Table XII. Localized In-Plane Force Constants for Ethylene for Various Representations for Nonbonded Interactions[a]

	representation			
	O[b]	A[c]	B[d]	C[e]
Diagonal Force Constants				
rC=C	11.64	11.62	11.62	11.63
rC—H	6.24	6.22	6.22	6.23
α	0.515	0.517	0.516	0.515
β	0.636	0.616	0.627	0.625
Stretch–Stretch Cross Terms				
rC=C,rC—H	0.110	0.105	0.108	0.108
rC—H,rC—H (gem)	0.053	0.067	0.059	0.058
Stretch–Bend Cross Terms				
rC=C,β	0.284	0.275	0.280	0.281
rC—H,α	0.159	0.153	0.156	0.157
rC—H,β	0.141	0.130	0.134	0.138
Stretch–Stretch′ Cross Terms				
rC—H,r′C—H (cis)	0.017	0.029	0.022	0.022
rC—H,r′C—H (trans)	−0.004	−0.014	−0.008	−0.007
Stretch–Bend′ Cross Terms				
rC—H,β' (cis)	−0.020	−0.016	−0.018	−0.018
rC—H,β' (trans)	0.051	0.044	0.049	0.048
Bend–Bend′ (θ–θ–ϕ) Cross Terms				
β,β' (cis)	−0.019	−0.022	−0.021	−0.021
β,β' (trans)	0.085	0.085	0.085	0.086

[a] Based on 6-31G* calculations carried out at the equilibrium geometry. See Table X for units for force constants and notation for the internal variables. [b] These "spectroscopic" force constants reproduce the calculated 6-31G* second derivatives. [c] Obtained after removal of contributions from exp-6 nonbonded interactions ($\epsilon^*_{\mathrm{H\text{-}H}}$ = 0.047 kcal/mol, $R^*_{\mathrm{H\text{-}H}}$ = 3.0 Å), as described in the text. [d] Obtained after removal of Lennard-Jones 9-6 contributions ($\epsilon^*_{\mathrm{H\text{-}H}}$ = 0.04 kcal/mol, $R^*_{\mathrm{H\text{-}H}}$ = 2.8 Å). [e] Obtained after removal of 9-6-1 Lennard-Jones plus coulombic contributions ($\epsilon^*_{\mathrm{H\text{-}H}}$ = 0.04 kcal/mol, $R^*_{\mathrm{H\text{-}H}}$ = 2.8 Å, q_{H} = +0.10).

particular, that a simple empirical expression nicely describes the diagonal localized force constants for angle bending at carbonyl groups. In contrast, the force constants employed in widely used empirical potentials fail to exhibit the trends observed in the experimental data. We have also found that published force fields for angle bending at a tetracoordinate center (i.e., at methylene groups in alkanes) are nearly diagonal in the localized representation, suggesting that neglect of cross terms in angle bending may be justified in developing an empirical potential. Thirdly, we have seen that virtual force constants can be employed to control the representation in dependent coordinates of stretch–bend and bend–bend′ cross terms, thereby providing a means for assessing model assumptions concerning the functional form and physical significance of such interactions. And finally, we have see that significant anharmonicity is present in the potential-energy surface for in-plane vibrations in ethylene and that such anharmonicities can be characterized by determining the dependence on molecular geometry of quadratic force constants obtained in the localized representation.

There are exciting times for those who work at the interface between biology and chemistry. For example, the new experiments made possible by the techniques of genetic engineering are yielding a wealth of new information on the relationship between protein structure and function.[48] But as Knowles notes,[48] the key to understanding this new information often lies not in experiment but in theory—in the ability to sort out through reliable calculations the factors which contribute to an experimental result. If theory is to serve in this role, better theoretical models will have to be developed. It would be most unfortunate if the vast amount of information on molecular properties compiled in "spectroscopic" force fields could not be utilized effectively in their development. The approach described in this paper suggests how it can be utilized.

Acknowledgment. I thank Drs. John Maple, Uri Dinur, and Arnold Hagler of Biosyn Technologies for making available the parameter-derivation software "PROBE"[33] used in the calculations on *N*-methylacetamide and on ethylene which were carried out to determine the magnitude of contributions to spectroscopic valence-coordinate force constants from nonbonded interactions. It also thank a referee for many clarifying suggestions and for identifying the need to justify the basis for comparing spectroscopic angle-bending force constants with those employed in empirical force fields.

Note Added in Proof. According to P. Kollman, additional AMBER force constants for angle bending at carbonyl carbon are cited in a forthcoming paper (Debolt, S.; Kollman, P. A. *J. Am. Chem. Soc.* In press); in the notation and units of Table VI, their values are H—C=O = 0.56, H—C—H = 0.49, and C—C—C = 0.98. Inclusion of these force constants would extend the generally good comparisons for the AMBER force field presented in Table VI and leave essentially unchanged the figures of merit cited there.

Energies and Isomerizations of $(CH)_{12}$ Hydrocarbons

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Abstract: Energy-optimized geometries of 15 isomeric $(CH)_{12}$ hydrocarbons are presented. Geometries were optimized with ab initio restricted Hartree–Fock calculations with the split-valence 3-21G basis set. Energies were calculated at those geometries with the polarized 6-31G* basis. Compound **8** is suggested as the most stable isomer of the $(CH)_{12}$ family. Previously calculated energetics for isomerizations of benzene dimers and molecules related to truncated tetrahedrane are reexamined. Other possible isomerizations and some new $(CH)_{12}$ isomers are considered.

Those compounds consisting entirely of carbons each bearing a single hydrogen, polymethine hydrocarbons, play an important role in organic chemistry. Among them are numbered the simple annulenes,[2] the prismanes,[3] dodecahedrane,[4] and the elusive

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molecule tetrahedrane.[5] Studies on them have been closely associated with the development of theories of aromaticity, molecular strain, and molecular rearrangements.

The 12-carbon branch of that family is exceedingly large. A 1984 review used graph-theoretical calculations to enumerate 357 different structural types.[6] This number excluded those described by nonplanar graphs and failed to distinguish between different stereoisomers of the molecules. At that time, 36 different $(CH)_{12}$ hydrocarbons were known, corresponding to 31 different structural types. For two of these, full structural characterization had not been accomplished.

In the intervening four years, several important members of the $(CH)_{12}$ family have been synthesized. Both the cis 2 + 2 dimer (**1**)[7] (the trans isomer, **2**, was already known[8]) and the C_{2h} quadruply bridged dimer (**3**)[9] of benzene have been prepared. The Diels–Alder dimer of benzene (**4**) has also been observed at low temperature and trapped.[10] Hexaprismane (**5**) has still eluded synthesis, but close approaches have been made.[11] The parent 4 + 4 dimer (**6**) also remains unknown. Analogous compounds involving naphthalenes[12] and anthracenes[13] are known, and bridged-halogenated molecules have recently been synthesized.[14] The preparation and properties of the spiro tetraene (**7**) have been the object of several studies.[15] A synthetic study aimed at the ring system of compound **8** has been reported.[16] The parent hydrocarbon was not obtained, although a dimethyl derivative had been prepared previously.[17]


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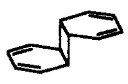
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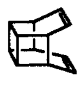
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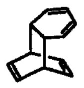
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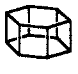
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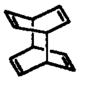
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Table I. Symmetries and Energies of the Hydrocarbons Studied[a]

compd	Balaban's no.	sym	energy 3-21G	energy 6-31G*	energy MNDO[b]	energy 6-31G*[c]
benzene		D_{6h}	(0)	(0)	(0)	
1a	4012	C_2	59.6	60.3		
1b	4012	C_{2v}	60.3	61.0	16	
2	4012	C_{2v}	56.0	57.5	15	
3	2034	C_{2v}	73.5	80.6		
4	4004	C_s	46.0	54.3[d]	31	
5	0061	D_{6h}	127.9	133.7	38	
6	4005	D_{2h}	69.9	81.8	45	
8	0201	D_{3d}	27.5	41.0		
9	0401	T_d	84.6	72.6		71.9
10	4001	S_4	81.2	90.1		91.1
11	3107	C_{3v}	55.6	55.5		56.1
12	2001	C_{2v}	37.1	54.4		
19	0241	C_{2v}	173.1	157.6		
20	0131	C_s	65.8	61.0		
21	0041	D_{2d}	48.5	70.5		
22	0222	C_{2v}	74.9	78.4		

[a] Energies are given in kcal mol^{-1} relative to two molecules of benzene. Energy (3-21G//3-21G) of benzene: −229.419 445 490 au. Energy (6-31G*//3-21G) of benzene: −230.703 066 409 au. [b] From ref 19; the value for 4 is from ref 20. [c] 6-31G*//STO-3G energies from ref 24. Arbitrarily set relative to twice the 6-31G*//3-21G energy for benzene from footnote *a*. [d] This value was calculated with the program GAMESS. Its energy is referenced to the 6-31G*//3-21G energy for benzene from footnote *a*.

Recent shock-tube data have been interpreted to suggest that benzene dimerizes at high pressures.[18] Interest in benzene dimers has centered on their stability and mode of dissociation, concerted or stepwise. Semiempirical MNDO and GVB calculations have been used to study the relative stabilities of some possible dimers,[19] with MNDO calculations applied to an examination of their reaction paths.[20] The latter study suggested **4** as the most likely benzene dimer. Some high-level calculations of hexaprismane have recently appeared, comparing it to other members of the prismane family.[21]

The highly symmetrical molecule truncated tetrahedrane (**9**) has also proven to be a challenging target. Synthetic efforts reported to date have all relied on Woodward's suggestion that it could be produced by an allowed ${}_{\pi}2_{a} + {}_{\pi}2_{a} + {}_{\pi}2_{a} + {}_{\pi}2_{a}$ photocyclization of the twisted tetraene, **10**.[22] Efforts to produce that tetraene have not been successful,[23] so the question of whether or not it provides an appropriate chromaphore has yet to be addressed. Lack of a chromaphore might not be a problem if, as a recent ab initio molecular orbital study suggests, the isomerization is exothermic.[24] In that event, catalytic methods, based on Lewis or Brønsted acids or radical ions, might be possible. Another related compound is the cyclopropatrishomobenzene (**11**). Compound **11** is also of interest as a possible trishomoaromatic molecule.


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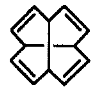
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This paper presents calculated structures and energies for a number of $(CH)_{12}$ hydrocarbons. First, we attempt to determine the most stable isomer of the family. We then present calculated energies for various isomers reported to date so that they can be compared across the board. Possibilities for fragmentation of benzene dimers and isomerization of molecules related to truncated tetrahedrane are re-examined. Finally, some new possibilities for isomerization of $(CH)_{12}$ hydrocarbons are proposed.

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Table II. Energies for Reactions at Various Levels[a]

method	eq 1[b]	eq 2[b]	eq 3[b]	eq 4[b]	eq 5[b]
RFH/3-21G	−0.4	56.0	18.4	32.1	18.5
RHF/6-31G*	13.6	33.9	20.4	20.7	13.3
RHF/6-31G**	13.0	31.8	19.3	19.3	12.9
RHF/6-311G**	7.7	30.1	15.1	20.1	13.0
RHF/6-31+G*	8.7	31.4	16.3		
MP2/6-31G*	27.1	34.7	29.7		28.5
expt[c]	11.9	30.6	18.2		

[a] Energies in kcal mol^{-1}. Derived from data in Table III (see supplementary material). [b] See text. [c] Calculated from data in ref 31.

Methods

Geometries were optimized using the force method[25] with the 3-21G basis set[26] using the GAUSSIAN-82 program.[27] Energies were calculated with the polarized 6-31G* basis[26] at the optimal geometries (RHF/6-31G*//RHF/3-21G). These calculations used GAUSSIAN-86, GAUSSIAN-88, or GAMESS.[27] The energetic results are given in Table I. Complete geometrical information is provided in the supplementary material.

It has been found that small split-valence basis sets such as 3-21G give a good accounting of the geometries of normal-valent molecules,[28] and we have recently shown that, for compounds containing a variety of small rings and multiple bonds, the geometries calculated with this smaller basis set are very similar to those obtained with the 6-31G* basis.[29]

Some direct results are available to support the use of 3-21G-optimized geometries instead of the more expensive 6-31G* ones. Geometries optimized at the 6-31G* level are available for benzene[30] and the two most symmetrical $(CH)_{12}$ isomers, hexaprismane[21] and truncated tetrahedrane.[24] The energies of the 6-31G*-optimized structures are lower than our 6-31G*//3-21G results by 0.0, 1.7, and 1.3 kcal mol^{-1}. Bond distances change by as little as 0.002 Å for the C–C bond in benzene; the largest change is 0.014 Å for either type of C–C bond in truncated tetrahedrane. Bond angles are comparably well reproduced.

In general, the highest possible point-group symmetry was assumed during the optimization. This minimizes the degrees of freedom of the molecule, simplifying the optimization process. Of course, the energetic minimum could well be a lower symmetry structure. The rigidity of most of these molecules, enforced by bridging, small rings, and multiple bonds, argues that such structures would not differ too much from the symmetrical forms. If this is so, their energies should be close to those reported here. Compound **1** is the least likely to attain its highest possible symmetry (C_{2v}); its geometry is discussed below.

In the case of truncated tetrahedrane, the high symmetry and large number of symmetrically related atoms caused problems with the force optimization in the GAUSSIAN-82 program. Three hydrogen atoms were distorted slightly to lower the symmetry from T_d to C_{3v}. In the final structure these hydrogens were distorted by less than 0.000 01 Å, indistinguishable from tetrahedral symmetry.

Due to the sizes of the systems involved, vibrational frequencies at the optimum geometries were not calculated. Such calculations would characterize the geometries as stable structures, transition structures, or higher-level stationary points on the potential surface.

While the 3-21G basis leads to reasonable geometries, reliable energetic results, especially on systems with the distorted bond angles found in small rings, require a basis set containing polarization functions. It has recently been shown that group additivity relationships can be used to convert Hartree–Fock energies to enthalpies of formation of hydrocarbons.[34,35] The methods reported to date find good agreement when 6-31G* energies are used. Additivity relationships based on 3-21G energies fail for strained molecules.[35] As Table I shows, there is poor agreement between the 3-21G and 6-31G* energies for the $(CH)_{12}$ hydrocarbons.

These group additivity methods use a single energy increment for all CH units and for molecules composed entirely of CH units would predict that relative energies from ab initio calculations would equal relative heats of formation. Thus, we take our relative energies as relative heats of formation. Direct calculation of heats of formation from electronic energies[33] would require vibrational frequencies, which were not obtained.

To see whether yet larger basis sets, or use of correlated wave functions, would lead to changes in our results, we have calculated RHF energies (at 3-21G optimized geometries) for ethylene, cyclopropane, and cyclobutane with the 3-21G, 6-31G*, 6-31G**, 6-311G*, and 6-31+G* basis sets[26] and MP2 energies with the 6-31G* basis set. Compounds **1a**, **4**, and **8** were also treated at these higher levels. The energies for the interconversion reactions below are given in Table II. The electronic energies from which they are calculated are given in Table III (see supplementary material).

$$2\,\text{cyclopropane} \rightarrow 3\,\text{ethylene} \qquad (1)$$

$$3\,\text{cyclobutane} \rightarrow 4\,\text{cyclopropane} \qquad (2)$$

$$\text{cyclobutane} \rightarrow 2\,\text{ethylene} \qquad (3)$$

8 1a

(4)

8 4

(5)

The 3-21G energies differ significantly from the larger basis set results and from the experimental heats of reaction.[31] As expected, the smaller basis destabilizes cyclopropane by about 7 kcal mol^{-1} and cyclobutane by about 2 kcal mol^{-1} relative to ethylene. No experimental data are available, but the change for eq 4 and 5 is consistent with this destabilization. The 6-31G* results are in good agreement with experiment. Adding a set of p-type functions to hydrogen (6-31G**) improves the agreement with experimental heats, but the change is not great. Neither do the energies for the $(CH)_{12}$ hydrocarbons change much.

A basis set with three sets of valence functions for carbon (6-311G*) has a noticeable effect on eq 1 and 3, as though the larger basis set stabilizes ethylene by 2 to 2.5 kcal mol^{-1}, but this stabilization is absent in the $(CH)_{12}$ compounds (eq 4 and 5). Since the small molecule reactions involve comparisons of molecules of different sizes, this may be a basis set superposition effect. Apart from this change, increasing basis set size produces only small changes in the energetics. The 6-31+G* basis set, in which carbon atoms are augmented with very diffuse functions, behaves similarly.

Correction for electron correlation at the MP2 level destabilizes ethylene by about 4.5 kcal mol^{-1} relative to cyclopropane or cyclobutane. This change leads to poorer agreement with experiment for eq 1 and 3. Similar behavior is observed for the $(CH)_{12}$ hydrocarbons in eq 5. The isomerization, which involves formation of 4 new double bonds, is calculated to be 15.5 kcal mol^{-1} more endothermic by the MP2 results than by RHF. This is 3.8 kcal mol^{-1} per double bond. Higher orders of perturbation theory would presumably lead to further changes in energies,[32] but calculations along these lines were not pursued.

In the following discussion the RHF/6-31G* energies are used. The main conclusions would not be changed if MP2 results were used. Energy

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(36) The lowest point on the $(CH)_{12}$ energy surface is two molecules of benzene. The relative energies in Table I reflect this fact, and several attempted syntheses of compound **10** have yielded only benzene, cf. ref 23.

differences would be of different sizes, but they would usually not change sign. The most stable isomer found has no double bonds. Equation 5 shows that MP2 results will make it appear even more stable relative to **4**. MP2 results should show increased stability with respect to other isomers as well. Most of the energy changes for isomerizations are either large or involve molecules with similar structural features. The most pronounced differences anticipated would be that **9** and **11** would be much nearer in energy, and **3** and **6** would no longer be nearly isoenergetic.

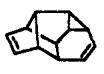
Results

The Global Minimum of the $(CH)_{12}$ System. Many kinds of hydrocarbon isomerizations are known. Under reversible conditions, isomerization will be controlled by the relative stabilities of the equilibrating species. So, it is of interest to determine relative energies and to find the most stable $(CH)_{12}$ hydrocarbon.[36] There are too many isomers to examine all possibilities with ab intio calculations. Instead, we limit the field by assuming that the presence of strained three- or four-membered rings or carbon–carbon double bonds will all destabilize molecules about equally. Likely candidates for the most stable isomer are those that have the fewest of these structural features. This analysis is simplified by Balaban's tables,[6] where isomers are ordered by just these three elements. There are 2 molecules with two strain elements each, 12 with three, and 64 with four.

This simple analysis should not be taken too far. The increase of strain with increasing number of double bonds and small rings is neither linear nor even monotonic. For example, compound **12** with two double bonds is only 1 kcal mol^{-1} more stable than **11**, which has four strain elements (three double bonds and a three-membered ring). Further, compound **2** with five strain elements (four double bonds and a 4-membered ring) is more than 30 kcal mol^{-1} more stable than **10**, which has only four strain elements (all double bonds).

The compounds with only two strain elements, compound **8** and the bridged sesquinorbornadiene **12**,[37] along with **4** and **11**, are the most stable of all those reported here. Compound **8** is calculated to be the most stable by more than 10 kcal mol^{-1}. We suggest that it will prove to be the most stable of all the $(CH)_{12}$ isomers. The nearest competitors studied here, compounds **2**, **4**, **11**, and **12**, all contain at least two double bonds. As noted above, calculations at the MP2 level should destabilize them further relative to **8**.

Using molecular mechanics,[38] we have examined all of the plausible stereoisomers of all of Balaban's structures. We find only two structures (**13** and **14**) comparable in energy to **8**. Due to their lack of molecular symmetry, these species have 66 independent geometrical parameters each. Geometry optimization of these molecules, even with the 3-21G basis, was not feasible. However, they cannot be ruled out as possibilities for the most stable isomer of the $(CH)_{12}$ family. A recent study by Dodziuk and Nowinski reported molecular mechanics calculations for **5**, **8**, and **9**.[39] The same energy ordering was found as in this work, but **8** was calculated to be much closer to **9** in energy.

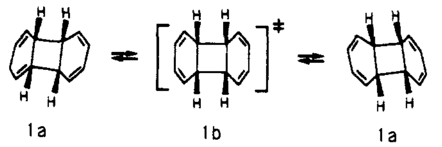

13


14

The stability of the carbon framework of **8** is consistent with its known chemistry. The formation of its only known derivative[17] involves a carbocation rearrangement from another $(CH)_{12}$ skeleton to give a *bisseco*-derivative. Closure of the three-membered rings by a Bamford–Stevens reaction also occurs cleanly.

Benzene Dimers. The relative energies of the benzene dimers reported here differ considerably from those of refs 19 and 20. The MNDO energies reported there are provided in Table I for comparison purposes. That work relied on MNDO geometry optimizations and minimal basis set ab initio molecular orbital calculations. These treatments lack the polarization functions necessary for describing the small rings involved. The GVB treatment and inclusion of configuration interaction added subsequently will not alleviate this problem, since they are based on the same, non-polarized basis. The unlikely stability attributed to hexaprismane is evidence of this deficiency.

Of all the molecules in this study, compound **1** is least likely to adopt its most symmetrical structure. A twisting distortion to C_2 (**1a**) from C_{2v} (**1b**) would relieve eclipsing and steric interactions between the six-membered rings. A geometry optimization was performed beginning with the twisted geometry predicted by molecular mechanics. The optimized geometry is indeed C_2, with the rings twisted nearly 20°. This structure is less than 1 kcal mol^{-1} lower in energy than the C_{2v} structure, which is presumably the transition structure for interconverting enantiomeric forms of **1**.



1a 1b 1a (6)

The relative energies of **1** and **2** from the MNDO calculations of ref 19 are similar to those found here. Since these compounds have similar structural features, MNDO treats them equally well (or equally poorly). Even when compound **1** is allowed to relax to C_2 symmetry, it is still less stable than the anti isomer. This opposes the suggestion, based on kinetic evidence, that the anti isomer is the more stable of the two.[7] Despite the energy ordering reported here, differential entropies or heat capacities may still make **2** less stable than **1** in terms of room temperature free energy.

The Diels–Alder adduct **4** proves to be the lowest energy benzene dimer. This is in contrast to previous work where the two 2 + 2 dimers are calculated to be more stable. Since the Diels–Alder is a Woodward–Hoffmann allowed reaction, **4** stands as the most plausible candidate for a benzene dimer. On the basis of a study of the reaction coordinate for benzene dimerization, a similar conclusion was drawn by Engelke.[20]

Despite its apparent strain, the quadruply bridged dimer, **3**, is calculated to be slightly more stable than para-bridged **6**. The relative energies of these two compounds are too close to guarantee this ordering, but it is clear that **3** and **6** cannot be much different in stability. A stepwise decomposition of hexaprismane to **6** would proceed through **3**. It is then unlikely to proceed to **6**, but rather will form the ortho-bridged dimer, **1**. That rearrangement is exothermic by 20 kcal mol^{-1}. The MP2 correction would make conversion of **3** to **6** endothermic by 10 kcal mol^{-1}.

Truncated Tetrahedrane Precursors. The relative energies of **9**, **10**, and **11** are not very different from those of Schulman and Disch.[24] That work reports 6-31G* energies calculated at STO-3G-optimized geometries. The difference between 3-21G and STO-3G geometries in these systems is small, so the energies are similar. Truncated tetrahedrane is predicted to be more stable than the S_4 tetraene by about 20 kcal mol^{-1}. Cyclopropatrishomobenzene is even more stable. Stepwise rearrangements from **10** to **9** will be hard pressed not to yield **11** instead. Photochemical routes may be required to effect this conversion.

Compound **11** is also interesting as a potentially aromatic molecule. Its three π bonds are held near in space, albeit their relative orientation is head-on rather than side-by-side as in benzene. The fact that the π systems are not directly connected to each other should have no effect on cyclic delocalization other than that expected from their increased separation. Several potential trishomoaromatic molecules, including 1,4,7-cyclononatriene,[40] triquinacene,[41] Paquette's C_{16} hydrocarbon,[42] and

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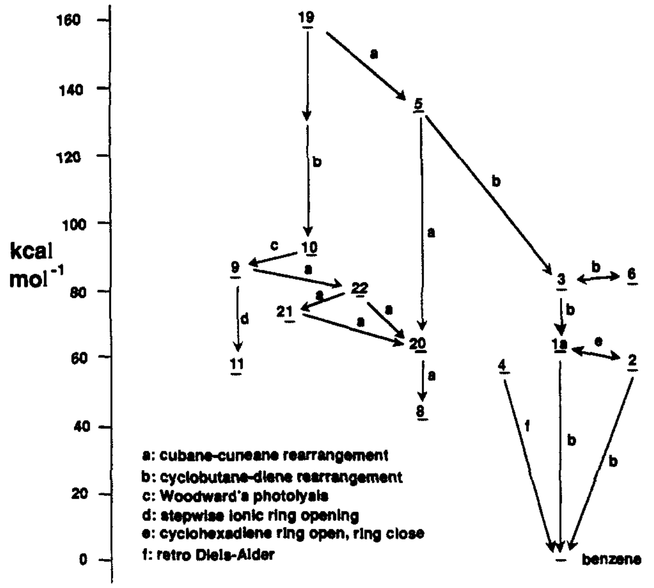


Figure 1. Relative energies of various hydrocarbons and possible isomerization reactions.

McMurry's triene[43] (**15**–**18**) have been studied in this context. No strong case for aromatic stabilization has yet been advanced.


15


16


17


18

Compound **11** is very similar to **15** in geometry. The distance between nonbonded sp^2 carbons is 2.46 Å in each case. Like **15**, it is unlikely to show aromatic delocalization. The calculated splitting between the a- and e-symmetry π orbitals is 0.05 au compared to 0.17 au for benzene at the same level of theory (6-31G*//3-21G).

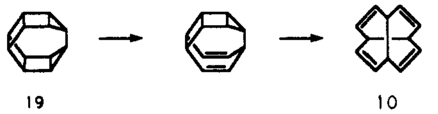
Possible Isomerization Products. Polycyclic hydrocarbons isomerize thermally,[44] photochemically, under the influence of Brønsted and Lewis acids, and in the presence of transition metals.[45] Recently, an entirely new class of hydrocarbon isomerizations has been discovered. These involve high-temperature heterogeneous reactions of hydrocarbons with metal catalysts. One spectacular result has been conversion of the hydrocarbon pagodane to dodecahedrane.[46]

Several isomerization reactions were mentioned above. We now consider some consequences of two types of isomerizations, their likely energetics, and products to be expected from them. These isomerizations are compared graphically in Figure 1. Prediction of the likelihood of these rearrangements would require study of the reactive intermediates (cations, diradicals, metal surface-bound species, etc.) and of the reaction coordinates involving those intermediates. Such studies are far beyond the scope of the present work. Instead, we present here a limited set of energies for neutral hydrocarbons that might be products or structurally related to intermediates in such rearrangements in order to arrive at a first guess about hydrocarbon isomerizations.

The most famous hydrocarbon isomerizations are those of cubane. In the presence of rhodium complexes, it isomerizes to tricyclooctadiene (eq 7). Similar reactions have been observed in other systems. Their common structural feature is the conversion of a strained cyclobutane to a pair of carbon–carbon double bonds.

(7)

The reversion of benzene dimers could be catalyzed in this way. The thermodynamics will be the same as discussed above for thermal ring opening. Conversion of hexaprismane to **3**, as well as opening of either **1** or **2** to benzene, is very exothermic. Of the intermediate reactions, opening of **3** to **1** is not very exothermic, and its opening to the para-bridged dimer, **6**, is predicted to be slightly endothermic. Many other possible cyclobutane–diene rearrangements among $(CH)_{12}$ hydrocarbons are possible. In an extreme case, tetraene **10** is one of several possible cyclobutane–diene rearrangement products of the very strained compound **19** (eq 8). The intermediate diene, an analogue of semibullvalene, was not considered in this study.

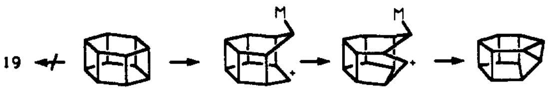

(8)

19 10

Another well-studied rearrangement of cubane is its conversion to cuneane in the presence of silver ion (eq 9).[47] This reaction proceeds through cationic intermediates beginning with opening of a bond in what is formally a bicyclo[2.2.0]hexane system.

(9)

Applying the cubane–cuneane formalism to hexaprismane would lead to compound **20**, which has not been previously studied. This rearrangement is tremendously exothermic, about 60 kcal mol^{-1} downhill in energy. Rearrangement from cleavage of a bond endocyclic to a 6-membered ring is also conceivable. This transformation leads to the cuneane-like hydrocarbon **19**. It is endothermic by 20 kcal mol^{-1} and should not be observed.

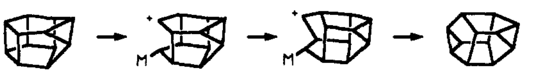


(10)

5 20

To date, efforts to observe a cubane–cuneane rearrangement in the homologous molecule pentaprismane have proven unsuccessful.[48] This may also be the case with hexaprismane, despite its tremendous strain. However, an argument can be advanced that the conversion of **5** to **20** will be more facile than the pentaprismane rearrangement.[49] In hexaprismane, the initial ring opening allows each cyclohexane ring to move from planarity, and the corresponding bond angles can relax from 120°. Since 5-membered carbocyclic rings prefer to be close to planar, the corresponding step for pentaprismane may not have as much driving force.

Further rearrangement of **20** converts it to the most stable $(CH)_{12}$ isomer, **8** (eq 11). This is exothermic by a further 20 kcal mol^{-1}.



(11)

20 8

Cubane–cuneane rearrangements could also form **20** from the symmetrical molecules **21** and **22**. The bonds that must open first are indicated by dashed lines in eq 12. One rearrangement begins with opening of the central bond of a bicyclo[2.2.0]hexyl system

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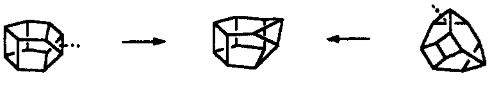
[49] This point is currently under study.

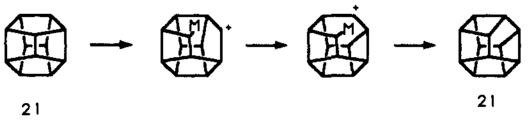
and the other with a cyclopropane ring, so both are plausible reaction paths. Initial cleavage of the other bond in the three-membered ring of **22** can lead to **21** directly.



(12)

Truncated tetrahedrane (**9**) can rearrange as well. The most likely path begins with cleavage of a cyclopropyl bond and leads to compound **22**. This creates a route from **9** to the most stable isomer, **8**.

Many other rearrangements of these hydrocarbons are possible, but they seem mechanistically less likely. Most, like the degenerate isomerization reaction of compound **21** (eq 13), involve initial cleavage of a relatively unstrained bond. Such reactions would require severe conditions, under which other processes would probably compete.



(13)

Conclusion

The chemistry of $(CH)_{12}$ hydrocarbons has been of interest for over 25 years, and recent results show no slowing of work in the area. Reports of preliminary investigations suggest that some very interesting members of this family will become available in the next several years. In advance of this, we have sought to discover likely chemical transformations of these molecules and to put our knowledge of their energetics on a more uniform footing. We believe that we have identified the most stable isomer of the family. Two other possibilities, **13** and **14**, have also been pointed out. Our relative energies for the benzene dimers should prove more accurate than those previously reported, and they can be compared to our results for other $(CH)_{12}$ hydrocarbons. We point out several relatively stable and symmetrical compounds, such as **20**, **21**, and **22**, which could prove of interest in the rearrangement chemistry of $(CH)_{12}$ hydrocarbons which will develop subsequently. It is particularly worth noting that compounds **5** and **9**, actively sought synthetic targets, may prove very susceptible to Lewis acid catalyzed rearrangement.

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Supplementary Material Available: Electronic energies for molecules used in constructing Table II and tables of internal (z matrix) and Cartesian coordinates for the optimized structures of all molecules in Table I (17 pages). Ordering information is given on any current masthead page.

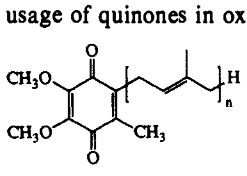
Interplay of Substituent Conformation and Electron Affinity in Quinone Models of Quinone Reductases

Howard H. Robinson and Scott D. Kahn*

Contribution from the Departments of Biophysics and Chemistry, University of Illinois, Urbana, Illinois 61801. Received August 9, 1989

Abstract: Nonempirical molecular orbital calculations were used to explore the electron affinities of model systems for ubiquinones and plastoquinones. An interconnection between substituent conformation on the quinone and the potential of the quinone–semiquinone couple is indicated. The role of this effect is discussed in the context of allosteric regulation/control of electron transfer reactions and/or charge storage in quinone-bearing proteins.

Quinones are lipid soluble enzyme cofactors that function as oxidation/reduction intermediaries between assemblies of the membrane-bound proteins of the energy conversion systems of photosynthetic and respiratory systems.[1] Ubiquinone (**1**) and plastoquinone (**2**) are biologically significant quinones, which possess alkoxy and alkyl substituents bound to the ring of a 1,4-benzoquinone, respectively. Within an energy conversion pathway, one set of enzymes reduces the quinone with two electrons and two protons to the neutral hydroquinone and another set of enzymes oxidizes the hydroquinones back to the quinone and liberates two electrons and two protons.[1] These oxidative and reductive processes must involve considerable reorganization of the quinone's electronic structure where the various charged transition states and intermediates are stabilized by the protein environment. For example, the radical anionic form of the quinone is known to be stabilized at the photosynthetic reaction center reductase quinone-binding site for minutes under certain conditions.[2] To help understand the mechanisms of both the oxidative and reductive reactions and, in particular, to understand how the radical anion is stabilized, we have undertaken a quantum mechanical analysis of the ground-state quinone and radical anionic form, the semiquinone. Knowledge concerning the influence of reaction site topology on the stability of the radical anion was sought by probing the relationship between quinone-substituent conformation and the electronic properties of the quinone moieties. Such information is needed to develop insight into nature's ubiquitous usage of quinones in oxido reductases.[3-5]



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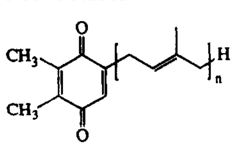

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*To whom correspondence should be addressed.

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