Potential Energy Surface of C_4Li_4

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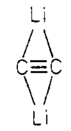
Abstract: The C_4Li_4 potential energy surface has been examined by using ab initio SCF and RMP2 calculations. Twelve structures were studied, the most stable of which is a novel D_{2h} tetralithiodiacetylene, lying 73.9 kcal/mol below two molecules of dilithioacetylene. Several other geometrical isomers of molecular formula C_4Li_4 have been characterized by using molecular orbital calculations at the SCF level and, in some cases, at the RMP2 level. A D_{2d} tetralithiodiacetylene was examined but is less stable than the D_{2h} structure by about 5 kcal/mol. All of the tetralithiotetrahedranes examined have at least one imaginary vibrational frequency, indicating that they are not minima on the potential energy surface. Three kinetically stable tetralithiocyclobutadienes were found, but these are of high energy.

Among the isomers of C_4H_4, cyclobutadiene and tetrahedrane exemplify the destabilizing effects of antiaromaticity and ring strain. It is of interest whether the corresponding isomers of the lithiated system, C_4Li_4, are equally destabilized. This work describes ab initio studies of a number of C_4Li_4 structures and provides a definite answer to this question. In addition, it suggests the existence of a novel stable dimer of dilithioacetylene, C_2Li_2. (A preliminary report of the possible synthesis of a C_4Li_4 species has appeared.)[2]

Calculations of dilithioacetylene have shown it to have a bridged structure of either C_{2v} (**1a**)[3] or D_{2h} (**1b**)[4] symmetry; the linear form (**1c**) is 6.8 kcal/mol less stable with SCF calculations employing carbon d orbitals.[3] For C_4Li_4, both face-lithiated (**2**) and classical (**3**) tetralithiotetrahedranes have been discussed,[2,5] but were later shown to possess two imaginary vibrational frequencies at the STO-3G and 4-31G levels,[6] implying kinetically unstable structures. We report here that the other proposed C_4Li_4 isomers, **4**[2] and **5**,[6] although possibly kinetically stable, lie roughly 100 kcal/mol above the structure of lowest energy, **6** (D_{2h} symmetry). The latter is 59-76 kcal/mol more stable than two C_2Li_2 monomers. Twelve dimer structures are discussed below.

1a, C_{2v}



1b, D_{2h}

$Li-C\equiv C-Li$

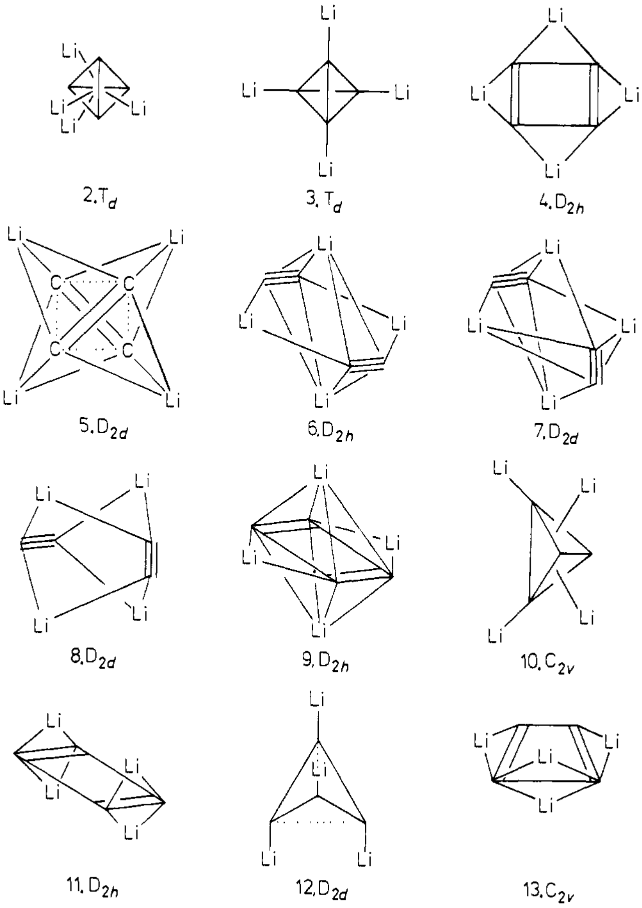
1c, $D_{\infty h}$

Methods

Both SCF and RMP2[7] calculations at Queens College, CUNY, were performed with machine-dependent programs (the Queens College Quantum Chemistry Package), while calculations at Los Alamos National Laboratory were performed with HONDO5.[8] The basis sets employed were STO-3G,[9a] 4-31G (5-21 for lithium),[9b] and three levels of 6-31G*,[9c] referred to as A (s, p, and d orbitals on lithium), B (s and p orbitals on lithium), and C (only s orbitals on lithium). Second-order correlation energies were obtained either by using all occupied orbitals in the sum-over-states expression or, in the frozen core (FC) approximation, by excluding excitations from C and Li 1s-like molecular orbitals. The effect of the FC approximation on geometry is small; thus, certain full RMP2 energies were computed at the RMP2(FC) optimized geometries. Similarly, energies at the 6-31G*C level were obtained at the 6-31G*B optimized geometries. Otherwise, geometries were optimized at the level of calculation for which the energies are reported.

All structures were first optimized at the STO-3G(SCF) level. Although the energies are crude, the geometries provide useful starting points for optimization at higher levels. The STO-3G basis set was also employed in calculations of the normal modes for the various dimer structures. An assumption made in this work is that structures which are kinetically unstable at the STO-3G level are unstable at any higher level. The converse, however, is false: several structures kinetically stable at the STO-3G level were found to be unstable at higher levels.

Chart I



2, T_d 3, T_d 4, D_{2h}

5, D_{2d} 6, D_{2h} 7, D_{2d}

8, D_{2d} 9, D_{2h} 10, C_{2v}

11, D_{2h} 12, D_{2d} 13, C_{2v}

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Table I. Bond Lengths (Å) and Energies (au) Calculated for the D_{2h} and $D_{\infty h}$ Forms of Dilithioacetylene

	level of calculation						
structure	4-31G-(SCF)	4-31G-(RMP2)	6-31G*A-(SCF)	6-31G*B-(SCF)	6-31G*C-(SCF)	6-31G*A-(RMP2, FC)	6-31G*A-(RMP2)
1b, D_{2h}							
energy	−90.43616[b]	−90.63951	−90.56231	−90.55570	−90.51745	−90.83298	−90.84489
R(CC)	1.260	1.300	1.250	1.250	1.250[a]	1.284	1.282
R(CLi)	2.059	2.060	2.027	2.034	2.034[a]	2.028	2.019
1c, $D_{\infty h}$							
energy	−90.44360[b]	−90.64216	−90.55119	−90.54877	−90.50699	−90.81766	−90.83067
R(CC)	1.240	1.278	1.235	1.235	1.235[a]	1.268	1.266
R(CLi)	1.886	1.907	1.900	1.901	1.901[a]	1.910	1.894
rel energy in kcal/mol **1b**–**1c**	4.7	1.7	−7.0	−4.3	−6.6	−9.6	−8.9

[a] Geometry not optimized. [b] Reference 4.

Table II. Energies of 12 Dilithioacetylene Dimers (Total Energies in au; Relative Energies in kcal/mol)

		level of calculation						
structure	unstable modes	STO-3G-(SCF)	4-31G-(SCF)	6-31G*A-(SCF)	6-31G*B-(SCF)	6-31G*C[a]-(SCF)	4-31G-(RMP2)	6-31G*A-(RMP2, FC)
2 (T_d)	2[b,c]	−178.74371 (99.3)	−180.75555 (143.9)		−181.04382 (104.8)	−180.94938 (119.2)		
3 (T_d)	2[b]	−178.63982 (164.5)	−180.66894 (198.3)					
4 (D_{2h})	0[b,c]	−178.76442 (86.3)	−180.80004 (116.0)		−181.03782 (108.5)	−180.94579 (121.5)		
5 (D_{2d})	0[b]	−178.80333 (61.9)	−180.81171 (108.7)		−181.05596 (97.2)	−180.91899 (138.3)		
6 (D_{2h})	0[b,c,d]	−178.90192 (0.0)	−180.98492 (0.0)	−181.22073	−181.21079 (0.0)	−181.13941 (0.0)	−181.39929[f] (0.0)	−181.78367[f]
7 (D_{2d})	1[d,e]	−178.88493 (10.7)	−180.97523 (6.1)		−181.20131 (5.9)	−181.13178 (4.8)		
8(D_{2d})	2[c]	−178.87071 (19.6)	−180.97171 (8.3)				−181.38615 (8.2)	
9 (D_{2h})	2[b]	−178.81827 (52.4)						
10 (C_{2v})	1[b]	−178.67700 (141.1)						
11 (D_{2h})	0[b]	−178.72200 (112.9)						
12 (D_{2d})	0[b]	−178.69696 (128.6)						
13 (C_{2v})	0[b]	−178.77028 (82.6)	−180.77762 (130.1)					
2 D_{2h} monomers		−178.80806 (58.9)	−180.87233 (70.7)	−181.12460 (60.3)	−181.11114 (62.5)	−181.03490 (65.6)	−181.27902 (75.5)	−181.66596 (73.9)

[a] Energies calculated at the 6-31G*B(SCF) geometries. [b] STO-3G(SCF) calculation. [c] 4-31G(SCF) calculation. [d] 4-31G(RMP2, FC) calculation. [e] This structure is stable at STO-3G(SCF) and borderline stable (lowest frequency near zero) at 4-31G(SCF) levels, respectively. [f] Calculated at the 4-31G(RMP2, FC) geometry.

Results

The dilithioacetylene structure has been reexamined at higher levels of calculation than reported previously. Additionally, the 12 dimer structures shown in Chart I have been investigated in detail. These structures have lines joining carbons and lithiums that are 1.8–2.3 Å apart. Triple, double, and single bonds have been assigned to carbon–carbon separations of 1.22–1.30, 1.35–1.43, and 1.48–1.64 Å, respectively; somewhat larger separations of 1.88–2.07 Å, found in **5** and **12**, are indicated by dotted lines. Several of the structures are derived from lithiated tetrahedranes (**2**, **3**, **10**, **12**) and cyclobutadienes (**4**, **9**, **11**, **13**), whereas others (**6**, **7**, **8**) retain a pair of C≡C moieties which interact only through bridging lithiums. We call the latter three structures tetralithiodiacetylenes.

Dilithioacetylene. New energies are given in Table I for the D_{2h} (**1b**) and $D_{\infty h}$ (**1c**) forms of dilithioacetylene optimized at the 4-31G(RMP2), 6-31G*A, B, and C(SCF), and the 6-31G*A-(RMP2) levels. As noted before,[4] whenever d orbitals are placed on carbon, the D_{2h} form is more stable than the $D_{\infty h}$ form; this is true even at the 6-31G*C(SCF) level, which contains only s orbitals on Li. On the other hand, even second-order correlation corrections to the 4-31G(SCF) calculation still favor the $D_{\infty h}$ form. The 6-31G*A(RMP2) calculation shows the D_{2h} form to be 8.9 kcal/mol more stable than the $D_{\infty h}$ form. An important change in geometry occurs at the RMP2 level with R(CC) for both isomers increasing in the 4-31G and 6-31G* bases by about 0.04 Å and 0.03 Å, respectively. Furthermore, as shown previously,[3] B_{1u} distortions of about 10° into C_{2v} symmetry lower the energy of the D_{2h} form by several calories/mole; hence, the D_{2h} form could be the transition state for C_{2v} interconversion.

Recently, it has been shown by Streitwieser that basis set superposition errors are significant for lithium-containing compounds;[10] this could manifest itself in the relative monomer energy differences and their geometries. Hence, we augmented the 6-31*B basis set with a diffuse ($\alpha = 0.06$) sp shell on carbon and deleted the outer Li p functions.[10] Reoptimization of the D_{2h} and $D_{\infty h}$ geometries of C_2Li_2 in this basis had only slight effects on the bond lengths ($D_{\infty h}$, R(C–C) = 1.238 Å, R(C–Li) = 1.900 Å; D_{2h}, R(C–C) = 1.249 Å, R(C–Li) = 2.034 Å); however, the $D_{\infty h}$–D_{2h} energy difference was reduced from 4.3 kcal/mol at 6-31G*B to 1.4 kcal/mol. With the augmented basis set, we were unable to determine whether the C_{2v} structure is a minimum because the C_{2v}–D_{2h} energy difference is vanishingly small and

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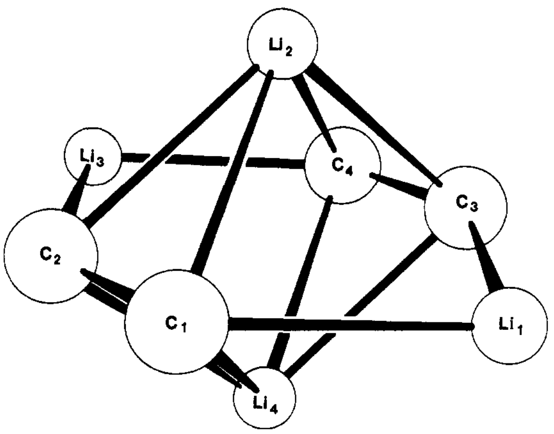

Figure 1. Perspective drawing of dilithioacetylene dimer **6**.

Table III. Geometrical Parameters (Å) and Vibrational Frequencies of Dimer **6**

	level of calculation				
optimized parameter	STO-3G-(SCF)	4-31G-(SCF)	4-31G-(RMP2, FC)	6-31G*A-(SCF)	6-31G*B-(SCF)
$R(C_1C_2)$	1.248	1.252	1.299	1.242	1.243
$R(C_1C_3)$	2.964	3.095	3.127	3.094	3.110
$R(C_1Li_1)$	2.039	2.132	2.167	2.131	2.152
$R(C_1Li_2)$	2.111	2.229	2.218	2.214	2.205

level of calculation	calculated frequencies, cm^{-1}[a]
4-31G(SCF)	A_g—2060, 524, 390, 206; Au—176; B_{1g}—431, 225; B_{2g}—424, 252; B_{3g}—396; B_{1u}—2041, 529, 313; B_{2u}—435, 328; B_{3u}—503, 393, 285
4-31G(RMP2, FC)	A_g—1724, 529, 388, 167; A_u—187;B_{1g}—432, 247; B_{2g}—437, 283; B_{3g}—422; B_{1u}—1703, 529, 310; B_{2u}—446, 318; B_{3u}—500, 422, 322

[a] The molecular *x* axis is Li_1–Li_3 and the *y* axis is Li_2–Li_4.

the calculated gradients are similarly small for both geometries. The effect of the diffuse shell was also tested at the 4-31G(SCF) and 4-31G(RMP2, FC) levels; the linear structure is favored by 2.2 and 0.4 kcal/mol, respectively.

Tetralithiodiacetylenes. The energies given in Table II show that the most stable dimer structure is **6**, a D_{2h} molecule (Figure 1) in which two lithiums and four carbons form a planar, hexagonal structure axially capped by the other two lithiums. The C_1C_2 distance of 1.24–1.30 Å implies a triple bond and is much shorter than the nonbonded distance between C≡C midpoints, 3.0–3.1 Å. The C–Li in-plane and axial separations are 2.0–2.2 and 2.1–2.2 Å, respectively, the axial C–Li distances being the longer at each level of calculation by from 0.05–0.08 Å.

Dimerization of two D_{2h} dilithioacetylenes to **6** is remarkably exothermic—by 70.7 and 60.3 kcal/mol at the 4-31G and 6-31G*A (SCF) levels, respectively; at the RMP2 level in the same bases, the exothermicities are 75.5 and 73.9 kcal/mol. The basis set superposition error for this structure determined by the counterpoise method[11] is estimated to be on the order of 10 kcal/mol at the 6-31G*A(SCF) level. A similar value was obtained by including a diffuse shell (α = 0.06) at both the 4-31G(SCF) and 4-31G(RMP2, FC) levels.

The vibrational frequencies of **6** determined at both 4-31G-(SCF) and 4-31G(RMP2, FC) levels are given in Table III. The fact that they are all real confirms that **6** is a true minimum on the C_4Li_4 calculated potential energy surface. The weak 4-31G-(SCF) vibrations at 176 cm^{-1} (A_u) and 225 cm^{-1} (B_{1g}) stiffened somewhat to 187 and 247 cm^{-1}, respectively, upon correcting for correlation to second order, although the lowest A_g vibration softened to 167 cm^{-1}.

When **6** is viewed as arising from parallel-oriented C_2 moieties bridged by lithiums, its similarity to the D_{2d} dimer **8** becomes apparent. The latter, whose lithiums lie in a square with orthogonally oriented C≡C groups above and below, is about 8 kcal/mol less stable than **6**; it is unstable with respect to two symmetry species at the 4-31G(SCF) level, although it is stable at the STO-3G level.

Dimer **7** is close in energy to **8** and can be thought of as arising from the interaction of two highly bent C_{2v} dilithioacetylenes (**1a**) with dihedral angles of about 108°. Although it is stable in the STO-3G basis, it is marginally stable and unstable with respect to A_2 distortions at the 4-31G(SCF) and 4-31G(RMP2, FC) levels, respectively.

Structures **6–8** can interconvert with small barriers, implying that they occupy a very flat region of the dimer ground-state surface; this situation is analogous to the flat monomer surface described by **1a–1c**. It is worth noting that the two C≡C moieties in **6–8** are linked only by C—Li—C bridges, whereas the other dimers investigated have carbon skeletons formed by covalent bonds with bridging lithiums appended.

Tetralithiotetrahedranes. Of the four structures derived from tetralithiotetrahedranes, only **12** appears to be a minimum at the STO-3G(SCF) level on the C_4Li_4 potential energy surface. The face-lithiated structure, **2**, which is the lowest energy tetrahedrane, is over 100 kcal/mol higher in energy than **6**. It is unstable with respect to an E symmetry species at both STO-3G and 4-31G levels and appears to rearrange in a symmetry-allowed manner to **5**, a D_{2d} homomer[12] of **7** with similar topology but different CC distances. Structure **5** may be considered to contain two orthogonal, weakly interacting C=C moieties with exterior bridging lithiums; it is a minimum at the STO-3G level but is unlikely to represent an observable structure because it can decompose exothermically to tetralithiodiacetylene. The highly energetic classical tetralithiotetrahedrane (**3**), which probably has much of the strain energy of tetrahedrane itself, is unstable with respect to E-type distortions. Displacement along these unstable modes followed by structure optimizations led to variants of **12** whose connectivities depend upon the distorting mode. Structure **12** is stable at the STO-3G level and can be considered to be either a distorted tetrahedrane or a puckered cyclobutadiene, but again is unlikely to represent an observable species.

Tetralithiocyclobutadiene. Of the cyclobutadiene-derived structures, **4**, **11**, and **13**[13] are minima at the STO-3G level. They appear to be on the order of 100 kcal/mol higher in energy than **6**.

Dimer **9** is a homomer of **6**, connected to it by a symmetry-forbidden diacetylene–cyclobutadiene-type dimerization. Structure **9**, which is 52.4 kcal/mol higher in energy than **6**, has two unstable modes at the STO-3G(SCF) level, as do several closely related isomers of **9**.

Discussion

Of the 12 dimers studied, only **6–8**, in which the acetylene moieties are retained, have energies lower than that of two dilithioacetylene monomers. The large dimerization energy and the retention of acetylenic character in tetralithiodiacetylenes are in accordance with the observed propensity of organolithiums to aggregate. In contrast, dimers with reorganized carbon–carbon frameworks, such as tetrahedranes and cyclobutadienes,[13] are of much higher energy. The C_4Li_4 case, therefore, differs from that of C_4H_4, in which cyclobutadiene is calculated to be nearly isoenergetic with two acetylenes and tetrahedrane lies only 25.5 kcal/mol higher.[14]

The retention of acetylenic character in the dilithioacetylenes and tetralithiodiacetylenes is one of several indications that the monomer and the dimer are ionic compounds, with Li cations bridging acetylide moieties. Thus, **1a** has a very large calculated dipole moment, 0.7 D, for only 6° bending at 6-31G*A. Although dimer **6** has no dipole moment, its 4-31G(RMP2, FC) quadrupole moments are those of a point-charge model in which carbon has

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−0.59 e and axial lithium +0.66 e.

The idea that lithium is acting principally as a cation in the dimer is further supported by the negligible effect of removing the Li 2p shell upon the dimerization energy, e.g., basis 6-31G*B vs. 6-31G*C. The effect upon the relative monomer energies is also small. Thus, a conclusion of this work is that electrostatic interactions provide much of the driving force to dimer formation. The dimerization energy for **6** is, in fact, comparable to that found for Li_2F_2, 60.4 kcal/mol.[15]

There has been considerable recent discussion of the nature of the C–Li bond. Arguments both for significant[16] and little[17] covalent character have been made based upon Mulliken populations and molecular structure on the one hand and projected electron densities on the other. The middle ground has been taken by Graham et al.,[18] who suggested a charge transfer of 0.55–0.60 e in CH_3Li. Given the acidic properties of acetylenes and strained rings, however, it is to be expected that dilithioacetylene should be more ionic than methyllithium. This ionic character is, in fact, exhibited in the high-melting, probably ionic crystalline form of Li_2C_2[19] and in the fact that Li_2C_2 melts participate in electrolysis.[20] While it can be argued that extensive ionic character appears only in condensed phases, aided by Madelung-type stabilization, it appears from the present studies that even the monomer and dimer are largely ionic.

We wish to point out that we find no evidence for lithium–lithium bonding in dimer **6**; it and the others are, therefore, fundamentally different from the hyperlithiated molecules reported recently.[21]

The effects of lithium substitution on ring strain and antiaromaticity can now be considered more clearly by using tetralithiodiacetylene as the reference point. On this basis, both the lithiated cyclobutadienes and tetrahedranes are destabilized by over 100 kcal/mol, values much larger than those calculated for cyclobutadiene and tetrahedrane. Even if two dilithioacetylenes are used as the reference point, energies of formation of lithiated cyclobutadienes and tetrahedranes are still higher than those calculated for their C_4H_4 counterparts. Consequently, replacement of hydrogen by lithium offers no stabilization for cyclobutadiene or tetrahedrane relative to the most stable C_4Li_4 structure.

Conclusions

All previously suggested structures for C_4Li_4 are found to be either kinetically or thermodynamically unfavorable (or both) compared with the lowest energy structure, **6**. This structure appears to have four lithium cations bridging two acetylide moieties. It is the lowest energy C_4Li_4 structure found and lies much below the energy of two separated dilithioacetylenes.

Registry No. 1c, 1070-75-3; **3**, 65982-76-5; **4**, 65982-75-4.

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On the Relationship between HMO and the Hydrogen Chain System

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Abstract: Answering the criticism against the recent publication on the stability of polygonal H_n hydrogen chain systems (HCS), the present communication points out that the comparison of the HCS model with HMO is meaningless and confirms that the HCS model is tenable in the fundamental study of aromaticity.

In a recent publication,[1] we proposed simple models using polygonal H_n systems (polygonal HCS[2]) which may serve as a fundamental understanding of aromaticity.

Haddon et al.[3] insist on the basic incompatibilities of the HMO and HCS analyses. Our proposal[1] is not aimed at substituting the HMO or related theories[4] by the HCS models, and therefore we do not need to give much comment on their criticism. However, it is worth noting that such a comparison is basically meaningless. This paper shows the reasons and gives a supplementary explanation to our previous report.[1]

The first reason is that there is an essential difference between a real molecule and such a model as HCS which never exists in nature. Namely, as far as the total energy is concerned, any kind of HCS model is higher in energy than the corresponding nH_2.

Table I. The Total and Electronic Energies of H_2 and Linear H_4 Systems at Optimized Structures (STO-6G)[a]

	H_2	H_4
R, Å	0.7103	0.8511
E^F total	−0.935611	−1.209290
E		
$\sum E_A$	−0.456351	−0.720772
$\sum E_{AB}$ neigh.	−0.106757	−0.109015
$\sum E_{AB}$ other		0.293939
total	−0.563108	−0.535850

[a] Energies are expressed per atom in terms of au.

Therefore, it is obvious that the sign of the delocalization energy per electron (DEPE)[5] in HF HCS models disagrees throughout with that of HMO. However, this does not simply mean that the HCS model is untenable in the analyses of aromaticity.

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[1] Ichikawa, H. *J. Am. Chem. Soc.* **1983**, *105*, 7467.

[2] Hydrogen chain system; we use the same terminology as in ref 3.

[3] Haddon, R. C.; Raghavachari, K.; Whangbo, M. H. *J. Am. Chem. Soc.*, in press.

[4] See ref 3–15 in ref 3.

[5] In accordance with ref 3, a positive value is used to denote stabilization.

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