

-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 Li₂F₂, 60.4 kcal/mol.¹⁵

There has been considerable recent discussion of the nature of the C-Li bond. Arguments both for significant¹⁶ and little¹⁷ 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 CH₃Li. 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 Li₂C₂¹⁹ and in the fact that Li₂C₂ melts participate in electrolysis.²⁰

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(16) (a) Dill, J. D.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 6159. (b) Clark, T.; Schleyer, P. v. R. *Chem. Commun.* **1978**, 137. (c) Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *Ibid.* **1980**, 672. (d) Clark, T.; Jemmis, E. D.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Organomet. Chem.* **1978**, *150*, 1.

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(18) Graham, G. D.; Marynick, D. S.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1980**, *102*, 4572.

(19) Juza, V. R.; Wehle, W.; Schuster, H. U. *Z. Anorg. Allg. Chem.* **1967**, *352*, 252. ($R_{CC} = 1.20 \text{ \AA}$, $R_{CLi} = 2.27 \text{ \AA}$.)

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 anti-aromaticity can now be considered more clearly by using tetra-lithiodiacetylene 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 C₄H₄ counterparts. Consequently, replacement of hydrogen by lithium offers no stabilization for cyclobutadiene or tetrahedrane relative to the most stable C₄Li₄ structure.

Conclusions

All previously suggested structures for C₄Li₄ 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 acetylene moieties. It is the lowest energy C₄Li₄ 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 HCS²) 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 proposal¹ is not aimed at substituting the HMO or related theories⁴ 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 nH₂.

(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.

Table I. The Total and Electronic Energies of H₂ and Linear H₄ Systems at Optimized Structures (STO-6G)^a

	H ₂	H ₄
<i>R</i> , Å	0.7103	0.8511
<i>E</i> ^F total	-0.935611	-1.209290
<i>E</i>		
∑ <i>E</i> _A	-0.456351	-0.720772
∑ <i>E</i> _{AB} neigh.	-0.106757	-0.109015
∑ <i>E</i> _{AB} other		0.293939
total	-0.563108	-0.535850

^aEnergies 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.

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

The second reason is based on the inherent vagueness of HMO, which need not be elaborated. As an example, we take the same problem as quoted in ref 3, i.e., the divergent results of DEPE between HMO butadiene and the HF HCS linear H_4 . Destabilization in HCS is a natural result and may be offset if one considers one or two factors such as long-range interaction and internuclear repulsion, both of which are not taken into account in HMO. Table I shows the total (E) and electronic (E^F) energies where E_A and E_{AB} denote the monocentric and bicentric terms,¹ respectively, and neigh. denotes the sum of the nearest neighboring interactions, e.g., for H_4 , it is ($E_{12} + E_{23} + E_{34}$).

In order to juxtapose the HF HCS model to HMO treatment, the long-range interactions are not incorporated, resulting in that DEPE for $2H_2 \rightarrow$ linear H_4 is +167 kcal/mol,⁵ and internuclear interaction is neglected so that DEPE becomes +172 kcal/mol, showing enormous stabilization. This example shows that if one tries to correlate the HF HCS results with those of HMO, one may not use the total energy but rather partitioned and/or partial energies with apparent physical meaning. Although the detailed analyses along this line may shed light on the role of HMO, it seems for us to be an unimportant task.

The relative stability of the cyclic system to the linear reference is a widely accepted definition of aromaticity.⁶ However, considering the sensitivity of ab initio MO theory on geometry, we do not think that such a comparison in the HF HCS model is workable since the geometrical environment between cyclic and linear systems is too different to ignore. Thus we only used the polygonal H_n systems to show the inherent stabilities of the $4n + 2$ cyclic HCS compared with the $4n$ cyclic HCS where the

(6) See ref 6-8 in ref 3.

environment is similar and that such a difference of energy may be correlated to the *kinetic (energy) pressure*.⁷

The foregoing communication³ also points out that unstability of the H_4 may be due to the higher HF solution (CDW) for singlet state and obtained triplet state (H_7^1) of H_4 and H_8 cyclic HCS's. We admit that we only handled the higher solution.

The lowest solutions that we found for D_{nh} H_4 and H_8 were the spin density wave (SDW) states,⁹ which are 31.0 and 34.1 kcal/mol lower than the H_4^t and H_8^s solutions, respectively. The order of total energy per atom¹⁰ is the following: $H_4^t(-0.47511) > H_4^s(\text{SDW: } -0.48747) > H_8^t(-0.50861) > H_8^s(\text{SDW: } -0.51542) > H_{10}(-0.52872) > H_6(-0.53035 \text{ au})$.¹ The unstable nature of H_4 and H_8 systems is again ascertained. Besides, analysis of the partitioned energies led to the same conclusion reported before.¹

Haddon et al.³ finally stress the discrepancies in the order for naphthalene, azulene, and [10]annulene geometries using a single common internuclear distance for each system. We have no comment on this, since in addition to the considerable geometrical differences between them, use of a single common H-H length for each system on geometry optimization seems to be an apparent arbitrary factor.

Registry No. Atomic hydrogen, 12385-13-6.

(7) In a previous report,¹ we used the abbreviated term *kinetic pressure* for *kinetic energy pressure* (Feiber, M. J.; Rudenberg, K. *J. Chem. Phys.* **1971**, *54*, 1495).

(8) Whangbo, M. H. *Acc. Chem. Res.* **1983**, *16*, 95.

(9) The total energies were obtained at their optimized structures. The optimized lengths (Å) of side are as follows: H_4^t (1.1471), H_4^s (1.2547), H_8^t (1.0050), and H_8^s (1.0362).

(10) In terms of au.

Comparison between the *s*-Cis and *Gauche* Conformers of 1,3-Butadiene

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Abstract: Geometries of stationary points for *s*-cis-1,3-butadiene and *gauche*-1,3-butadiene have been predicted via molecular electronic structure theory. Both double- ζ (DZ) and double- ζ plus polarization (DZ+P) basis sets were used in conjunction with the self-consistent-field (SCF) and configuration interaction (CI) methods. At the DZ SCF level, *s*-cis-1,3-butadiene was characterized as a transition state for the isomerization of the two possible *gauche*-1,3-enantiomers, which were shown to be genuine local minima. The barrier to planarity at this level of theory was predicted to be 0.4 kcal/mol, and the torsional angle for the *gauche* structure is 33.2°. The same qualitative result was found at the DZ+P SCF level, with the rotational barrier being 0.7 kcal and the torsional angle 37.8°.

Experimental and Theoretical Background

It is now well established that the compound 1,3-butadiene is a mixture of two conformers: the more stable *trans*-1,3-butadiene^{1,2} and another structure which is often presented as *s*-cis-1,3-butadiene in textbooks.³⁻⁶ The question as to whether the second stable conformer is actually *s*-cis- or rather *gauche*-1,3-butadiene (twisted) has been the subject of discussion for some time.⁷⁻⁹

For experimental chemists, an unequivocal answer to this question has been hindered by the difficulty of obtaining direct evidence concerning the less stable conformer. In 1973, however, Lipnick and Garbisch¹⁰ opted for the *gauche*-1,3-butadiene as the second stable conformer on the basis of NMR spectroscopy. In

his 1975 Raman study, Carreira¹¹ concluded that the second equilibrium geometry of 1,3-butadiene is the planar *s*-cis structure,

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(2) Kuchitsu, K.; Fukuyama, T.; Morino, Y. *J. Mol. Struct.* **1968**, *1*, 463.

(3) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; pp 291-292.

(4) Mislow, K. "Introduction to Stereochemistry"; Benjamin: New York, 1966; p 75.

(5) Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed.; Cornell University Press: Ithaca, NY, 1969; pp 61-62.

(6) Kagan, H. "Organic Stereochemistry"; Halsted/Wiley: New York, 1979; pp 53-54.

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(10) Lipnick, R. L.; Garbisch, E. W., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 6370.

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