a good deal of bond breaking would have to occur in this mechanism as well. It is interesting that secondary KIE's which have been reported in the literature for homolysis of C–C bonds are in the range of 1.13–1.15,[30] close to the value measured here assuming 3-bond cleavage, and may reflect a similar fraction of σ bond cleavage in the transition state.

Conclusion

Although the observed KIE and the results of the calculations demonstrate that a concerted but nonsynchronous 3-bond cleavage of **1** by C is viable, they do not rule out the intermediacy of **2** or product-determining cleavage to **4** + **6**. However, the fact that no cyclobutane is formed in this reaction argues against the intermediacy of **2**. Since **2** represents a limit in a spectrum of transition states for the deoxygenation of **1**, it is reasonable to assume that modifications of substrate and/or products could lead to reactions in which **2** is an intermediate. This may be the case in the deoxygenation of **1** by C_2O[4] and the C atom desulfurization of tetrahydrothiophene[1] in which cyclobutane is formed in addition to **4**. It is possible that the increased exothermicity of the C atom deoxygenation of **1** as compared to the other two reactions is channeled into breaking the C_2–C_3 bond in the transition state. Finally is should be pointed out that, while the observed isotope effects demonstrate that **1** is not deoxygenated upon every collision with C atoms, they leave open the question of whether complex **3** is an actual energy minimum.

Experimental Section

Reaction of Atomic Carbon with 1. Carbon atoms were generated by the thermolysis of 5-diazotetrazole (**7**)[15] and reacted with gaseous **1**. In a typical reaction, **7** (from 1 mmol of amino precursor) was coated on the walls of a 500-mL flask and 0.6 mmol of gaseous **1** was introduced and **7** decomposed by heating the surface of the flask at 100 °C for 3 min. The products of seven such reactions were pumped into traps at −130 and −196 °C. The contents of the −196 °C trap were analyzed by IR for **4**. The yield of **4** averaged 1.5 × 10^{-2} mmol/flask. Analysis of the contents of both traps for cyclobutane, cyclopentanone, and dihydropyran by GC did not reveal these compounds. A similar analysis of the products of the reaction of arc generated carbon with **1** at 77 K revealed only ethylene.

Reaction of Atomic Carbon with a Mixture of 1 and 1-d_8. The reaction was carried out as described above with an equimolar mixture of **1** and **1**-d_8 (0.65 mmol). The contents of the −196 °C trap were analyzed for the deuterated ethylenes by IR spectroscopy. Only **4** and **4**-d_4 were present. The **4**:**4**-d_4 ratio was determined by IR with standards of known concentrations. The reaction was run twice, each time combining the contents of eight flasks giving an average yield of **4** of 4.70 × 10^{-3} mmol and of **4**-d_4 of 1.77 × 10^{-3} mmol leading to an average ratio of **4**:**4**-d_4 = 2.7 ± 0.2.

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A $(CH)_{12}$ Hydrocarbon of T_d Symmetry

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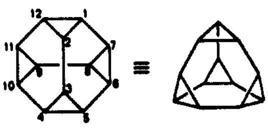
Abstract: We show by ab initio calculations at the 6-31G* SCF level that the $(CH)_{12}$ hydrocarbon **1** is kinetically stable in T_d symmetry. The calculated vibrational frequencies of **1** and of cubane, which serves as a model, are given. The lowest frequency of **1**, 375 cm^{-1}, is found for a t_1 mode. Structures of C_{3v} symmetry such as the triene **2** can be reached by t_2 distortions; however, the lowest frequency t_2 fundamental of **1** is calculated to be 500 cm^{-1}.

Few organic molecules or ions have the high symmetry of the cubic or icosahedral point groups. Those that do may become the subject of intense synthetic and theoretical interest, especially when they are also highly strained. In some cases, for example tetrahedrane[1] and dodecahedrane,[2] theoretical treatments have preceded their synthesis and structure determination. In fact, tetrahedrane has yet to be synthesized, and while its tetra-*tert*-butyl derivative has been prepared,[3] the X-ray structure of this compound is sufficiently complex that its interpretation indicating T symmetry[4] relies in part upon calculations.

The subject of this paper is compound **1**, whose presumed T_d symmetry derives from a carbon skeleton that is a tetratruncated tetrahedrane containing planar, saturated six-membered rings.[5]



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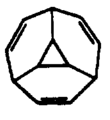

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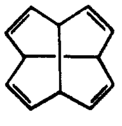

3

Several synthetic efforts have been directed toward **1** or its isomeric triene **2**[6] and tetraene **3**.[7] On the theoretical side, **1** has been considered from the viewpoint of orbital symmetry[8] and by ab initio molecular orbital theory assuming T_d symmetry.[9] Because of its high strain energy, ca. 108 kcal/mol, one can reasonably ask whether **1** is kinetically stable in T_d symmetry, would have

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Table I. Vibrational Frequencies of Cubane (cm^{-1})

symmetry	calcd	obsd	symmetry	calcd	obsd
a_{1g}	2993	2999	a_{2u}	2957	2965
a_{1g}	963	1002	a_{2u}	1020	1030
e_g	1107	1078	e_u	1168	1151
e_g	874	899	e_u	600	617
t_{1g}	1144	1130	t_{1u}	2974	2982
t_{2g}	2966	2973	t_{1u}	1263	1231
t_{2g}	1233	1185	t_{1u}	825	852
t_{2g}	816	821	t_{2u}	1078	1036
t_{2g}	649	667	t_{2u}	814	829

this structure only on the average, or would rearrange via a symmetry-allowed transition[8] to the lower energy isomer **2**. This triene is ca. 15 kcal/mol more stable than **1**, whereas **3** is ca. 21 kcal/mol less stable.[9]

Results

The geometry of **1** was optimized at the SCF level in the 6-31G* basis set. The bond lengths (Å) of **1** are as follows: C_1C_2, 1.505; C_1C_7, 1.500; and CH, 1.076. (The near equality of the two CC bond lengths may be an artifact of the 6-31G* SCF calculation.) The total energy of **1** is calculated to be −461.2922 au[10] which, using the atom equivalents of Ibrahim and Schleyer,[11] leads to a $\Delta H_f°$(298 K) of 93 kcal/mol. In T_d symmetry, the 66 vibrational fundamentals of compound **1** are as follows: a_1 (4), a_2 (2), e (6), t_1 (7), and t_2 (9). The force-constant matrix was computed by finite differences of analytical SCF gradients. The eigenvalues of this matrix are all positive, thus confirming the kinetic stability of the T_d structure. (An earlier analysis at the STO-3G level,[9] which reached the same conclusion, cannot be considered definitive owing to the minimal basis and its lack of polarization functions on the strained carbons.)

More relevant are the calculated fundamental frequencies of **1**, which would indicate the depth of the potential in the harmonic approximation and assist in its identification by vibrational spectroscopy. Ab initio vibrational frequencies at the 6-31G* SCF level can differ from experiment by 10% or more. However, as will be seen from the strained, highly symmetric (O_h) cubane molecule used here as a model $(CH)_n$ system, scaling the calculated frequencies leads to satisfactory agreement with the experimental values. The vibrational spectrum of cubane has been well studied both experimentally[12] and theoretically.[13]

When the calculated 6-31G* frequencies of cubane are fitted to the observed values by the method of least squares, reasonable agreement is obtained for all but the lowest a_{2u} mode, which is in error by 170 cm^{-1}. However, reassignment of the lowest fundamental to 1030 cm^{-1} from 839 cm^{-1} brings all the frequencies into substantial agreement with experiment, as shown in Table I.[14] This reassignment was also suggested by Dunn et al.[13b] on the basis of a more detailed analysis. The root mean square deviation of the cubane 6-31G* SCF values from experiment (Table I) is 26 cm^{-1}, the largest error being 48 cm^{-1}. The agreement is not as good as that obtained by Dunn et al., who scaled the 4-21G force-constant matrix (with more parameters than are used here) to fit the observed frequencies. However, since our intent is to examine the vibrational frequencies of **1**, whose structure differs significantly from that of cubane, our use of the least-squares procedure seems adequate.

We note that our 6-31G* SCF frequencies of cubane are similar to those reported by Almlöf and Jonvik[13a] at the SCF level in a basis set of 4s,2p contracted gaussians. They examined the role of carbon d orbitals only for the two a_{1g} modes, which probably explains why a least-squares fit of their frequencies to the experimental data (after reassignment of the a_{2u} mode) gives a root mean square deviation more than twice that of the 6-31G* values.

Table II. Scaled Vibrational Frequencies (cm^{-1}) of $C_{12}H_{12}$ (T_d)

a_1	731	1199	1351	3031			
a_2	681	1105					
e	433	657	1011	1086	1383	3008	
t_1	375	765	877	1065	1107	1312	2996
t_2	500	710	933	989	1160	1363	1434
	3001	3022					

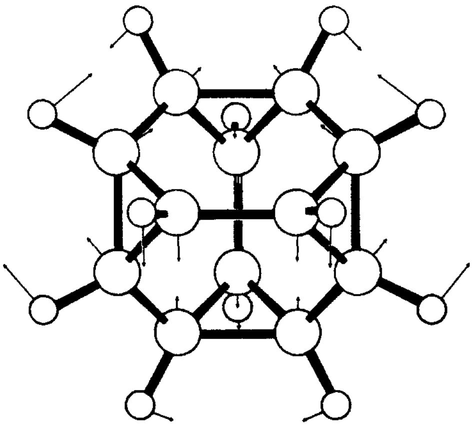

Figure 1. Distortion of compound **1** according to the eigenvector of its 6-31G* force-constant matrix having the lowest eigenvalue. The extent of this t_1 distortion has been exaggerated for clarity.

The calculated frequencies of **1** are given in Table II.[15] The zero-point energy of **1** is 125.9 kcal/mol, in good agreement with the value predicted by an empirical formula, 125.8 kcal/mol.[16] The lowest frequency, 375 cm^{-1}, is found for a t_1 mode. It is sufficiently large to ensure that **1** is indeed kinetically stable in T_d symmetry. For comparison, the lowest frequency fundamental observed in cubane is 617 cm^{-1} (600 cm^{-1} calculated) for an e_u mode. Figure 1 depicts an exaggerated distortion of **1** according to the t_1 eigenvector of the 6-31G* force-constant matrix having the lowest eigenvalue. The energy increase for a distortion having atomic displacements of up to 0.2 au is still in agreement with the harmonic approximation.

Discussion

Since the theoretical result is unlikely to change significantly at higher levels of calculation, it provides strong evidence for the T_d symmetry of compound **1**. We note that neither of its two lowest frequency fundamentals can be regarded as initiating a *direct* transit toward the more stable triene **2**: only t_2 modes can produce structures of C_{3v} symmetry. The lowest frequency t_2 fundamental is 500 cm^{-1}; the barrier for this transit is estimated to be 24 kcal/mol.[9] An indirect transit via C_3 symmetry is possible in principle from a t_1 distortion.

Compound **1** is more stable than hexaprismane, of current synthetic interest,[17] whose heat of formation, calculated from its 6-31G* SCF energy of −461.1957 au, is 153.6 kcal/mol. The D_{6h} structure of hexaprismane has been demonstrated at the 3-21G SCF level, where the lowest frequency is calculated to be 431 cm^{-1} (unscaled).[18]

When compound **1** is prepared, the spectroscopic data would include the expected proton and ^{13}C singlets with chemical shifts characteristic of cyclopropanes. However, fluxional behavior could also lead to the same NMR spectra and, without a reliable the-

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(10) Due to a less stringent criterion for integral retention in ref 9, the total energy given there is lower by 0.0003 au than the present value.

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(14) ν(scaled) = 0.9128ν(unscaled) − 31.66, in cm^{-1}.

(15) We have computed the following freqencies (cm^{-1}) for the perdeuterio analogue $(CD)_{12}$: a_1 707, 851, 1369, 2272; a_2 587, 917; e 423, 532, 765, 956, 1290, 2252; t_1 335, 609, 812, 895, 931, 1062, 2243; t_2 484, 588, 741, 822, 922, 1179, 1389, 2247, 2264.

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oretical calculation, could not be ruled out. This is an aspect of the more general problem of demonstrating that a species is actually kinetically stable in its presumed symmetry. Unfortunately, even when structural and spectral data are available, crystal packing forces, the locations of counterions, thermal motions, imprecise positioning of hydrogens in X-ray structures, and incomplete or erroneous assignment of fundamental vibrational frequencies in Raman and infrared spectra can all lead to incorrect or ambiguous conclusions. Similarly, microwave spectroscopy and electron diffraction have limitations in their ranges of utility. Thus, theoretical confirmation by a reliable computational method has become desirable.

Acknowledgment. This research was supported, in part, by Grants 667253, 668248, and 669274 of the PSC-CUNY Research Award Program of the City University of New York and a grant of computing time from the City University Committee on Research Computing. Part of this work was conducted, with vector programs developed by us (The Queens College Quantum Chemistry Package), with use of the Cornell National Supercomputer Facility, a resource of the Center for Theory and Simulation in Science and Engineering at Cornell University, which is funded in part by the National Science Foundation, New York State, and the IBM Corporation and members of the Corporate Research Institute.

Structures and Charge Distributions in Alkoxide Ions

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Abstract: The structures of methoxide ion, ethoxide ion, *tert*-butoxide ion, fluoromethoxide ion, and trifluoromethoxide ion were obtained via geometry optimizations with the 6-31G* and 6-311++G** basis sets. In all cases, the carbon–oxygen bond shortened about 0.1 Å on going from the alcohol to the alkoxide ion, whereas the bonds attached to the alcohol carbon increased in length. The origin of the changes in bond lengths was studied with use of Bader's theory of atoms in molecules. Two types of interactions were found. With C–H or C–C bonds, the oxygen in the alkoxide ions was found to repel charge from the adjacent carbon, and onto the groups attached to this carbon. This results in a larger volume element for the ion and a decrease in the classical electrostatic energy. The coulombic attraction between the alkoxy oxygen and the carbon leads to a shorter bond. With C–F bonds, the charge polarization is so large that little further polarization can occur on going to the alkoxide ion. Here, charge transfer from the oxygen to the electron-deficient carbon was found. The energy changes in the ionization of the alcohols and of acetic acid were studied. The change in energy of the hydroxy proton on ionization accounts for half of the difference in ionization energy of ethanol and acetic acid.

It has been found from X-ray crystallographic studies that the C–O bond of trifluoromethoxide ion is unusually short and that the C–F bonds are unusually long, compared to those of trifluoromethanol. Ab initio calculations reproduced the experimental result.[1] We should like to report that these structural features are not unique to this alkoxide ion, but they are generally found.

Geometry optimization of methoxide ion with the 6-31G* basis set[2] gave $r(\mathrm{CO}) = 1.311$ Å and $r(\mathrm{CH}) = 1.133$ Å as compared to the values for methyl alcohol of $r(\mathrm{CO}) = 1.400$ and $\mathrm{r(CH)} = 1.085$ Å (av) (Table I).[3] It was possible that the short CO bond length arose from an inadequate basis set in which the oxygen makes use of some of the carbon orbitals in order to describe its relatively diffuse charge distribution. Therefore, the optimizations were repeated with the 6-311++G** basis set which is triple-ζ for the valence electrons and includes both diffuse functions and polarization functions at all atoms. The methanol geometry was essentially unchanged, and the methoxide ion had somewhat less extreme structural changes (Table I). The CO bond length was still 0.074 Å less than that for methanol, and the CH length was 0.038 Å greater.

The geometry changes were clearly due to the charge at oxygen, for lithium methoxide had a calculated structure much closer to that of methanol (Table I). As expected for an ion pair, the C–O–Li geometry was found to be linear.

The structures of ethoxide ion and ethanol, fluoromethoxide ion and fluoromethanol, as well as trifluoromethoxide ion and trifluoromethanol were obtained with both the 6-31G* and 6-311++G** basis sets. The gauche rotamer of fluoromethanol was found to be 4.9 kcal/mol more stable than the trans rotamer[4] with use of the 6-31G* basis. In the case of *tert*-butoxide ion and *tert*-butyl alcohol, it was not possible to use such a large basis set. Here, geometry optimizations were carried out with only the 6-31G* basis.

Before analyzing the origins of the structural changes, it is important to see whether or not key experimental data, the acidity of the alcohols, were satisfactorily reproduced by the calculations. Correction for electron correlation might be important in these cases that involve bond cleavage, and so the energies of methoxide ion and methanol were obtained with the Møller–Plesset perturbation theory through the fourth order (full MP4).[5] The energies are given in Table II and are converted to relative energies in Table III. The energy changes on ionization oscillated with increasing correction for electron correlation and averaged 395 kcal/mol with an uncertainity of about 2 kcal/mol.

Before comparing the result with the experimental value, it was necessary to correct for the loss of one O–H stretching mode and two C–O–H bending modes. Calculations of the vibrational frequencies for methanol and methoxide ion showed that the

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