

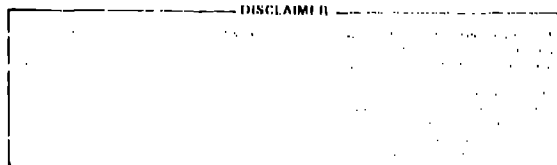
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TITLE: MOLECULAR-ORBITAL CALCULATIONS FOR POLYNITROPOLYHEDRANES

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MASTER

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MOLECULAR-ORBITAL CALCULATIONS FOR POLYNITROPOLYHEDRANES

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From the beginning, theoretical calculations have resulted in a better understanding of polynitropolyhedranes. I participated in research involving the polynitropolyhedranes first at the University of Texas, with Michael Dewar and Jack Alster, where we investigated the effects of nitro substitution on polyhedranes using largely MINDO/3, then at Los Alamos National Laboratory where I am currently evaluating various synthetic pathways to polyhedranes using theoretical calculations. The following slides summarize the effort to date.

As the first slide indicates, replacement of a C-H bond with a C-NO₂ bond in the cases shown has less than a 10-kcal effect on the heat of formation of a hydrocarbon. Somewhat surprisingly, however, sequential replacement of C-H bonds with C-NO₂ bonds in pentacyclo[4.2.0.0.^{2,5}0.3,⁸0^{4,7}]octane (cubane) results in a rather large lowering of the heat of formation, as the second slide illustrates. This implies that the nitro substitution in cubanes may be strengthening bonds within the cubane framework.

The third and fourth slides summarize some calculated C-H and C-NO₂ bond strengths in the nitro substituted cubanes. Although the results indicate that successive nitration results in a weakening of C-H and C-NO₂ bonds, the weakening amounts to only 8 kcal in the tetranitrocubane. As a result, we expect tetranitrocubanes to be stable to the homolytic cleavage of C-H and C-NO₂ bonds.

The next slide demonstrates that nitro substitution usually weakens the adjacent C-C bond by stabilizing radical fragments. In contrast, as slide 6 demonstrates, MINDO/3 predicts that nitro substitution may actually increase the strength of the adjacent C-C bonds within the cubane framework. This is shown by the increase of the activation enthalpy for the illustrated cubanes.

From these results, we conclude that nitro substitution does not weaken bonds within the cubane framework and that polynitropolyhedranes ought to be as stable as the parent polyhedrane. Consequently, polynitrocubanes should be stable enough to be synthesized and tested as explosives.

Slide 8 summarizes the results of calculations that indicate that tetranitrotetrahedrane may also be an explosive of exceptional performance (if it can be made). The next two slides demonstrate behavior of tetrahedranes upon nitration which is analogous with that of the cubanes. This indicates that polynitrotetrahedranes may be no less stable than tetrahedrane. Unfortunately, tetrahedrane itself is notoriously unstable. On the other hand, tetra-*t*-butyl-tetrahedrane is a stable compound. This suggests that tetranitrotetrahedranes possibly might be stable, isolable compounds too.

Slide 11 outlines a report, by Schleyer, of the synthesis of tetralithio-tetrahedrane. Although preliminary, this report suggests a possible synthetic pathway to the nitrotetrahedranes. It seems likely that, if tetralithiotetrahedrane does indeed exist, a simple nitration reaction may yield the desired compound. This is illustrated in slide 12.

Because of this, the effects of lithium substitution on strained rings were investigated using theoretical calculations. As a measure of ring strain, the group separation method was used, as illustrated on slide 13.

Slides 14 and 15 present the results of *ab initio* calculations, which suggest that the monolithiated polyhedrane and the conjugate base of the polyhedrane show a sizable relief of ring strain. The similarity between the

calculated ring strains of the lithiated polyhedrane and the conjugate base of a polyhedrane indicate that the carbon-lithium bond is highly ionic, as slide 16 states.

Slide 17 suggests that the incorporation of an unhybridized anionic carbon atom may account for the relief of ring strain observed in the conjugate bases of polyhedranes. This is because the unhybridized carbon entails less ring strain upon incorporation into a polyhedrane framework than does a hybridized carbon. The next slide documents an experimental report which suggested this concept without a theoretical background.

Our results have indicated that lithium substitution can lead to a relief of ring strain; however, this is a result of an ionic carbon-lithium bond which places a large negative charge on carbon. Because it seemed likely that charge-charge repulsions in polylithium compounds might lead to destabilization of a polylithiopolyhedrane, we investigated the C_4Li_4 potential energy surface in more detail than had been previously reported.

Slide 19 summarizes the calculated relative energies of five C_4Li_4 isomers. The planar tetralithiocyclobutadiene, 1, is predicted to be the global minimum whereas the face-lithiated tetrahedrane, 2, is predicted to be the lowest energy tetrahedrane.

Slides 20-22 summarize the results of vibrational frequency calculations for the tetralithiotetrahedranes. These results show 4 and 3 to be hilltops on the potential energy surface, as indicated by the two imaginary vibrational frequencies in each case. This suggests that these compounds are not isolable. Slide 21 shows that 3 has but one imaginary vibrational frequency, indicating it to be a transition state. Again, this means 2 is not a minimum on the potential energy surface.

Slides 23 and 24 summarize the results of vibrational frequency calculations for the tetralithiocyclobutadienes. In contrast with the results for the tetralithiotetrahedranes, both 1 and 5 are predicted to be minimum on the potential energy surface. As such, attempts to isolate these compounds may be carried out with some hope of success.

These results indicate that the synthesis of tetranitrotetrahedrane from tetralithiotetrahedrane is not a promising route. Alternatively, sequential base-promoted nitrations of cubanes seem a much more promising route for obtaining polynitrocubanes.

QUESTIONS AND ANSWERS

Question

How can you directly compare ΔH_f° of mononitrocubane and dinitrocubane directly since they have different formulas? I think that this must relate to the fact that (by coincidence) $\Delta H_f^\circ(\text{CH}_4) \cong \Delta H_f^\circ(\text{CH}_3\text{NO}_2)$. But in going from $\text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{NO}_2$ there is a difference in ΔH_f° of -18.0 kJ/mol and for



you use homodesmotic relationships to assess stability?

Arthur Greenberg

New Jersey Institute of Technology

Answer

To quantitatively assess ring strain, homodesmotic relationships would, indeed, be proper; however, I used the H_f 's directly as a qualitative guide. These qualitative results were then substantiated by the calculations in which bond strengths were calculated. Bond strengths give a true measure of the stability of a molecule to unimolecular decomposition. Homodesmotic relationships, on the other hand, give a number that is an aggregate of several effects

and, as such, are less useful for determining the stability of the substituted polyhedranes.

Incidentally, MINDO/3 calculations indicate a change of +8 kcal/mol for t-butane \rightarrow t-nitrobutane; this is presumably due to steric effects. In contrast, the ΔH_f of tetrahedrane \rightarrow nitrotetrahedrane is -30 kcal/mol.

Question:

(1) You used group separation reactions to discuss polyhedryl lithiums and anions. Shouldn't you also use this approach for the (poly) nitropolyhedranes?

(2) For the use of unhybridized carbon, isn't there trouble because of only using one lobe of the p orbital? However, consider acetylene and its anions--i.e., have $s^2 p^1 p^1 p^1$.

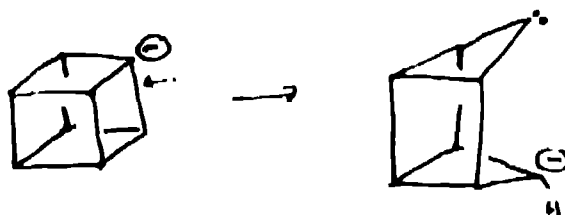
Joel F. Liebman

University of Maryland Baltimore County

Answer

(1) See response to Arthur Greenberg.

(2) This may be true, but appears not to cause a problem because of the differing angular dependencies of p and sp^3 orbitals (which are oriented at 90° and 109.5° , respectively). It is this differing angular dependency that makes the incorporation of the unhybridized anionic center appear likely. Furthermore, by using an unhybridized atom, one "saves" the $2s \rightarrow 2p$ excitation energy required for the atom to hybridize. A final point is that breaking the bond adjacent to the anionic center would result in a carbene on one side and an anion on the other (shown below). This, I would think, would be a rather highly endothermic reaction.



Question

Have you considered early 60's work on C_3Li_4 (West) and other work by Gelman (degradation of many chloro-aromatics and other compounds to Li_2C_2) and the related experimental problems?

Ron Husk

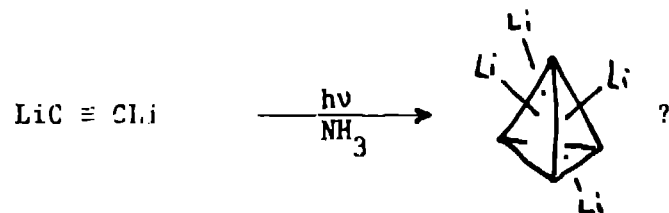
Army Research Office

Answer

Polylithium compounds seem to be plagued by problems. We expect, however, to be able to perform sequential anion formation to generate polyhedrane derivatives. Mono-anion formation is, of course, quite common.

Question

A recent paper by Lagow et al. indicates that Li_2C_2 is the most stable lithium carbide. Have you calculated the energetics of the photochemical reaction reported by Schleyer for the preparation of Li_4C_4 :



We have repeated the proposed Schleyer reaction many times and have been unable to trap the Li_4C_4 as a covalent R_4C_4 derivative.

R. Bruce King

University of Georgia

Answer

I have found that tetralithiotetrahedrane lies 74.0 kcal above two dilithioacetylenes (cyclic, most stable) at the split valence level. This is in contrast to split valence calculations, previously performed by others, which indicate that tetrahedrane lies only 50.6 kcal above two molecules of acetylene.

My results (slides 20-22) indicate that you will not be alone in failing to trap tetralithiotetrahedrane.

Question

Have you calculated C_4^{4-} ? It might have six π electrons and six in MO's for the 2s AO's, leading to σ and π aromatic structures simultaneously. (Same result if the σ AO's are hybridized.)

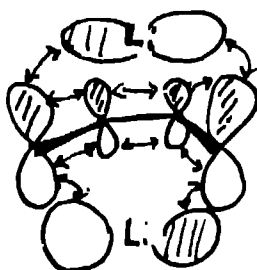
Michael J. S. Dewar

The University of Texas

Answer

This is a very interesting suggestion. My present results suggest that the tetralithiocyclobutadienes are σ and π antiaromatic; that is, $4e^-$ in the π system and $8e^-$ in the σ system. This presumably results in their rectangular structure.

Incidentally, I have been unable to find any evidence of Li p orbitals being involved in an anti-Hückel aromatic ring as Schleyer has suggested.



$4e^-$; anti-Hückel aromatic

MINDO/3

Comparison of calculated (experimental^a) heats of formation (kcal/mol) of hydrocarbons and nitro hydrocarbons.

R	H	NO2
CH ₃	- 6.3 (-17.9)	-10.0 (-17.9)
C ₂ H ₅	-20.0 (-20.2)	-21.0 (-24.4)
(NO ₂)C ₂ H ₄	-21.0 (-24.4)	-21.0 (?)
3° Adamantyl	2.2 (32.9)	10.0 (?)

^a)Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds" Academic Press; New York; 1970.

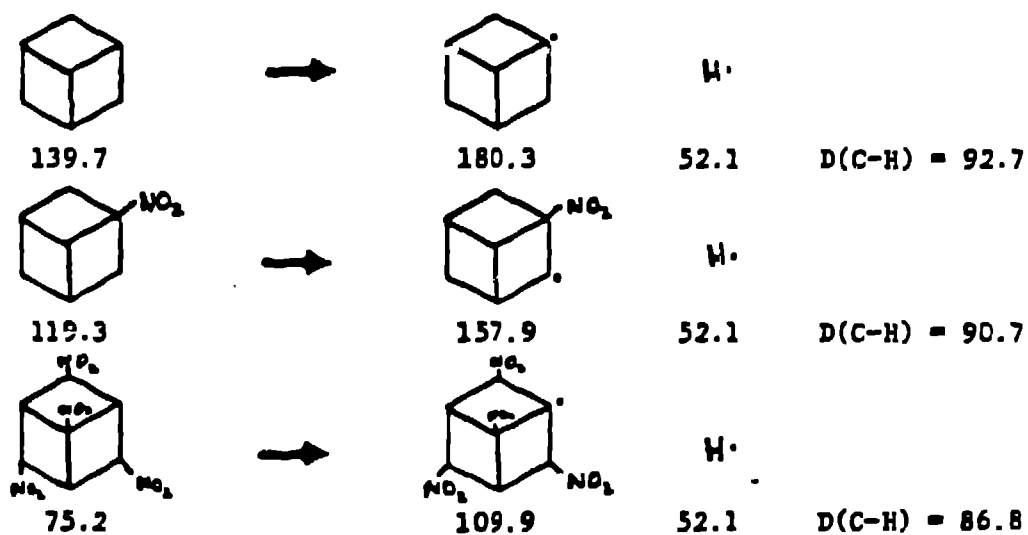
MINDO/3

Calculated heats of formation (kcal/mol) of nitro substituted pentacyclo (4.2.0.0.^{2,5} 0.^{3,8} 0^{4,7}) octanes.

Substitution	H _f
none	139.7
1 nitro	119.3
1,2 dinitro	102.7
1,3 dinitro	102.1
1,4 dinitro	101.5
1,3,5 trinitro	87.1
1,3,5,7 tetranitro	75.2







MINDO/3

Calculated C-H bond strengths (kcal/mol) in cubanes.



MINDO/3

Calculated C-N bond strengths (kcal/mol) of some nitro cubanes.

 119.3	→	 180.3	NO ₂ 8.1* D(C-N) = 69.1
 102.7	→	 157.9	NO ₂ 8.1* D(C-N) = 63.3
 75.2	→	 128.0	NO ₂ 8.1* D(C-N) = 60.9

*this value refers to the experimental heat of formation of this molecule.






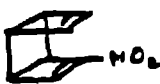
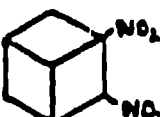


MINDO/3

Calculated C-C bond strengths (kcal/mol) of some
substituted ethanes.

$\text{CH}_3\text{--CH}_3$	\longrightarrow	2 CH_3	
-21.		41.	D(C-C) = 103.
$\text{NO}_2\text{H}_2\text{C--CH}_3$	\longrightarrow	CH_2NO_2 + CH_3	
-21.		20. 41.	D(C-C) = 82.
$\text{NO}_2\text{H}_2\text{C--CH}_2\text{NO}_2$	\longrightarrow	2 NO_2CH_2	
-21.		20.	D(C-C) = 61.

MINDO/3

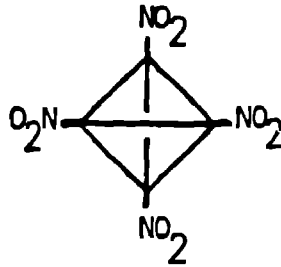
Calculated bond strengths (kcal/mol) and activation
enthalpies of some nitro cubanes.

	\longrightarrow		\longrightarrow	
139.7	$H^* = 32$	163.0	$H^* = 9$	123.1
	\longrightarrow		\longrightarrow	
119.3	$H^* = 40$	135.4	$H^* = 13$	96.4
	\longrightarrow		\longrightarrow	
102.7	$H^* = 42$	129.6		73.4

CONCLUSION:

IN CUBANES, AND PROBABLY ALL POLYHEDRANES, REPLACEMENT OF C-H BONDS WITH C-NO₂ BONDS DOES NOT SIGNIFICANTLY WEAKEN THE BONDS WITHIN THE MOLECULE. THIS LEADS TO THE CONCLUSION THAT NITROPOLYHEDRANES, AND PARTICULARLY NITROCUBANES, SHOULD BE STABLE ENOUGH TO BE SYNTHESIZED AND TESTED AS EXPLOSIVES.

CALCULATED CJ PARAMETERS OF PNT:



$$H_F = 30.8 \text{ KCAL/MOL}$$

$$\text{DENSITY} = 2.11 \text{ g/cc}$$

	P_{CJ} (KBAR)	T_{CJ} (K)	D_{CJ} (M/S)
JD	457.0	5153	9000
3KW (CO ₂ $c_v=630$)	494.7	2740	9948
3KW (CO ₂ $c_v=600$)	431.8	3440	9071

J PARAMETERS CALCULATED BY ALSTER, ET AL. FOR NITROCUBANES INDICATE THAT THEY TOO MAY BE EXCEPTIONALLY POWERFUL EXPLOSIVES.

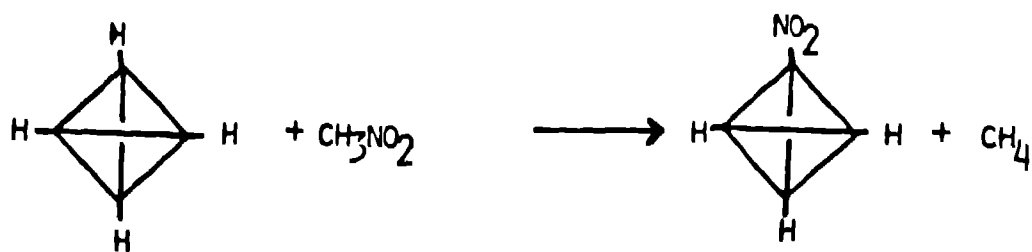
MINDO/3

Calculated heats of formation (kcal/mol) and bond
lengths (Å) of nitro substituted tetrahedranes.

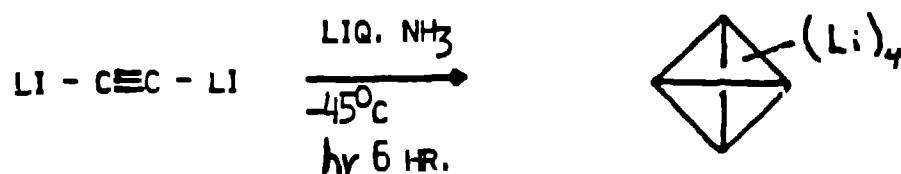
Number of nitro groups	R_f	R_{C-N}	R_{HC-CH}	R_{NO_2C-CH}	$R_{NO_2C-CNO_2}$
0	126.0		1.50		
1	96.0	1.39	1.49	1.51	
2	71.3	1.40	1.48	1.51	1.54
3	50.5	1.41		1.49	1.53
4	30.8	1.42			1.53

Comparison of MINDO/3 (kcal/mol) and ab initio (au)
single point calculations for tetrahedrane, nitro-
methane, nitrotetrahedrane, and methane.

	$E(C_4H_4)$	$E(CH_3NO_2)$	$E(CH_4)$	$E(C_4H_3NO_2)$	H_{rxn} (kcal/mol)
MINDO/3	126.0	- 10.0	- 6.3	96.2	-25.9
STO-3G	-151.7041	-240.4109	-39.7257	-352.3757	2.9
4-31G	-153.3380	-243.2622	-40.1386	-356.4384	2.0



CONSIDER, HOWEVER, A RECENT REPORT OF THE SYNTHESIS OF TETRALITHIOTETRAHEDRANE
 (G. RAUSCHER, T. CLARK, D. POPPINGER, AND P. SCHLEIER, "C₄Li₄, TETRALITHIOTETRAHEDRANE?"
 ANGEW. CHEM. INT. ED. ENGL. 17, 276-278 (1978))



$$^{13}\text{C}_{\text{NMR}} = 75.0 \text{ PPM} \longrightarrow ^{13}\text{C}_{\text{NMR}} = 57.2 \text{ PPM}$$

FIELD DESORPTION MASS SPECTRUM - M/E = 76 AND 75 (ISOTOPE OF LITHIUM)

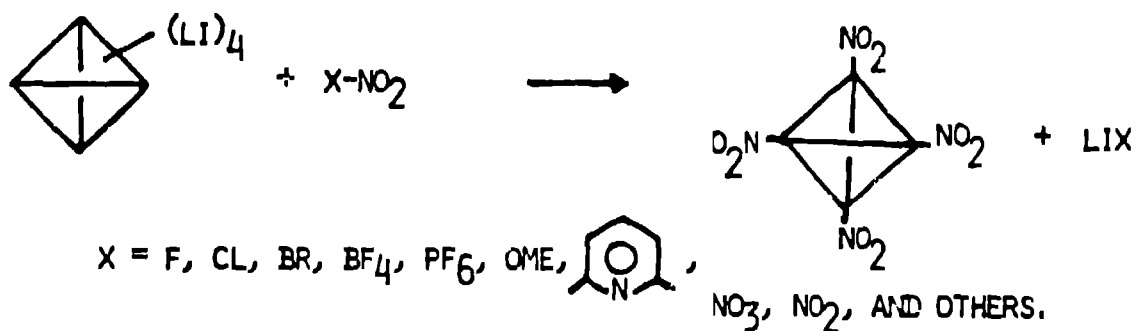
NO PEAKS $[\text{C}_2\text{Li}_2]^+_N$ N = 1; N = 3, 4, 5, ...

THE RAMAN (C≡C) VIBRATION AT 1885 CM⁻¹ DISAPPEARS.

A WHITE AMMONIA-FREE POWDER WHICH ABSORBS AT 688, 612, AND 448 CM⁻¹ IN
 THE IR RESULTS.

NITROTETRAHEDRANES MAY BE ACCESSIBLE FROM C_4Li_4 VIA
REAGENT.

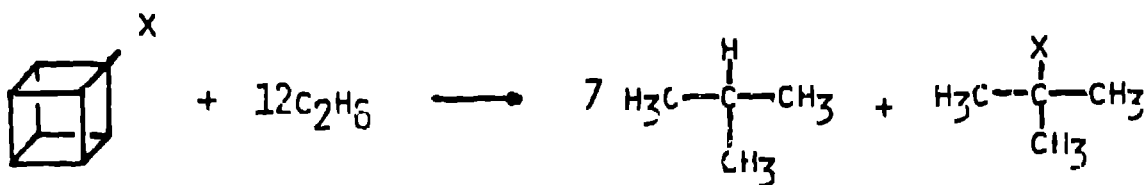
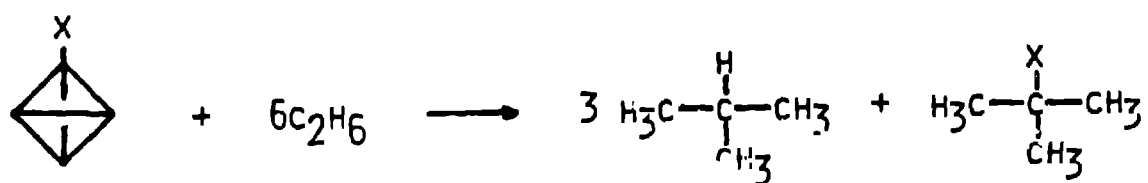
REACTION WITH A SUITABLE NITRATING



C_4Li_4 MAY ALSO REACT WITH CO_2 , HALOGENS, TRIMETHYL-
STANNYL HALOGENS TO GIVE DERIVATIVES WHICH MIGHT BE
SILYL HALOGENS, OR TRIMETHYL-
CONVERTED TO NITRO GROUPS.


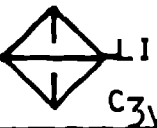

BECAUSE THIS SEEMS TO BE A PROMISING GENERAL SYNTHETIC ROUTE TO POLYNITROPOLYHEDRANES, WE EXAMINED FURTHER THE EFFECTS OF LI ON STRAINED RINGS.

WE ESTIMATED RING STRAIN USING THE GROUP SEPARATION METHOD.



THE NEGATIVE OF THE CALCULATED H_R FOR THE ABOVE PROCESSES IS TAKEN AS THE RING STRAIN.

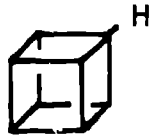
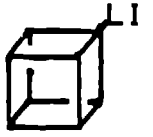
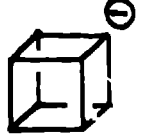
FOR THE TETRAHEDRANES, STO-3G AND 4-31/5-21G CALCULATIONS WITH COMPLETE GEOMETRY OPTIMIZATION WITHIN THE SPECIFIED POINT GROUP THE FOLLOWING RESULTS

	CALCULATED RING STRAIN (KCAL/MOL)		
			
STO-3G	195.5	164.4	158.8
4-31/ 5-21G	163.1	133.3	133.7

LITHIUM SUBSTITUTION DOES STABILIZE RINGS.

ANIONS ALSO SHOW SIMILAR RELIEF OF RING STRAIN.

SIMILAR CALCULATIONS FOR CUBANES GAVE THE FOLLOWING RESULTS.

	CALCULATED RING STRAIN (KCAL/MOL)		
	 O_H	 C_{3v}	 C_{3v}
STO-3G	175.3	160.7	158.8
4-31/	172.3		
5-21G			

AGAIN, IT IS OBSERVED THAT THE LITHIATED AND ANIONIC CUBANES SHOW SIMILAR RELIEF OF RING STRAIN.

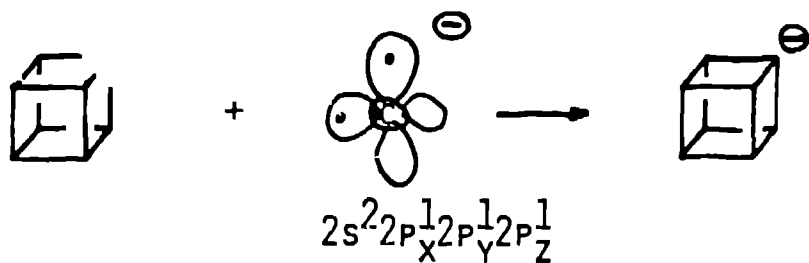
THE OBSERVED SIMILARITIES BETWEEN THE LITHIUM CONTAINING COMPOUNDS AND THE CONJUGATE BASES IS CONSISTENT WITH AN IONIC CARBON-LITHIUM BOND.

I BELIEVE THAT, IN THIS CASE, THE EMPTY P ORBITALS ON LITHIUM PLAY LITTLE OR NO CHEMICAL ROLE.

FURTHERMORE, RELIEF OF RING STRAIN MAY RESULT FROM THE INCORPORATION OF AN UNHYBRIDIZED ANIONIC CENTER.

THE VALENCE ELECTRONIC CONFIGURATION OF C^- IS $2s^2 2p_x^1 2p_y^1 2p_z^1$.

THIS ARRANGEMENT HAS THREE UNPAIRED ELECTRONS IN MUTUALLY PERPENDICULAR ORBITALS PERFECTLY SUITED FOR INCORPORATION INTO THE CUBYL ANION.



THIS EFFECT HAS PROBABLY ALREADY BEEN OBSERVED EXPERIMENTALLY.¹



$J(^{13}\text{C-H}) = 160\text{Hz}$
ABOUT 32% S CHARACTER



$J(^{13}\text{C-H}) = 155\text{Hz}$
ABOUT 30% S CHARACTER

RELATIVE RATE

OF EXCHANGE WITH
CSCHA, 50°

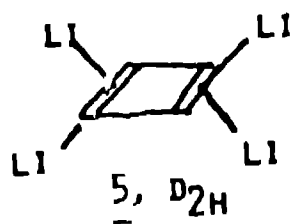
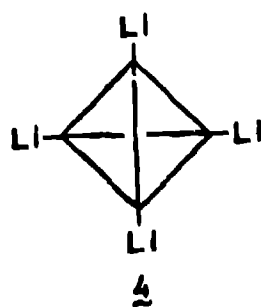
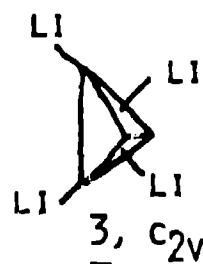
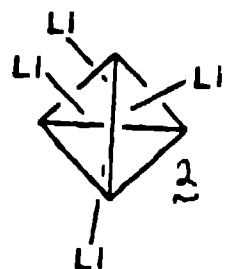
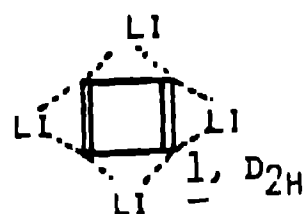
= ABOUT 10^{-3}

= 1

STOCK AND LUH: "WE INFER THAT THE LARGE ENHANCEMENT OF ACID STRENGTH
ORIGINATES IN THE ALTERED HYBRIDIZATION AT THE ANIONIC
CARBON ATOM TO AN ORBITAL WITH SIGNIFICANTLY ENHANCED
S CHARACTER."

1. LUH, T.-Y.; STOCK, L.M. J. AM. CHEM. SOC. 1974, 96, 3712-3713.

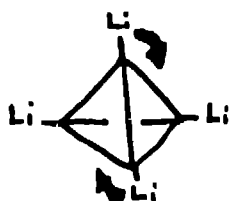
INTRIGUED BY SCHLEYER'S REPORTED ISOLATION OF TETRALITHIOTETRAHEDRANE,
WE INVESTIGATED THE C_4Li_4 POTENTIAL ENERGY SURFACE.



RELATIVE ENERGIES (KCAL/MOL)

	STO-3G	SPLIT VALENCE
1	00.0	00.0
2	13.0	27.9
3	54.8	
4	78.1	82.8
5	26.6	

THE CALCULATION OF FORCE CONSTANTS FOR THE CORNER-LITHIATED
TETRALITHIOTETRAHEDRANE INDICATES THAT THIS STRUCTURE IS A HILLTOP.
IT HAS TWO NEGATIVE FORCE CONSTANTS AND IS NOT A MINIMUM.



CALCULATED VIBRATIONAL FREQUENCIES (cm^{-1})
AT THE
STO-3G LEVEL

169i	(2)
56	(3)
87	(3)
444	(2)
674	(1)
735	(3)
1098	(3)
1623	(1)

PARENTHESES INDICATE THE DEGREE OF DEGENERACY.

FORCE CONSTANT CALCULATIONS FOR THE C_{2v} STRUCTURE INDICATE THAT IT IS A TRANSITION STATE BECAUSE IT HAS ONLY ONE NEGATIVE FORCE CONSTANT. THIS TRANSITION STATE DECOMPOSES TO TWO DILITHIOACETYLENES AND RESULTS IN A SCRAMBLING OF THE CARBONS AND LITHIUMS.



CALCULATED VIBRATIONAL FREQUENCIES (cm^{-1})
AT THE
STO-3G LEVEL

388i

52

71

123

140

263

299

532

585

638

689

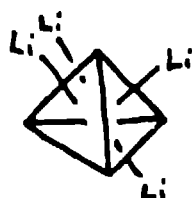
811

816

856

935, 1126, 1160, 1493

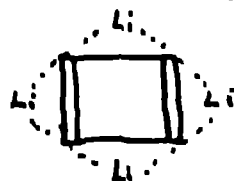
FORCE CONSTANT CALCULATIONS FOR THE FACE-LITHIATED TETRAHEDRANE
 INDICATE THAT THIS STRUCTURE IS ALSO A HILLTOP.



CALCULATED VIBRATIONAL FREQUENCIES (cm^{-1})

	STO-3G	SPLIT VALENCE
1E	225i	154i
1T ₁	272	250
1T ₂ *	352	298
2E	658	612
2T ₂ *	738	617
1A ₁	793	657
3T ₂ *	976	847
2A ₁	1292	1073

FORCE CONSTANT CALCULATIONS FOR TETRALITHIOCYCLOBUTADIENE INDICATE THAT IT IS A TRUE MINIMUM ON THE POTENTIAL ENERGY SURFACE.



CALCULATED VIBRATIONAL FREQUENCIES (CM⁻¹)
*IR active

	STO-3G	SPLIT VALENCE
1B _{1U} *	114	122
1B _{3G}	169	234
2B _{1U} *	217	154
1B _{1G}	290	262
1B _{3U} *	361	308
1B _{2U} *	376	279
1B _{2G}	384	281
1A _U	478	500
1A _G	614	491
2B _{1G}	652	556
2A _G	729	609
2B _{2U} *	735	635
3B _{1G}	829	750
2B _{3U} *	887	714
3B _{2U} *	1004	803
3A _G	1224	999
3B _{3U} *	1554	1483
4A _G	1623	1508

ADDITIONALLY, FORCE CONSTANT CALCULATIONS INDICATE THAT THERE IS ANOTHER CYCLOBUTADIENE WHICH IS ALSO A MINIMUM.



CALCULATED VIBRATIONAL FREQUENCIES (cm^{-1})

144

186

210

312

357

365

368

554

562

615

639

650

801

886

1134

1295

1512

1535