311 43 | 56.3 |
| **6** | $C_{2v}$ | −127.764 27 | −127.797 50 | 98.3 | −129.251 97 | 93.7 |
| **7** | $C_{2v}$ | −127.777 52 | −127.819 52 | 84.5 | −129.198 02 | 127.5 |
| **13** | $C_s$ | −127.865 73 | | | | |
| $C_3HLi_3$ | | | | | | |
| **23** | $C_s$ | | −134.692 25 | | −136.233 08 | |
| **21** | $C_s$ | −134.615 48 | | | | |
| **22** | $C_s$ | −134.623 64 | | | | |
| **25** | $C_{3v}$ | −134.612 45 | | | | |
| $C_3Li_4$ | | | | | | |
| **27** | $D_{2d}$ | | −141.384 93 | 35.6 | −143.049 83 | 19.0 |
| **28** | $D_{2h}$ | | −141.387 16 | 34.2 | −143.050 63 | 18.5 |
| **29** | $C_{3v}$ | | −141.418 87 | 14.3 | −143.060 35 | 12.4 |
| **30** | $D_{2d}$ | | −141.416 00 | 16.1 | −143.028 64 | 32.3 |
| **31** | $D_{2h}$ | | −141.405 64 | 22.6 | −143.073 48 | 4.2 |
| **36** | $C_{2v}$ | | −141.441 66 | 0.0 | −143.080 11 | 0.0 |

[a] Total energies in hartrees. Relative energies in kilocalories/mole.

**Table II.** STO-3G Optimized Geometries of $C_3H_3Li$ Isomers[a,c,e]

| molecule | parameter | value | parameter | value |
|---|---|---|---|---|
| **1** $C_{3v}$ | $C_1C_2$ | 1.193 (1.216) | $C_2C_3$ | 1.485 (1.461) |
| | $C_1Li$ | 1.828[b] (1.896) | $C_3H$ | 1.089 (1.085) |
| | $\angle HCC$ | 110.8 (111.4) | | |
| **11** $C_s$ | $C_1C_2$ | 1.264 (1.277) | $C_2C_3$ | 1.356 (1.341) |
| | $C_1Li$ | 1.914 (2.000) | $C_2Li$ | 1.892 (2.039) |
| | $C_3Li$ | 2.246 (2.469) | $C_3H$ | 1.080 (1.075) |
| | $C_1H$ | 1.080 (1.068) | $\angle C_1C_2C_3$ | 157.6 (161.4) |
| | $\angle LiC_1C_2$ | 69.5 (73.2) | $\angle HC_1C_2$ | 129.8 (130.0) |
| | $\angle OC_3C_2$[d] | 156.9 (167.4) | $\angle HC_3H$ | 114.8 (116.3) |
| **3** $C_s$ | $C_1C_2$ | 1.299 (1.304) | $C_1C_3$ | 1.541 (1.594) |
| | $C_2C_3$ | 1.466 (1.480) | $C_1Li$ | 1.881 (1.916) |
| | $C_2H$ | 1.074 (1.063) | $C_3H$ | 1.086 (1.079) |
| | $\angle LiC_1C_3$ | 147.5 (144.2) | $\angle HC_2C_3$ | 144.4 (143.2) |
| | $\angle OC_3C_2$[d] | 156.5 (157.6) | $\angle HC_3H$ | 111.8 (112.9) |
| **5** $C_s$ | $C_1C_2$ | 1.272 | $C_1C_3$ | 1.525 |
| | $C_3Li$ | 1.999 | $C_3H$ | 1.091 |
| | $C_1H$ | 1.075 | $\angle C_1C_3C_2$ | 49.2 |
| | $\angle HC_1C_3$ | 145.3 | $\angle LiC_3C_1$ | 123.9 |
| | $\angle HC_3C_1$ | 111.9 | $\phi HC_1C_2C_3$ | 175.0 |
| | $\angle HC_3Li$ | 118.1 | | |

[a] $\phi$ = dihedral angle. [b] The C–Li distance in LiCCH is 1.836 Å (ref 3). [c] 4-31G optimized values in parentheses. [d] $OC_3$ is the bisector of $\angle HC_3H$. [e] Bond lengths in ångstroms and bond angles in degrees.

on optimization. Earlier CNDO/2 calculations gave similar conclusions regarding the favored structure of allenyllithium.[19] **11** is less stable than **1** by 11.7 kcal/mol at STO-3G and 12.7 kcal/mol at 4-31G/5-21G (Table I). Even though rearrangement is observed during derivatization reactions in solution,[7f] relaxation of the $C_s$ symmetry constraint did not reveal any low-energy pathway for rearrangement of **11** to the thermodynamically more stable isomer **1**; both are energy minima.

The stability of propyne over cyclopropene (30.0 kcal/mol

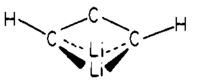
**Table III.** STO-3G Optimized Geometries of $C_3H_2Li_2$ Isomers[a,b]

| molecule | parameter | value | parameter | value |
|---|---|---|---|---|
| **4** $C_{2v}$ | $C_1C_2$ | 1.343 | $C_2C_3$ | 1.518 |
| | $C_1Li$ | 1.850 | $C_3H$ | 1.086 |
| | $\angle C_1C_3C_2$ | 52.5 | $\angle LiC_1C_3$ | 150.1 |
| | $\angle HC_3C_1$ | 120.2 | $\angle HC_3H$ | 111.8 |
| **4a** $C_{2v}$ | $C_1C_2$ | 1.378 | $C_1C_3$ | 1.518 |
| | $C_3H$ | 1.081 | $C_1Li$ | 1.941 |
| | $C_3Li$ | 2.922 | $\angle C_1C_3C_2$ | 54.0 |
| | $\angle HC_3H$ | 112.0 | | |
| **6** $C_{2v}$ | $C_1C_2$ | 1.289 | $C_2C_3$ | 1.496 |
| | $C_1H$ | 1.077 | $C_3Li$ | 2.092 |
| | $\angle C_1C_3C_2$ | 51.0 | LiLi | 2.441 |
| | $\angle LiC_3C_1$ | 124.5 | $\angle HC_1C_3$ | 145.9 |
| **7** $C_{2v}$ | $C_1C_2$ | 1.325 | $C_2C_3$ | 1.424 |
| | $C_1H$ | 1.081 | $C_3Li$ | 2.584 |
| | $\angle C_1C_3C_2$ | 55.4 | LiLi | 3.258 |
| | $\angle HC_1C_3$ | 148.8 | $\angle LiC_3C_1$ | 124.0 |
| **16** $C_{2v}$ | $C_1C_2$ | 1.325 | $C_1H$ | 1.075 |
| | $C_2Li$ | 1.889 | $\angle C_1C_2C_3$ | 142.9 |
| | $\angle HC_1C_2$ | 129.7 | $\angle LiC_2Li$ | 91.5 |
| **17** $C_s$ | $C_1C_2$ | 1.260 | $C_2C_3$ | 1.443 |
| | $C_1Li_1$ | 1.820 | $C_3H$ | 1.082 |
| | $C_1Li_2$ | 2.070 | $C_2Li_2$ | 1.888 |
| | $C_3Li_2$ | 2.024 | $C_2Li_1$ | 2.269 |
| | $\angle Li_1C_1C_2$ | 93.1 | $\angle C_1C_2C_3$ | 153.0 |
| | $\phi HC_3C_2C_1$ | 116.1 | $\angle HC_3C_2$ | 113.7 |
| **18** $C_{2v}$ | $C_1C_2$ | 1.286 | $C_2C_3$ | 1.372 |
| | $C_1Li$ | 1.925 | $C_2Li$ | 1.834 |
| | $C_3H$ | 1.080 | $\angle HC_3C_2$ | 121.6 |
| **19** $C_2$ | $C_1C_2$ | 1.333 | $C_1Li$ | 1.839 |
| | $C_1H$ | 1.086 | $\angle C_1C_2C_3$ | 158.6 |
| | $\angle HC_1C_2$ | 119.7 | $\angle LiC_1C_2$ | 73.0 |
| | $\phi HC_1C_2C_3$ | 140.2 | $\phi LiC_1C_2C_3$ | 50.1 |
| **20** $C_{2v}$ | $C_1C_2$ | 1.297 | $C_2C_3$ | 1.315 |
| | $C_1Li$ | 1.770 | $C_3H$ | 1.076 |
| | $\angle LiC_1C_2$ | 120.8 | $\angle HC_3C_2$ | 121.4 |

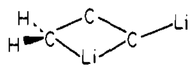
[a] $\phi$ = dihedral angle. [b] Bond lengths in angstroms and bond angles in degrees.

at STO-3G)[18] is also reflected in the monolithium derivatives. **1** is 40.5 kcal/mol more stable than **3** and 71.5 kcal/mol more stable than **5** (Table I). Vinylic hydrogens of cyclopropene are more acidic than the methylene hydrogens;[11b] correspondingly, 1-lithiocyclopropene is more stable than 3-lithiocyclopropene.

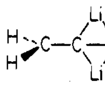
**$C_3H_2Li_2$.** A previous theoretical study of $C_3H_2Li_2$ isomers using the CNDO/2 semiempirical method and partial geometry optimizations considered a limited number of structures.[20] The present results are significantly different. Initially, the conventional structures, **4**, **6**,[5h] **12**, **13**, **14**, and **15**, in standard geometry were examined. As expected, the acetylide structure (**12**) was the best at this level. The less stable **13** was not optimized further. A $C_{2v}$ structure (**16**) with centrally bridged lithiums, indicated to be the most stable by a previous CNDO/2 calculation,[20] was also included in the initial set of structures to be optimized. Upon optimization of **12**, the propargylic lithium moves to a bridging position. The resulting structure, **17**, is the most stable of all $C_3H_2Li_2$ isomers we have been able to find. Similarly, the two lithiums of **14** bridge on optimization within $C_{2v}$ symmetry to give **18**. **18** is not a local minimum, however. When the symmetry constraint is relaxed to $C_s$, further optimization gives **17**, the most stable isomer. While the previous semiempirical study found **16** to be more stable than any other isomers considered, we find **16** to be less stable than **17** by 26.7 kcal/mol at STO-3G (25.9 kcal/mol at 4-31G/5-21G) (Table III). **16** is not a local minimum at the STO-3G level; reduction of the symmetry to $C_2$ and optimization lead to the doubly bridged structure **19**, only 12.6 (STO-3G) or 12.9 kcal/mol (4-31G/5-21G) less stable than **17**. No pathway is apparent for the interconversion of **17** and **19**. Thus, the structure of 1,3-dilithioallene (**19**) can be considered to be intermediate between the centrally bridged **16** and the localized allene **15**. Depending on the substituents and on the conditions, the actual structure might be shifted toward



16, $C_{2v}$

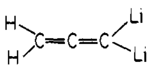


17, $C_s$

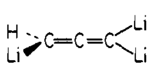


18, $C_{2v}$

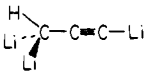
19, $C_2$



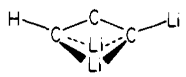
20, $C_{2v}$



21, $C_s$



22, $C_s$



23, $C_s$

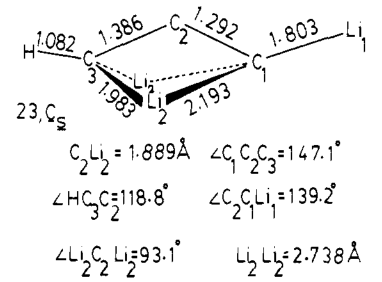


**Figure 1.** Structure of $C_3HLi_3$ at STO-3G level (distances in angstroms, angles in degrees).

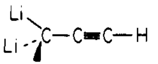
either extreme. Such changes have been inferred from spectroscopic studies.[8]

Another point interested us. The planar 1,1-dilithioallene (**20**) was just as stable as the perpendicular form **14** at standard geometries! However, the improvement in energy upon optimization within the constraints of $C_{2v}$ symmetry was much less for **20** than for **14**, since the latter gave doubly bridged **18**.

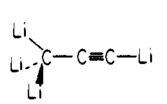
1,2-Dilithiocyclopropene (**4**) is less stable than **17** by 51.3 kcal/mol (STO-3G). 3,3-Dilithiocyclopropene, in perpendicular (**6**) and the more favorable planar (**7**) geometries (STO-3G), was, as expected, much higher in energy.[5h] Optimization of the planar 3,3-dilithiocyclopropene (**7**) leads to a structure with considerable bonding between the two lithiums which is best regarded as a weak complex between singlet cyclopropylidene and $Li_2$ (see Discussion). At 4-31G/5-21G the relative stabilities of **6** and **7** are reversed; **6** is more stable than **7**. Optimization at 4-31G and the use of more flexible bases are expected to decrease the energy of **7** more than that of **6**, but such studies were not performed. The cyclic structure of $C_2Li_2$[5a] suggests an analogous double-bridged structure **4a** for 1,2-dilithiocyclopropene. At STO-3G//STO-3G, **4a** is more stable than **4** by 9.7 kcal/mol.

**$C_3HLi_3$.** Taking hints from the most stable acyclic structures of $C_3H_3Li$, $C_3H_2Li_2$, and $C_3Li_4$,[5c] we expect conventional structures like **21** and **22** to be less stable than geometries like **23** or **24**. $Li_3CC{\equiv}CH$ (**25**) is also expected to be less stable because it lacks the favorable acetylide structure. **23** and **24** were optimized as the most likely candidates, but **24** merged into **23** (Figure 1) during energy minimization. Standard geometry calculations (STO-3G) indicate **21**, **22**, and **25** to be less stable than the optimized structure **23** by 48.2, 43.1, and 50.1 kcal/mol, respectively. Cyclic structures were not considered, as no basically new features were expected.

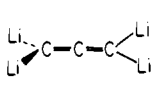
24, $C_1$



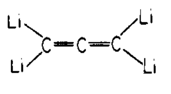
25, $C_{3v}$



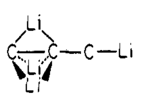
26, $C_{3v}$



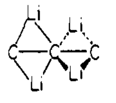
27, $D_{2d}$



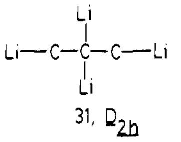
28, $D_{2h}$



29, $C_{3v}$

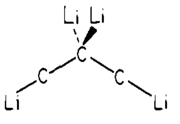


30, $D_{2d}$



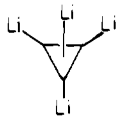
31, $D_{2h}$

**$C_3Li_4$.** Tetralithiopropyne, a readily available lithiocarbon,[7] was the subject of a preliminary report.[5c] The conventional structures, **26** and **27**, and the planar allene, **28**, were considered first. **26** collapsed to a triply bridged structure, **29**. **28** ($D_{2h}$) is more stable than **27** by 0.5 kcal/mol at 4-31G/5-21G. Even though **27** was a minimum within $D_{2d}$ symmetry, a tetrabridged structure **30** was found to be more stable at the STO-3G level. At 4-31G/5-21G, however, **30** turned out to be the least stable of all these isomers. In this study of 20 molecules **30** is one of only two cases for which the STO-3G relative energies deviate qualitatively from those at the 4-31G/5-21G level. A planar $D_{2h}$ structure, **31**, proved not to be a local minimum. Distortion of **31** to $C_{2v}$ symmetry by decreasing the $LiC_2Li$ angle destabilizes the system if the atoms around C-2 are moved in opposite directions toward a *tetrahedral* arrangement to give **32**. Such distortion ultimately would lead to tetralithiocyclopropene (**33**). Standard geometry calculations (Table I) on **32**, **33**, **34**, and **35** showed them not to be competitive energetically and hence were not considered further. Distortion of **31** to $C_{2v}$ symmetry by bridging the CCC unit leads to the most stable $C_3Li_4$ structure obtained (**36**).

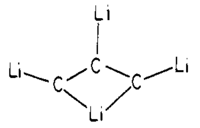


32, $C_{2v}$

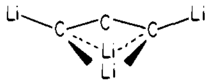
33, $C_{2v}$



34, $C_{3v}$



35, $C_{2v}$



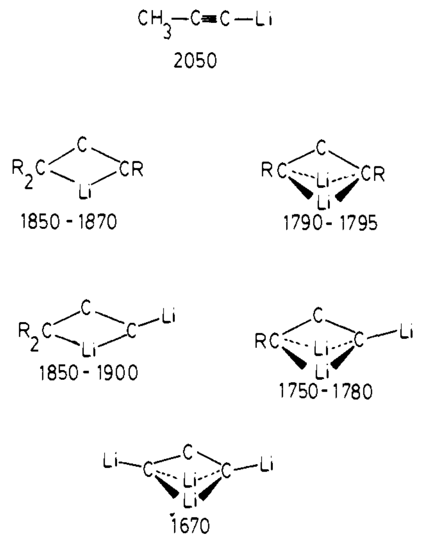
36, $C_{2v}$

Further reduction of symmetry of a $C_2$ geometry similar to **19** resulted in destabilization.

## Discussion

Two basically different bonding arrangements exist in lithiopropynes (or lithioallenes) as exemplified by the monolithium derivatives, **1** and **11**. **1**, with conventional acetylide bonding, is 12 kcal/mol more stable than **11**, where the lithium bridges the CCC unit. Indeed, in solution monolithiation of propyne gives 1-lithiopropyne (**1**).[7,8] Experimentally, allenyllithium (**11**) is found to give both 3-propenyl and allenyl products.[7g] The structure of **11** (Table II) explains such results. As in allyllithium (**8**),[5d] the Li lies nearest to $C_2$ but its bonding overlap with that atom is nearly zero (−0.02, STO-3G). Bonding overlap, greater to $C_1$ (0.48) than to $C_3$ (0.24), is facilitated by the bent framework (∠CCC = 157.6°). Significant bending is found in all other structures involving bridging lithiums (Table II).

Scheme I.[7c] IR Frequencies (cm$^{-1}$)



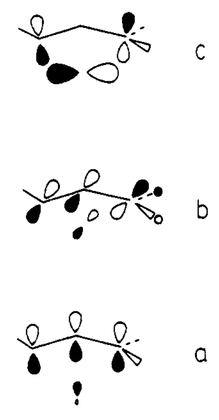


**Figure 2.** Representations of the three highest occupied molecular orbitals of $C_3H_3Li$ (**11**).

**Figure 3.** Highest occupied molecular orbital of (a) "planar" 3,3-dilithiocyclopropene (**7**); (b) "tetrahedral" 3,3-dilithiocyclopropene (**6**).

The three highest occupied MOs of **11** shown in Figure 2 account for the bonding satisfactorily. The carbon p orbitals lying in the carbon plane (Figures 2a,c) are similar to those in allyllithium (**8**) with the exception that in **8** the $\pi$ orbitals lie perpendicular to the plane formed by the three carbon atoms.[5d] The ethylenic $\pi$ bond in **11**, perpendicular to the carbon plane, interacts in bonding and antibonding combinations with the $\pi$-type orbitals of the $CH_2$ group. Figure 2b represents the antibonding combination. The interaction between lithium and the terminal carbons $C_1$ and $C_3$ is bonding in both MOs of Figures 2a and 2c. However, in the MO represented in Figure 2b lithium is bonding with respect to the acetylenic carbon $C_1$, but antibonding with the propargylic carbon $C_3$. Correspondingly, in the optimized structure of **11**, lithium is nearer to $C_1$ than to $C_3$; bonding to $C_1$ is also greater. Substituents may alter the degree of bonding between lithium and $C_1$ or $C_3$. If this is increased strongly at both positions separate isomers corresponding to propargylic and allenic structures may be possible (i.e., two energy minima). The infrared spectrum of monolithio-1,3-bis(trimethylsilyl)-3-phenylpropyne, for example, has been interpreted to indicate a mixture of such propargylic and allenic isomers.[21]

The preferences for these two types of bonding (acetylide and bridging) can explain the relative stabilities of the polylithio derivatives. The rules are simple: Li prefers an acetylide position if one is available; the next best alternative (some 12 kcal/mol less favorable in energy) involves bridging a CCC unit. Only one acetylide bond is possible in $C_3H_2Li_2$. An arrangement with two terminal lithiums would necessitate that the two remaining hydrogens be attached to the central carbon atom. A dicarbene, $LiCCH_2CLi$, which can be considered to be a ring-opened form of 1,2-dilithiocyclopropene (**4**), would result. Instead, replacement of a hydrogen in **1** by lithium should give **17**. In fact, lithiation of either **1** or **11** is found experimentally to produce the same dilithio derivative[7g] for which structure **17** is likely. Both **12** and **14** collapse to **17** on optimization. The similarity between structures **11** and **17** is striking.

Allene or propyne also give the same thermodynamically more stable dilithio derivative **17** upon dilithiation.[7g] The energetically next best isomer **19** is obtained only when the formation of a Li-acetylide bond is precluded by 1,3 disubstitution.[7f] The activation energy for interconversion of **17** and **19** may be sufficiently high so that derivatives of either **17** or **19** can be observed in solution. However, reactions of **17** or **19** often give both allenic and propargylic products. Substituents may determine the degree to which a dilithioallene resembles **15**, **16**, or **19**. Solvation is also known to influence the preferred structure in such cases.[8]

Replacement of one more hydrogen in **17** by lithium should lead to a trilithio derivative with two bridging lithiums and one acetylide lithium. We find the bridging lithiums to be symmetrically placed above and below the CCC plane (**23**) in $\pi$ planes about 90° apart. Lithiation of **19** also should give the same trilithio derivative **23**. It is still meaningful to designate the terminal C-Li bond in **23** "acetylide" despite the bending of both CCC and CCLi angles (Figure 1). The most stable $C_3Li_4$ structure (**36**) is now easy to understand. Replacement of the hydrogen in **23** by lithium gives **36** with two acetylide-type C-Li bonds and two bridging lithiums. Both propyne and allene give the same tetralithio derivative experimentally.[7]

West has tabulated the IR absorption bands in the 1600–2000-cm$^{-1}$ region for various lithiated propynes and allenes.[7c] The propargylide "dianion" ($\simeq$**17**) and allenic "monoanion" ($\simeq$**11**) absorb in the same frequency range. Trilithiopropargylides ($\simeq$**23**) and dilithiated allenes ($\simeq$**19**, **16**) also have similar IR frequencies. This may not be coincidence. Structural similarities of **17** and **11** as well as **23** and **16** may also be responsible for such absorption frequencies. Compounds with the same number of bridging lithiums seem to absorb around the same frequency (Scheme I).

Among the cyclopropenes only mono- and dilithio derivatives were considered in detail. Tetralithiocyclopropene (**33**) was found to lie very high energetically (Table I). In accordance with experimental observations,[11b] lithium prefers vinylic to methylenic positions. The electronic structure of 3,3-dilithiocyclopropene is of particular interest. The Li-Li distance in the planar structure (**7**) is 2.44 Å, shorter than that in the $Li_2$ molecule (2.68 Å at STO-3G);[22] the C-Li distance of 2.58 Å (2.01 Å in $CH_3Li$ at STO-3G level) is rather long.[22] The HOMO of **7** is represented by Figure 3a, indicating the delocalization of the Li-Li bond to the ring. At the same time the "$\pi$" electrons are no longer localized on $C_1$–$C_2$. In contrast, the HOMO of **6**, the *tetrahedral isomer*, consists of the antibonding combination of the $C_1$–$C_2$ $\pi$ bond and the $\pi$-type $CLi_2$ orbitals so that $C_1$–$C_3$ and $C_2$–$C_3$ become antibonding (Figure 3b). Synthesis of unsubstituted 3,3-dilithio derivatives will certainly be difficult, as the thermodynamically more stable 1,2 isomer (**4**) will be obtained preferentially. Furthermore, at the STO-3G level, **7** is indicated to be stable toward disso-

**Table IV.** Isodesmic Reaction Energies Relative to Methyllithium Using Energies Given in Tables I and V

| no. | reaction | $\Delta H$, kcal/mol STO-3G opt | $\Delta H$, kcal/mol 4-31G//STO-3G |
|---|---|---|---|
| 1 | $CH_3CH{=}CH_2 + CH_3Li \rightarrow C_3H_5Li$ (**8**) $+ CH_4$ | −33.9 | −23.3 |
| 2 | $CH_3CH_3 + CH_3Li \rightarrow CH_3CH_2Li + CH_4$ | 3.1 | 5.0 |
| 3 | $H_2C{=}CH_2 + CH_3Li \rightarrow LiCH{=}CH_2 + CH_4$ | −19.2 | 0.8 |
| 4 | $HC{\equiv}CH + CH_3Li \rightarrow LiC{\equiv}CH + CH_4$ | −40.3 | −32.9 |
| 5 | $CH_3C{\equiv}CH + CH_3Li \rightarrow C_3H_3Li$ (**1**) $+ CH_4$ | −39.4 | −30.8 |
| 6 | $CH_2{=}C{=}CH_2 + CH_3Li \rightarrow C_3H_3Li$ (**11**) $+ CH_4$ | −44.6 | −18.9 |
| 7 | $CH_3C{\equiv}CLi$ (**1**) $+ CH_3Li \rightarrow C_3H_2Li_2$ (**17**) $+ CH_4$ | −33.2 | −8.0 |
| 8 | $C_3H_3Li$ (**11**) $+ CH_3Li \rightarrow C_3H_2Li_2$ (**17**) $+ CH_4$ | −44.9 | −20.9 |
| 9 | $C_3H_2Li_2$ (**17**) $+ CH_3Li \rightarrow C_3HLi_3$ (**23**) $+ CH_4$ | −27.2 | −7.5 |
| 10 | $C_3HLi_3$ (**23**) $+ CH_3Li \rightarrow C_3Li_4$ (**36**) $+ CH_4$ | −34.3 | −17.1 |
| 11 | cyclopropene $+ CH_3Li \rightarrow C_3H_3Li$ (**3**) $+ CH_4$ | −28.9 | −20.7 |
| 12 | cyclopropene $+ CH_3Li \rightarrow C_3H_3Li$ (**5**) $+ CH_4$ | 2.1 | 6.3 |
| 13 | $C_3H_3Li$ (**3**) $+ CH_3Li \rightarrow C_3H_2Li_2$ (**4**) $+ CH_4$ | −22.5 | −8.3 |
| 14 | $C_3H_3Li$ (**5**) $+ CH_3Li \rightarrow C_3H_2Li_2$ (**6**) $+ CH_4$ | −6.4 | 12.2 |
| 15 | cyclopropane $+ CH_3Li \rightarrow$ cyclopropyllithium $+ CH_4$ | −2.3 | 2.8 |

**Table V.** Total Energies for Reference Molecules

| molecule | point group | energy using STO-3G optimized geometry STO-3G | energy using STO-3G optimized geometry 4-31G/5-21G |
|---|---|---|---|
| $CH_4{}^a$ | $T_d$ | −39.726 86 | −40.139 76 |
| $CH_3Li^b$ | $C_{3v}$ | −46.421 59 | −46.959 62 |
| $C_2H_6{}^a$ | $D_{3d}$ | −78.306 18 | −79.115 82 |
| $C_2H_5Li^c$ | $C_s$ | −84.996 05 | −85.927 65 |
| $C_2H_2{}^a$ | $D_{\infty h}$ | −75.856 25 | −76.709 99 |
| $C_2H_4{}^a$ | $D_{2h}$ | −77.073 96 | −77.921 88 |
| $C_2HLi$ | $C_{\infty v}$ | −82.615 14$^d$ | −83.582 33 |
| $C_2H_3Li$ | $C_s$ | −83.799 30 | −84.740 44 |
| $C_3H_6{}^c$ | $C_s$ | −115.660 30 | −116.904 59 |
| propyne$^e$ | $C_{3v}$ | −114.448 98 | −115.699 69 |
| allene$^e$ | $D_{2d}$ | −114.421 72 | −115.698 36 |
| cyclopropene$^e$ | $C_{2v}$ | −114.401 16 | −115.641 68 |

[a] W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974). [b] J. D. Dill, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Am. Chem. Soc.*, **99**, 6159 (1977). [c] Reference 5d. [d] Reference 17. [e] L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 5339 (1971).

ciation into cyclopropenylidene (singlet) and $Li_2$ by only 1.4 kcal/mol.[23]

Isodesmic reactions[24] are useful to indicate the stabilities of the organolithium compounds, relative to a standard of reference, e.g., monomeric $CH_3Li$ (Table IV). In order to provide calibration, the relative stabilities of allyllithium, ethyllithium, vinyllithium, and ethynyllithium are also compared. Since the STO-3G basis tends to overemphasize the involvement of p orbitals on lithium, the less exothermic 4-31G/5-21G energies will form the basis for discussion. Reaction 1 is exothermic by 23.3 kcal/mol in accordance with the delocalized nature of allyllithium.[5d] Ethyllithium is less stable relative to methyllithium (reaction 2) by a small magnitude.[21] The acidity of an $sp^2$ C–H bond is believed to be larger than that of an $sp^3$ C–H bond,[6,25] but reaction 3 is slightly endothermic. The value, 0.8 kcal/mol, is less than that of reaction 2, indicating that vinyllithium is more stable than ethyllithium. Lithium acetylide is more stable than $CH_3Li$ by 32.9 kcal/mol, a larger value than for allyllithium. A methyl substituent does not change the energies appreciably; $CH_3CCLi$ is almost as stable as HCCLi relative to $CH_3Li$ (reaction 5). The stability sequence, $C_2H_5Li < C_2H_3Li < C_2HLi$, has also been obtained by Streitwieser's group.[6]

Although in both cases replacement of $C(sp^2)$ hydrogens is formally involved, the nature of allenyllithium is quite different from that of vinyllithium. The greater stability of allenyllithium (reaction 6 is exothermic by 18.9 kcal/mol) can be explained by the bonding advantages of bridged structure **11**. In this respect allenyllithium is more similar to allyllithium than to vinyllithium. Each additional lithiation is thermodynamically favorable but by different amounts, depending on whether a bridging lithium (reactions 7 and 9) or an acetylide lithium (reactions 8 and 10) is being introduced. The exothermicity of these reactions explains the easy formation of $C_3Li_4$. Starting from propyne, reactions 5, 7, 9, and 10 lead to $C_3Li_4$. When allene is the starting material, reactions 6 and 8 begin the process leading to the same $C_3Li_4$.

**Ionic or Covalent Bonding.** The bonding in organolithium compounds is regarded differently. Streitwieser has argued that the C–Li bond is largely ionic,[6] while we have stressed the multicenter covalent nature of lithium bonding, particularly in the polylithio compounds, which our calculations reveal to have such peculiar structures.[5]

While adhering to our viewpoint, we wish to point out that an ionic model may be used to rationalize the structures described in this paper. In this model, the $Li^+$ cations associate themselves electrostatically with the carbon center or centers of highest negative charge. In an ethynyllithium, $RC{\equiv}C^-Li^+$, the negative charge is localized in the sp orbital and the $Li^+$ is aligned along the CC bond. The two $Li^+$ ions in $C_2Li_2$ either may both line up with the CC bond or may bridge the CC bond, on opposite sides, between the two negatively charged ends. Previous calculations indicate that $C_2Li_2$ prefers a doubly bridged cyclic structure $CLi_2C$ but the energy difference is not large.[5a] On this basis, we considered a doubly bridged structure **4a** for 1,2-dilithiocyclopropene. In fact, **4a** is calculated to be 9.7 kcal/mol more stable than the classical structure **4** at the STO-3G level.

Allyllithium, according to this model, has the negative charge of the allyl anion delocalized to $C_1$ and $C_3$; the $Li^+$ lies above the carbon plane, as close as possible to the two negative end carbons. The allenyl anion is similarly delocalized; the $Li^+$ in allenyllithium is expected to occupy a bridging position similarly. West has represented 1,3-dilithioallene as $[HCCCH]^{2-}2Li^+$.[7c] The two $Li^+$ ions would be bridging the CCC unit, so that $Li^+$–end carbon distances will be identical. Similarly a doubly bridged structure is also applicable for $C_3Li_4$. Thus the general features of these compounds can be arrived at using an ionic model. However, structures different from that of the parent hydrocarbons do not indicate absence of covalent character. All of these structures can be explained by invoking the overlap between orbitals of the alkyl group and those of the lithium atoms. We prefer to look at these compounds as having multicenter covalent bonding with partial ionic (polar) character. The bridging structures of allyllithium and allenyllithium involve overlap between the p orbitals of

Table VI. Higher Level Calculations on $C_3H_3Li$ Species[a]

| molecule | 4-31G | 4-31G geometries[b] | |
|---|---|---|---|
| | | MP2/4-31G[c] | 6-31G*[d] |
| **1** | −122.571 05 (0.0) | −122.850 55 (0.0) | −122.735 16 (0.0) |
| **11** | −122.553 21 (11.2) | −122.832 58 (11.3) | −122.721 49 (8.6) |
| **3** | −122.496 30 (46.9) | −122.777 57 (45.8) | −122.677 61 (36.1) |

[a] Energies in hartrees; relative energies (in parentheses) in kcal/mol. [b] See Table II. [c] J. S. Binkley and J. A. Pople, *Int. J. Quantum Chem., Symp.*, **9**, 229 (1975); J. A. Pople, J. S. Binkley, and R. Seeger, *ibid.*, **10**, 1 (1976). [d] P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973).

lithium and the nonbonding $\pi$ orbitals with which the bridging lithiums can interact as in allyllithium explaining these arrangements. Ionic bonding in methyllithium implies the interaction of $CH_3^-$ with $Li^+$. As the number of lithium atoms in a molecule increases the extent of ionic character should decrease. A totally ionic structure for $CLi_4$ would require $C^{4-}$ surrounded by four lithium cations. Such a high buildup of negative charge on carbon is unlikely. Back-donation to the lithiums would occur; $CLi_4$ may be more covalent than methyllithium. On the same basis $C_3Li_4$ would be more covalent than other polylithioallenes and propynes. Experimental observations seem to support this idea. At least under some conditions, $C_3Li_4$ appears to be soluble even in *n*-hexane.[7c,26]

The greater stabilities of 1-lithio- and 1,2-dilithiocyclopropenes over 3-lithio derivatives are indicated by isodesmic reactions 11–14. While formation of 1-lithiocyclopropene is 20.7 kcal/mol exothermic, formation of 3-lithiocyclopropene is 6.3 kcal/mol endothermic. The antiaromatic (4$\pi$ electrons) character of the cyclopropenyl anion is chiefly responsible for the high energy of 3-lithiocyclopropene (**5**). The greater acidity of strained vinylic hydrogens, in accordance with experimental observations, is shown by the greater exothermicity of reaction 11 over reaction 3. Ethylene cannot be lithiated by direct exchange but lithiation of cyclopropene, e.g., with phenyllithium, is easily achieved.[9,10] The doubly bridged structure **4a** for 1,2-dilithiocyclopropene is more stable than **4** by 9.7 kcal/mol. 1,2-Dilithiocyclopropene is known experimentally in solution,[9,10] but not its structure. Our calculations refer to isolated molecules in the gas phase and may not correspond to structures in solution. However, in view of the unusual structures of alkyllithiums known[3,4] these compounds invite experimental structural studies.

## Conclusions

Lithio derivatives of $C_3H_4$ isomers are studied using ab initio molecular orbital theory. Experimentally sequential replacement of all four hydrogens in allene or propyne can be achieved using lithiating agents. Two basically different types of bonding are available for lithium in these open-chain $C_3$ compounds. The more stable is the familiar acetylide type, with one lithium attached to one of the two end carbons. In the second, Li bridges C-1 and C-3 as in allyllithium. Since there are two end carbons two acetylide-type bonds are possible, provided that there are no substituents. The most stable arrangement of $C_3Li_4$ thus becomes **36** with two acetylide and two bridging lithiums. Only mono- and dilithio derivatives of cyclopropene were considered. Substitution of the vinylic hydrogens is energetically favorable compared to that of methylenic hydrogens. Isodesmic reactions indicate that polylithiation is exothermic for each step so that, starting from propyne or allene, tetralithio derivatives are produced easily.

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## Addendum

A referee questioned the reliability of the STO-3G minimal basis geometries for molecules of such unusual structure. Consequently, we have reoptimized the structures of the $C_3H_3Li$ isomers, **1**, **3**, and **11**, at the 4-31G/5-21G level. The results, included in Table II, show little change in geometries, especially in consideration of the rather flat energy surfaces involved. The relative energies of the three isomers (compare Table I with Table VI) change 1.5 kcal or less on optimization at the higher level. Hence, there is no indication that 4-31G reoptimization of the $C_3H_2Li_2$ and higher structures would reveal changes sufficiently large to justify the large expenditure of computer time required.

Instead, we examined the three $C_3H_3Li$ isomers at higher theoretical levels (Table VI). Electron correlation (MP2/4-31G results) was found to have a very minor effect on the relative energies. As expected, inclusion of d-type polarization functions (6-31G* results) reduced the relative energy of the three-membered ring derivative, **3**, significantly; however, the stability order was unaffected.

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# Accurate Binding Energies of Diborane, Borane Carbonyl, and Borazane Determined by Many-Body Perturbation Theory

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**Abstract:** Binding energies including valence-shell electron correlation are obtained from many-body perturbation theory (MBPT) for diborane, borane carbonyl, and borazane. Results are given for basis sets of double $\zeta$ quality and for basis sets with polarization functions added on all atoms. The binding energies ($-\Delta E$) are found to be (respectively) 35, 21, and 30 kcal/mol. Correlation effects account for 48, 62, and 32% of the binding. The size-consistent nature of the MBPT method enables the computation of enthalpies of reaction for four different reactions involving monoborane, diborane, carbon monoxide, and borane carbonyl. When the theoretical values are corrected for vibrational zero-point energies and the experimental data are adjusted for temperature effects, the results agree (within 5%) and thus confirm the set of experimental enthalpies corresponding to $\Delta H$ (300 °C) = $-34$ kcal/mol for the association reaction yielding diborane. The result for the binding energy of borazane constitutes a prediction in the absence of an experimental value.

## I. Introduction

Binding energies of molecules having weak dative bonds have been difficult to ascertain, either experimentally or theoretically. Experimentally, there have been several problems, particularly for complexes of monoborane. First, $BH_3$ has a very short lifetime (owing to its reactivity) which does not permit direct determination of its energy. Of more significance, proper interpretation of experimental data (from electron impact of products of pyrolysis or kinetic studies) requires the knowledge of reaction mechanisms.[1] Complications arise from multiple rates resulting from surface and gas-phase reactions.[2,3] Additionally, mass spectrographic analysis of products (used in conjunction with appearance potentials) does not necessarily lead to infallible conclusions regarding energy disposal.

Historically, there has been either a lack of experimental evidence (in the case of borazane) or the presence of conflicting results (for diborane). Furthermore, the possibility of error propagation is present because of the common use of energetic relationships between molecules. For example, the dissociation (binding) energies of $B_2H_6$ and $H_3BCO$ are related (as we shall see in the Discussion) by the equation[4]

$$D(B_2H_6) - 2D(H_3BCO) = 9.1 \text{ kcal/mol} \tag{1}$$

Unfortunately, internal checks of consistency do not preclude the presence of errors and may succeed only in deferring their detection.

Theoretical difficulties arise primarily because correlation effects[5] account for a significant and sometimes dominant part of the binding energy. By coincidence, in some cases, the early self-consistent field (SCF) calculations obtained reasonable values owing to cancellation of the errors resulting from the use of inadequate basis sets and from the neglect of correlation. However, this was not consistently the case, and typically systematic improvement of basis sets destroyed the fortuitous SCF agreement. Thus, as improved methods are available,[6-11] theoretical (re)examinations of reactions of molecules of this type are in order. In this regard, there have been discourses concerning the proper treatment of the correlation problem.[6-18] The many-body perturbation theory (MBPT) methods[6,7] which we shall employ will also have distinct computational advantages, as discussed in sections II and IV.

## II. Methodology

Sophisticated ab initio quantum mechanical methods based on many-body perturbation theory (MBPT) are now available for the calculation of correlated energies for closed-shell (or UHF open-shell) ground-state systems. The calculation of the total correlated energy

$$E_{\text{total}} = E_{\text{SCF}} + E_{\text{corr}} = E_0 + \Delta E \tag{2}$$

(where $E_0 = \Sigma_i^{\text{occ}}\epsilon_i$ and $E_{\text{SCF}} = E_0 + E_1$) is based on the linked diagram expansion[18]

$$\Delta E = \sum_{n=0}^{\infty} \langle \Phi_0 | V[(E_0 - H_0)^{-1} V]^n | \Phi_0 \rangle_{\text{L}} \tag{3}$$

where L indicates the limitation to linked diagrams. $\Phi_0$ is the SCF reference function and $\{\epsilon_i\}$ are the (Hartree–Fock) orbital energies. $V$ comes from the Moeller–Plesset separation of the Hamiltonian[19]

$$H = H_0 + V \tag{4}$$

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