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New strained organic molecules: theory guides experiment

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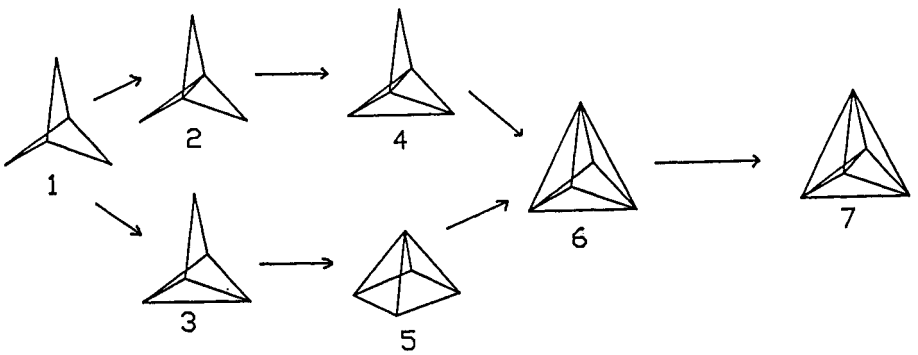
Abstract - The experimental program in this laboratory for the preparation of rare gas matrix-isolated hydrocarbons with highly strained carbon centers by gas-phase dehalogenation of polyhalides is guided by calculations of molecular geometry and vibrational spectra. In this communication are reported 6-31G SCF and MP2 as well as MNDO results for the highly strained molecules derived from the known stable hydrocarbons, bicyclo[1.1.1]pentane and [1.1.1]propellane. Several of these improbable looking structures are calculated to be stable in low temperature inert gas matrices. The calculated ab initio SCF and MNDO symmetries, bond lengths (Å), strain energies, and lowest vibrational frequencies are listed with the formulas.

INTRODUCTION

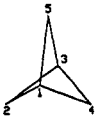
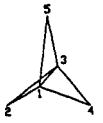
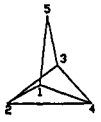
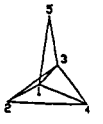
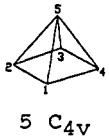
Gas-phase dehalogenation of organic dihalides with alkali metal vapors followed by trapping of the products in an argon matrix offers access to highly reactive molecules of unusual structures.[1] In recent years, the method was used to obtain the IR spectra of [2.2.1] propellane[2] and [2.1.1] propellane[3]. The synthesis of the last member of the series of simple propellanes, [1.1.1]propellane, which is stable and does not require such special techniques,[4] represents a landmark in the quest for highly strained small-ring organic molecules. Clearly, however, it does not represent the end of a road. One direction in which new horizons beckon leads us to hydrocarbons formally derived from bicyclo[1.1.1]pentane by the removal of not only one pair of hydrogen atoms and addition of one new bond, as in producing [1.1.1]propellane, but by a repeated sequence of such steps:



In principle, our dehalogenation - matrix isolation procedure could permit the generation of such currently improbable-looking species if we manage to synthesize the requisite starting polyhalides. Each such synthesis requires considerable effort and it would therefore appear prudent to inquire whether the synthetic targets represent stable structures. As the degree of steric strain increases, intuition rapidly becomes a rather unreliable guide -- after all, not so long ago, the [1.1.1]propellane structure itself looked improbable. For the purpose of matrix isolation spectroscopy, stability means merely the absence of unimolecular decomposition modes with activation barriers lower than, say, 5 or 10 kcal/mol, i.e., the existence of local minima on the ground state potential energy hypersurface. Stated in this way, the problem is clearly answerable in terms of currently available theoretical methods.

In addition to providing information on the energies and structures of the potential synthetic targets, the calculations also yield their vibrational frequencies. These are important not only because they provide some indication about the depth of the potential energy well, but also since the identification of the new matrix-isolated hydrocarbons, if they should indeed be formed, will clearly rely heavily on their vibrational spectroscopy. Because of the contemplated mode of synthesis, it is also of interest to check whether the target molecules do not have an unusually high electron affinity. This might lead to complications due to electron transfer from metal atoms in the matrix. Last but not least,

Table I. Optimized structures for 1 - 7.

molecule symmetry[a]	geometry parameters[b]	MNDO	HF 6-31G*	MP2 6-31G*	Exp. Results
	$r(C_1-C_2)$	1.573	1.546		1.557
	$r(C_1-C_3)$	1.895	1.870		- - -
	$r(C_2-C_4)$	2.175	2.132		- - -
	$r(C_1-H)$	1.083	1.082		1.097
	$r(C_2-H)$	1.101	1.085		1.102
1 D_{3h}	HC_2H	123.3	111.0		111.2
	$r(C_1-C_2)$	1.556	1.503	1.514	1.525
	$r(C_1-C_3)$	1.631	1.544	1.592	1.596
	$r(C_2-C_4)$	2.296	2.233	2.230	- - -
	$r(C_2-H)$	1.097	1.076	1.088	1.106
2 D_{3h}	HC_2H	109.9	118.7	114.9	116.0
	$r(C_1-C_2)$	1.556	1.509	1.517	
	$r(C_1-C_3)$	1.988	1.940	1.945	
	$r(C_1-C_5)$	1.549	1.534	1.535	
	$r(C_2-C_4)$	1.492	1.435	1.453	
	$r(C_1-H)$	1.078	1.075	1.086	
	$r(C_2-H)$	1.068	1.068	1.078	
	$r(C_5-H)$	1.102	1.086	1.097	
	HC_5H	108.7	110.7	111.0	
	HC_1C_5	129.1	132.4	132.9	
	HC_2C_4	142.7	137.6	136.7	
3 C_{2v}	$[C_5C_1C_3C_2]$[c]	141.5	141.6	141.4	
	$r(C_1-C_2)$	1.532	1.455	1.476	
	$r(C_1-C_3)$	1.757	1.628	1.688	
	$r(C_1-C_5)$	1.540	1.508	1.516	
	$r(C_2-C_4)$	1.537	1.492	1.506	
	$r(C_2-H)$	1.065	1.065	1.076	
	$r(C_5-H)$	1.099	1.077	1.090	
	HC_2C_4	143.4	144.9	143.8	
	HC_5H	110.7	114.8	114.6	
4 C_{2v}	$[C_5C_1C_3C_2]$[c]	142.2	141.8	141.5	
	$r(C_1-C_2)$	1.482	1.434	1.445	
	$r(C_1-C_3)$	2.095	2.028	2.044	
	$r(C_1-C_5)$	1.692	1.620	1.645	
	$r(C_1-H)$	1.077	1.068	1.080	
5 C_{4v}	HC_1C_5	130.8	121.3	119.4	
	$r(C_1-C_2)$	1.542	1.464	1.473	
	$r(C_1-C_3)$	2.032	1.806	1.781	
	$r(C_2-H)$	1.079	1.066	1.077	
6 D_{3h}	$r(C_2-C_4)$	2.001	2.056	2.109	
	$r(C_1-C_2)$	1.545	1.487[d]	1.489	
	$r(C_1-C_3)$	1.619	1.710[d]	1.909	
7 D_{3h}	$r(C_2-C_4)$	2.279	2.107[d]	2.002	

(a) Determined by optimization at the MNDO and HF/6-31G* levels, assumed at the MP2 level; (b) Bond lengths in Å, bond angles in degrees; (c) dihedral angles; (d) at the HF level the D_{3h} structure is not stable and at the MP2 level the stability has not been tested.

the calculations will provide information about the nature of bonding in the target molecules, several of whose structures violate the usual bonding concepts to a remarkable degree.

METHOD OF CALCULATION

Although the structures in question are very different from any of those used in the parameterization of semiempirical methods, we felt that it would be useful to perform initial geometry optimizations by the extremely rapid MNDO method.[5] Further calculations were performed using the GAUSSIAN 82 program[6] and the 6-31G* basis set with six cartesian d components. The geometries were first optimized at the Hartree-Fock SCF level and then at the second-order level of many-body perturbation theory (MP2), using analytical gradient procedures. In the MP2 calculation all electrons were correlated but the point group derived from the SCF calculation was imposed. Harmonic normal mode vibrational frequencies have been calculated only at the SCF level so far. Heats of formation and strain energies were calculated, using the group-equivalent schemes of Wiberg[7] and Schleyer et al.[8], respectively, at the SCF level. Ultimately, we expect to base all our conclusions exclusively on results obtained at the MP2 level since we view the SCF approximation as suspect for molecules of this kind, and to probe even beyond, but this is unfortunately not yet possible in this progress report.

RESULTS AND DISCUSSION

The calculated geometries are presented in Table I; for all of the species they correspond to local minima at the HF and MNDO levels, except for 7 at the HF level and for **5** at the MNDO level. The computed lowest vibrational frequencies are quite high, supporting the absence of extremely small reaction barriers. The HF and MP2 total energies together with HF dipole moments and the lowest SCF harmonic vibrational frequencies are given in Table II. Table III contains the heats of formation and strain energies at the HF and MNDO levels. Heats of hydrogenation are presented in Table IV.

Table II. Calculated Total Energies, Dipole Moments and Lowest Vibrational Frequencies.

molecule	Total energies[a]		HF/6-31G*	
	HF/6-31G*	MP2/6-31G*	μ	ν̃
1	-193.90568		0.0	591 (e')
2	-192.69107	-193.37471	0.0	577 (e')
3	-192.68524	-193.35305	-0.58	512 (b_2)
4	-191.42314	-192.10369	0.33	475 (b_2)
5	-191.45834	-192.12403	1.97	414 (e')
6	-190.17886	-190.84288	0.0	653 (e')
7	-188.83663	-189.51932	0.0	i297 (e")

(a) In Hartrees; (b) All electrons were correlated; (c) Dipole moment in Debye; (d) The lowest vibration (cm^{-1}).

Table III. Calculated Heats of Formation[a,b] and Strain Energies[a,c].

molecule	ΔH_f(298 K)		Strain Energy	
	MNDO	HF/6-31G*	MNDO	HF/6-31G*
1	58.3	50.4	78.0	70.1
2	172.7	88.5	188.7	104.5
3	100.7	96.0	114.4	109.8
4	237.8	164.0	247.8	174.0
5	-----[d]	143.8	-----[d]	152.7
6	346.5	222.6	351.8	228.0
7	492.0	-----[d]	493.5	-----[d]

(a) kcal/mol;
(b) based on Wiberg's group equivalent table[7];
(c) based on the group equivalent table suggested by Schleyer et al.[8];
(d) unstable at this approximation.

Table IV. Heats of Hydrogenation[a]

2	→	1	-46.9
3	→	1	-49.6
4	→	2	-79.1
4	→	3	-76.4
5	→	3	-54.1
6	→	5	-87.2
6	→	4	-64.9

[a] $\Delta H°$ (0K) in kcal/mol

The known hydrocarbons **1** and **2** provide a good starting point for a discussion. Our optimized geometries agree well with those calculated previously[9] and with experiment.[10] The MNDO method tends to overestimate and the HF method tends to underestimate the experimental C-C bond lengths. The experimental heat of formation is not known for **1** but the two methods of calculation are in reasonable agreement. However, MNDO overestimates the heat of formation for **2** very badly, while the HF value agrees well. Even the earlier ab initio calculation[11] without any polarization functions predicted ΔH_f(298 K) for **2** to be about 96 kcal/mol, and MINDO/3 predicts ΔH_f (298 K) to be 101 kcal/mol.[12] Based on these facts, we conclude that the MNDO method is unlikely to provide reliable heats of formation for molecules **3**-**7**. Even though we list the results of MNDO calculations, our discussion will be based on the ab initio results.

3: Although the parent hydrocarbon is unknown, its derivatives have been synthesized and are stable.[13] Results of a previous calculation[14] at the extended Hückel level were used to discuss the possibility of bond stretching isomerism between **3** and a biradical obtained by stretching the C_2-C_4 bond, and of rearrangements of the carbonium ion resulting from hydride abstraction on C_5. It is interesting to compare the computed geometries of **3** and of bicyclo[1.1.0]butane, available at the HF/6-31G* level.[15] The dihedral angle between the $C_1C_2C_4$ and $C_3C_2C_4$ planes is 93.9° as compared to a value of 72.7° in bicyclo[1.1.0]butane. The computed C_1-C_2 bond length in **3** is longer by about 0.02 Å, and the C_2-C_4 bond length shorter by about 0.03 Å and thus noticeably shorter than normal. The hydrogens at C_2 and C_4 do not show appreciable deviation from the bicyclobutane geometry.

With respect to **1**, the C_1-C_5 distance in **3** decreased by 0.012 Å, the C_1-C_3 distance increased by 0.07 Å, and the methylene hydrogens remain unaffected. The dihedral angle between the $C_1C_2C_3$ and $C_1C_3C_4$ planes decreased by 43.2° from the 120° value in **1**.

The shortening of C_2-C_4 bond and the lengthening of C_1-C_2 bond compared to bicyclobutane probably reflect the more strongly bent nature of the C_2-C_4 bond due to an increase in p character of the C_2-C_4 bond and a concomitant increase in the s character of C_1-C_2 and C_2-H bonds.

Relative to its isomer **2**, **3** is predicted to be 3.7 kcal/mol higher in energy at the HF level and this difference is seen in the computed strain energy as well. It is 13.6 kcal/mol higher at the MP2 level and the inclusion of correlation thus seems to be much more important for **2** than for **3**. In agreement with the known properties of its substituted derivatives, **3** should not be a particularly difficult synthetic target.

4: This tetracyclic compound can be viewed as a cyclopropane ring fused to one of the edges of tetrahedrane. No previous calculations are available. Compared to tetrahedrane at the HF level, the C_2-C_4 bond length is longer by 0.03 Å and the C_1-C_2 bond length is shorter by 0.008 Å. The fusion of a cyclopropane ring at the C_1-C_3 bond edge causes the C_1-C_3 bond to lengthen by 0.165 Å compared to tetrahedrane and by 0.131 Å compared to cyclopropane. The hydrogens attached to C_2 and C_4 do not change much as compared to tetrahedrane. The C_1-C_3 bond is expected to be quite similar to the C_1-C_3 bond in [1.1.1]propellane. However, the bonding between C_2 and C_4 increases strain in the molecule and causes the C_1-C_3 bond to lengthen by 0.084 Å. The C_1-C_5 bond is longer by 0.011 Å than the C-C bond in cyclopropane. The methylene hydrogen positions do not change much relative to **2** and **3**.

As usual, the MP2 bond lengths are larger than the corresponding HF bond lengths. The C_1-C_3 bond length increases by 0.06 Å whereas all the others only by about 0.02 Å. This shows that a high level of electron correlation is important particularly in describing the bridgehead-bridgehead bond.

The calculated strain energy of **4** is about 19 kcal/mol higher than the sum of strain energies of cyclopropane and tetrahedrane. The hydrogenation of **4** to form **2** is more exothermic by 2.7 kcal/mol compared to the formation of **3**, and in this sense the C_1-C_3 bond is slightly stronger than the C_2-C_4 bond. We conclude that **4** represents a promising synthetic target, particularly since the usual plague of the efforts to synthesize unsubstituted tetrahedrane, rearrangement to cyclobutadiene,[16] should be prevented by the presence of the additional three-membered ring.

5: Three-dimensional cage compounds are fairly common among boron hydrides, carboranes and transition metal compounds, but extremely rare among hydrocarbons. The simplest such structure is the as yet unknown parent tetrahedrane. The next member in the family of three-dimensional cage hydrocarbons is **5**, commonly known as [3.3.3.3]fenestrane or pyramidane.[17] The isolectronic protonated form, $C_5H_5^+$, was predicted to be stable in a pyramidal C_{4v} structure a long time ago.[14,18] Various derivatives of $C_5H_5^+$ have been identified,[19] but the neutral compound **5** or its derivatives have never been synthesized. It has already been reported[20] that the pyramidal form of **5** corresponds to a local minimum and is stable towards isomerization at the MINDO and HF/STO-3G and 4-31G levels of calculation. Since pyramidane is clearly highly strained, it is desirable to include polarization functions and electron correlation to improve the reliability of the calculations.

At the HF/6-31G* level, a C_{4v} structure indeed remains as a local minimum for **5**. However, MNDO calculations do not show a local minimum for the C_{4v} structure. In comparison with the STO-3G geometry,[20] the apex-basal C_1-C_5 distance is decreased from 1.678 Å to 1.620 Å at the 6-31G* level. The addition of correlation at the MP2 level predicts the C_1-C_5 bond length to be 1.645 Å. The basal C_1-C_2 bond lengths are predicted to be 1.434 Å at the HF/6-31G* level and 1.445 Å at the MP2 level compared to the STO-3G value of 1.453 Å. The C-H bond lengths change from 1.068 Å at HF/6-31G* to 1.08 Å at MP2. The most interesting aspect of the pyramidal structure is the displacement of H atoms from the planar positions towards the apical carbon atom. As pointed out earlier,[21] this is due to the more effective overlap between the p orbital of the apex carbon and the tilted π orbitals of the planar ring. The direction of bending, towards or away from the apical carbon, is expected to depend on the number of carbon atoms in the ring, the effective size of the p orbital of the apical carbon and the ring-apex distance. In the case of **5**, the H atoms were predicted[21] to move towards the apex carbon. In agreement with this prediction, the H atoms are shifted by 7.5° at the HF and by 9.0° at the MP2 level. The out-of plane bending of the H atoms lowers the HF energy by 3.0 kcal/mol. The dipole moment of **5** calculated with 4-31G[20] and 6-31G* basis sets at the HF level were found to be the same, about 2 Debye, even though the atomic charges derived from Mulliken Population analysis are quite different. The 4-31G basis set[20] predicts the charge on the apical carbon atom to be -0.114 and that on the basal carbon atoms to be -0.211 units, whereas the 6-31G* set predicts the charges to be -0.185 and -0.193, respectively.

The HF energy difference between the two isomers **4** and **5** is 21.9 kcal/mol, with **5** more stable. At the MP2 level, this energy difference is reduced to 12.7 kcal/mol. As we mentioned earlier, this result is consistent with the effect of electron correlation being particularly important for the "inverted" bridgehead-bridgehead bonds. If we consider the molecules **4** and **5** to have eight formal C-C bonds, the strain energy per C-C bond is about 19.1 kcal/mol in **5** as compared to 21.8 kcal/mol in **4**. Even **5** does not look like an impossible target molecule.

6: The introduction of a C_4-C_5 bond in **4** or the introduction of a C_1-C_3 bond in **5** leads, after geometry optimization, to the same result, a local minimum in the potential energy surface at a D_{3h} geometry for C_5H_2. This structure corresponds to two face-fused tetrahedranes and belongs to the class of three-dimensional caged hydrocarbons. No trigonal bipyramidal hydrocarbons seem to have been previously calculated to be stable.[21] From extended Hückel calculations,[14] it was concluded that the D_{3h} trigonal bipyramidal structure for $(CH)_5^+$ corresponds to an energy saddle point. However, the closo carborane, $C_2B_3H_5$, is known to exist in a trigonal bipyramidal structure.[22] The compound **6** is isoelectronic with it and is derived from the hypothetical $C_5H_5^{+++}$ trication by triple deprotonation. Therefore, a trigonal bipyramidal structure for **6** is actually highly likely. To obey the (2n+2)-electron count as in closo boranes and carboranes,[23] the two CH groups at the bipyramidal capping positions in **6** contribute 3 electrons each, and each of the three carbon atoms in the trigonal positions contributes 2 electrons, and keeps two in a lone pair, making up a total of 12 electrons for the framework bonding. It is interesting to see how the cage structure forces the molecule to behave as if it were electron deficient by expelling electrons into lone pairs.

At the HF level, the lowest vibrational frequency is quite high, 653 cm^{-1} (e′ symmetry). The C_1-C_2 bond length was found to be essentially the same as the C-C bond length of tetrahedrane at the same level of theory. However, the three C-C bonds shared between two tetrahedranes are longer by 0.343 Å than in tetrahedrane (ca. 1.463 Å). As usual, the C_1-C_2 bond length increased when electron correlation at MP2 level was included, from 1.464 Å to 1.473 Å. However, for the C_1-C_3 bond we found that at MP2 level the bond length decreased from 1.806 to 1.781 Å. The C-H bond lengths were found to be slightly shorter than normal.

The hydrogenation of **6** can result in the formation of **5** or **4**. At the HF level, contrary to what we observe for compounds **2**, **3**, and **4**, the hydrogenation that results in the breaking of the C_1-C_5 bond is more exothermic by 22.3 kcal/mole compared to the breaking of the C_1-C_2 bonds. The isodesmic reaction of **6** with a cyclopropane to yield two tetrahedranes is endothermic by 26.6 kcal/mole.

The strain energy of **6** is awesome. If we consider the number of formal C-C bonds to be nine, the strain energy per C-C bond is 25.4 kcal/mole, much larger than the strain energy per C-C bond in previously calculated highly strained hydrocarbons. Clearly, although extremely attractive and possibly perfectly stable once isolated in a matrix, **6** will not be an easy target.

7: The removal of all the hydrogens from **1** takes us into the regime of atomic clusters. Recently, experimental advances in the production of atomic clusters and ab initio theoretical calculations have provided much insight into the structure and bonding aspects of carbon clusters.[24] Much of the initial theoretical work on carbon clusters assumed linear structures for carbon clusters with fewer than six atoms. The structure that is relevant to this work is the D_{3h} trigonal bipyramidal arrangement of five carbon atoms, and

this corresponds to a minimum at the MINDO/2 level.[25] In this calculation, the D_{3h} structure was found to be energetically lower than the linear structure. We also note that the MNDO calculations indicate a stable structure at D_{3h} symmetry for C_5. More recent ab initio calculations at various levels of sophistication have shown that the linear structure for C_5 is more stable than the trigonal bipyramidal form by about 94.5 kcal/mol (at the MP4/6-31G* level).[24c] Our calculations at the HF/6-31G* level show that the D_{3h} structure does not correspond to a local minimum. Although it is possible that such a structure is stabilized by electron correlation, we see little hope for it as a synthetic target.

CONCLUSIONS

Our calculations suggest that the highly improbable looking hydrocarbons **3-6** will be quite stable under conditions of matrix isolation. Problems with electron transfer from alkali atoms also present in the matrix may be encountered for those with particularly low energies of the lowest unoccupied molecular orbital: **6** (2.9 eV) and **5** (3.7 eV); the others have LUMO energies at 4.8 eV (**2**) and higher. This is only an extremely crude indicator of electron affinity but may serve as a warning. To correctly describe the bonding in these compounds, particularly the ones with "inverted" bridgehead-bridgehead bonds, higher levels of electron correlation are clearly required. In particular, our conclusion that the bridgehead-bridgehead bond is stronger than the methylene-methylene carbon bond, which is currently based on the HF/6-31G* level investigation of the hydrogenation reactions of **2**, **3** and **4**, must be viewed with caution because it is well known that electron correlation is very important for the correct description of the heats of hydrogenation reactions.

Additional work with correlated wavefunctions is necessary to understand the degree to which these molecules have biradicaloid nature, to study bond-breaking isomerism, to calculate the heats of hydrogenation reaction more accurately, and to predict their vibrational spectra more reliably. These efforts are underway. Semi-empirical methods like MNDO and MINDO/3 do not appear to be reliable for compounds of this class.

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