aluminum. The relationship between experimentally determined ionization potentials and bond strengths in Me$_3$Al(PMe$_3$) and Me$_2$(BHT)Al(PMe$_3$) shows that the Al–P σ bond in Me$_3$Al(PMe$_3$) is stronger than that in Me$_2$(BHT)Al(PMe$_3$). The source of the weaker Al–P σ bond in Me$_2$(BHT)Al(PMe$_3$) traces to phenoxide π donation from an oxygen p π orbital into the empty Al–P σ^* orbital. The loss of observable vibrational fine structure in the Ph π b$_1$ ionization between the free and coordinated ligand and the change in the band shape and position of the Al–P σ ionization between Me$_3$Al(PMe$_3$) and Me$_2$(BHT)Al(PMe$_3$) provide the evidence of phenoxide π donation. The Al–P σ ionization occurs at higher binding energy in Me$_3$Al(PMe$_3$) than in Me$_2$(BHT)Al(PMe$_3$), indicating that the positive charge potential of the Al center is greater in Me$_3$Al(PMe$_3$). Although π donation into the vacant 3p orbital of a planar, three-coordinate, Al center is expected, the presence of π bonding in four-coordinate Al compounds is a new observation. We are continuing our studies in this area in order to investigate the generality and influence of this interaction on the chemistry of aluminum compounds.

Acknowledgment. D.L.L. acknowledges support by the U.S. Department of Energy (Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research; Grant DF-SG02-86ER135101), the National Science Foundation (Grant CHE8519560), and the Materials Characterization Program, Department of Chemistry, University of Arizona. A.R.B. acknowledges support by the Petroleum Research Fund administered by the American Chemical Society, and ICI-Materials Division.

An Experimental and Computational Investigation of the Mechanism of the Deoxygenation of THF by Atomic Carbon

Michael L. McKee,* Gitendra C. Paul, and Philip B. Shevlin*

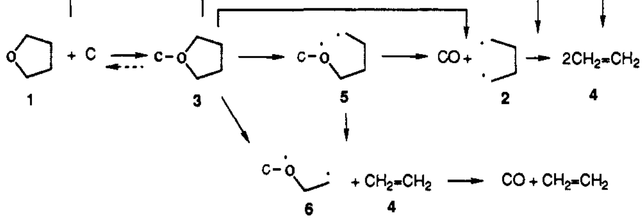
Contribution from the Department of Chemistry, Auburn University, Auburn, Alabama 36849.

Received August 4, 1989

Abstract: An ab initio investigation (MP2/6-31G*//3-21G) of the deoxygenation of tetrahydrofuran (**1**) to ethylene and CO by atomic carbon reveals a low-energy concerted pathway, which yields the products directly in a 3-bond cleavage. The geometry of the transition state for this process, calculated at the HF/3-21G level, indicates a nonsynchronous process in which the C–O bonds are cleaved to a greater extent than the C–C bond. When C atoms are reacted with a 1:1 mixture of **1** and **1**-d_8, the products are ethylene and ethylene-d_4 in a 2.7:1 ratio. This ratio represents a mean secondary kinetic isotope effect (KIE) k_H/k_D = 1.13 per H and is close to a value of 1.12 calculated from the computed amount of rehybridization in the transition state and the corresponding equilibrium isotope effects.

The deoxygenation of tetrahydrofuran (**1**) by atomic carbon,[1] which results in exclusive cleavage to C_2H_4 and CO, is an interesting reaction in that it offers a wide variety of mechanistic possibilities regarding the timing of bond making and breaking (Scheme I).[2] Although it is tempting to postulate the intermediacy of the cisiod tetramethylene biradical **2**, other reactions in which **2** and its derivatives have been generated lead to cyclobutanes as well as ethylenes.[1,3,4] Since no cyclobutanes are generated in the deoxygenation of **1**, it may be that the products in Scheme I result from a concerted 3-bond cleavage of 2 C–O bonds and a C–C bond. In this study, we report an experimental and computational evaluation of the timing of bond breaking in this interesting reaction.

Scheme I



Computational Results. The Gaussian 82[5] and 86[6] programs were used to investigate this reaction theoretically. Geometries were optimized at the HF/3-21G level, and single-point calculations were made on these geometries at the MP2/6-31G* level. Frequencies were calculated at the HF/3-21G level and used to calculate zero-point corrections. Tables I and II give the energies of intermediates and transition states calculated at various levels in this investigation. The energy of C(^{1}D) was estimated as the calculated (UMP2/6-31G* with spin contamination projection[7]) energy of C(^{3}P) plus the experimental singlet–triplet separation of 30 kcal/mol, a procedure that has worked well in the past.[8-10] The lowest energy pathway for singlet carbon and **1** is assumed to lead to the closed shell solution for complex **3**, between C and **1**, a situation that has applied to the reactions of C with other substrates.[8-10]

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Table I. Absolute Energies (hartrees) of Species Relevant to the Cleavage of THF by C(^{1}D)

	mol symm	3-21G	6-31G*	PMP2/6-31G*[a]	ZPE(NEV)[b]
C(^{3}P)[c]	K	−37.481 07	−37.680 86	−37.732 97	0.00 (0)
1	C_2	−229.699 16	−230.973 61	−231.668 27	78.72 (0)
1	C_s	−229.697 18	−230.972 83	−231.667 41	78.69 (1)
3	C_2	−267.124 62	−268.579 83	−269.367 13	80.18 (0)
3	C_s	−267.121 94	−268.577 21	−269.363 90	80.13 (1)
TS3-4	C_2	−267.084 80	−268.553 21	−269.423 51	77.40 (1)
TS3-4	C_{2v}	−267.083 00	−268.549 66	−269.414 67	77.73 (2)
CO[d]	$C_{\infty v}$	−112.093 30	−112.737 26	−113.020 13	3.31 (0)
4[d]	D_{2h}	−77.600 99	−78.031 69	−78.284 09	34.57 (0)
$COCH_2CH_2$[c]	C_s	−189.568 48	−190.623 97	−191.122 90	37.16 (2)
2[c,d]	C_{2h}	−155.170 26	−156.033 63	−156.507 74	67.35 (2)
$CO(CH_2)_4$[c]	C_s	−267.209 73	−268.695 49	−269.455 60	75.77 (2)

[a] The frozen core approximation is used. [b] Zero-point energy (kcal/mol) and number of imaginary frequencies in parentheses. [c] The energy of the triplet state is calculated with the effect of spin contamination projected out at the MP2/6-31G* level. [d] Geometry available at the 3-21G level from: Whiteside, R. A.; Frisch, M. J.; Pople, J. A. *Carnegie-Mellon Quantum Chemistry Archive*, 3rd ed.; Carnegie-Mellon: Pittsburgh, 1983.

Table II. Relative Energies (kcal/mol) of Species Relevant to the Cleavage of THF by C(^{1}D)[a]

	3-21G	6-31G*	MP2/6-31G*	MP2/6-31G* + ZPC
C(^{1}D)[b] + **1**	−4.9 (1.2)	−16.9 (0.5)	8.1 (0.5)	6.6
3	0.0 (1.7)	0.0 (1.6)	0.0 (2.0)	0.0
TS3-4	25.0 (1.1)	16.7 (2.2)	−35.4 (5.5)	−38.2
CO + $2C_2H_4$	−107.1	−138.6	−138.8	−146.5
$COCH_2CH_2$ + C_2H_4	−28.2	−47.6	−25.0	−33.4
2 + CO	−87.2	−119.9	−100.9	−110.6
$CO(CH_2)_4$	−53.4	−72.6	−55.5	−68.3

[a] The value in parentheses is the increase in energy (kcal/mol) that results when the geometry is optimized in C_s (C_{2v} for TS) rather than C_2 symmetry. [b] No calculations were made on C(^{1}D). The energy of C(^{1}D) was determined as the energy of C(^{3}P) plus 30 kcal/mol, which is the experimental singlet–triplet separation. Moore, C. E. *Natl. Bur. Stand.* (*U.S.*) *Circ.* **1949**, *1*, No. 467.

Experimental measurements indicate that the C_2 conformer of **1** is more stable than the C_s conformer by 0.1 kcal/mol,[11-13] in agreement with a theoretical value of 0.7 kcal/mol (6-31G*//6-31G*).[14] The value determined here at the MP2/6-31G*//3-21G level is 0.5 kcal/mol. The energy of complex **3** between C and **1** was determined in C_s and C_2 symmetry. The C_2 conformer was 2.0 kcal/mol lower in energy than the C_s conformer at the MP2/6-31G* level with the HOMO and LUMO predominately on the monovalent carbon. Although **3** is predicted to be less stable than C(^{1}D) + **1** at lower levels of theory, at the MP2/6-31G* level it is bound by 6.6 kcal/mol.

The transition state for a concerted 3-bond cleavage of **3** to CO + **4** (**TS3-4**) is optimized in C_2 symmetry at the 3-21G level with barrier heights of 25.0 and 16.7 kcal/mol respectively at the 3-21G and 6-31G* levels. An examination of the geometry of **TS3-4**, shown in Figure 1, demonstrates that cleavage of the C–O bonds is more pronounced than that of the C–C bond in the transition state. However, the negative mode has a substantial component involving cleavage of the C_2–C_3 bond as well as the C–O bonds, indicating that this is a transition state for a concerted, but nonsynchronous, 3-bond cleavage. The effect of correlation on the energy of **TS3-4** is dramatic, dropping the energy 35.4 kcal/mol below **3** at the MP2/6-31G*//3-21G level, indicating that the transition state for deoxygenation is probably earlier than that calculated at the 3-21G level and that there may be little or no barrier calculated for loss of CO at the higher level. In order to explore this possibility, single-point calculations were performed on 3-21G optimized geometries of **3** with one or two parameters changed. When the forming CO bond was shortened from 1.616 Å to 1.3 Å, the MP2/6-31G* energy of **3** dropped 7.2 kcal/mol. When the C–O distance was held at 1.3 Å and the distance of CO from the remainder of the complex was increased, the MP2/6-31G* energy decreased. While it is true that the single-determinant wave function used here will favor concerted cleavages in the C + **1** system over mechanisms involving biradicals such as **2**, **5**, and **6**, these computational data indicate a rather small barrier to concerted 3-bond cleavage in the deoxygenation of **1** by atomic carbon, a reaction calculated to be exothermic by 153.1 kcal/mol (experimental = 158.4 kcal/mol). The thermodynamics (but not the barriers) for formation of **2**, **5**, and **6** were also calculated by assuming that singlet and triplet states of these biradicals, with their widely separated spins, were similar in energy. Tables I and II demonstrate that cleavage to **2**, **5**, and **6** + **4** is exothermic by 117.2, 74.9, and 40.0 kcal/mol, respectively, indicating that these pathways may be accessible in the deoxygenation of **1** by C.

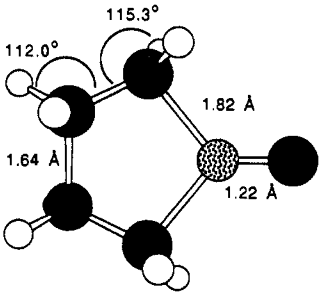

Figure 1. Geometry of **TS3-4** calculated at the 3-21G level.

Competitive Deoxygenation of 1 and 1-d_8 by C Atoms. The deoxygenation of **1** by arc generated C is interesting in that **4** is the only hydrocarbon produced.[1] This is in contrast to the deoxygenation of **1** by C_2O,[4] the desulfurization of tetrahydrothiophene,[1] and other reactions of **2** that all give some cyclobutane along with **4**.[3] We have carried out the deoxygenation of gaseous **1** with C atom generated by the decomposition of 5-diazotetrazole (**7**)[15] and reinvestigated the deoxygenation by arc generated C and confirm that no cyclobutane is generated in either of these reactions. We have also searched for cyclopentanone and dihydropyran, products of a formal C–O insertion by C to generate 2-oxacyclohexanylidene,[4,16] and find neither of these compounds.

A classic method of evaluating concert in reactions involving rehybridization at carbon is the measurement of the secondary deuterium kinetic isotope effects (KIE's) involved.[17] In the present case, we have carried out the deoxygenation of gaseous **1** with C atoms generated by the thermolysis of 5-diazotetrazole (**7**) and have measured the competitive secondary deuterium isotope effects

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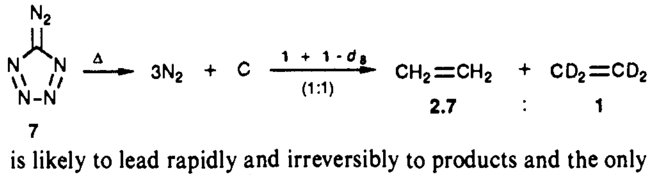
involved. Thus when C atoms, from the decomposition of **7**, are reacted with an equimolar mixture of **1** and **1**-d_8 at 80 °C, C_2H_4 and C_2D_4 are formed in a 2.7:1 ratio. Since any cleavage of **2** is likely to lead rapidly and irreversibly to products and the only products detected are CO and **4**, the partition between deuterated and nondeuterated products depends upon the relative rates of deoxygenation of **1** and **1**-d_8. Thus, the observed KIE is derived from the initial deoxygenation of **1** and irreversible formation of **3** is ruled out.

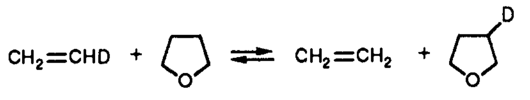


Discussion

The fact that there is a substantial normal secondary KIE in the deoxygenation of **1** by C is consistent with a reaction in which sp^3 carbons are converted to sp^2 carbons as in Scheme I. A secondary KIE > 1 in going from sp^3 to sp^2 is attributed to the fact that the C–H bending frequency, and the associated zero-point energy, decreases more than the C–D bending frequency and its zero-point energy in going to the transition state for rehybridization.[18] If we assume that rehybridization of C–H bonds is the primary factor giving rise to our observed KIE's, we may use our observed KIE of 2.7 to derive a KIE per D for the possible product-determining cleavages depicted in Scheme I. If α and β are the KIE's per deuterium for rehybridization of the respective C–H bonds α and β to the oxygen in **1**, the observed KIE will be $(\alpha)^m(\beta)^n$ where m and n are the number of C–H bonds undergoing rehybridization at the α and β sites, respectively, in the product-determining step.[19] Thus in product-determining cleavage of **3** → **5**, our k_H/k_D of 2.7 leads to a KIE per D of $(2.7)^{1/2}$ = 1.64. Concerted cleavage of both α C–O bonds to give **2** would result in an observed KIE of $(2.7)^{1/4}$ = 1.28. Product-determining **3** → **6** + **4** cleavage would result in cleavage of an α and a β bond with rehybridization at 3 carbons and would have an observed mean KIE of 1.18/D. Concerted 3-bond cleavage with simultaneous rehybridization of 4 carbons would require $\alpha\beta = (2.7)^{1/4}$ = 1.28 giving an observed mean KIE of 1.13/D.

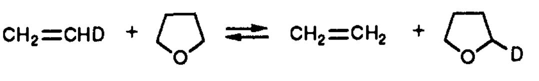
Having determined what the experimental KIE's per D would be for four possible product-determining cleavages, we may now ask which of these values are reasonable and hence evaluate the viability of these possible product-determining steps. If the KIE's are due to rehybridization, they should not exceed the equilibrium isotope effects (EIE's) for the corresponding rehybridizations in eqs 1 and 2. EIE's are often estimated from the corresponding fractionation factors (FF's) of Hartshorn and Shiner,[20] which are the hypothetical equilibrium constants between deuterium on the C–H bond of interest and the C–H bond of acetylene. As a model for the FF of the β carbon of **1**, we use the FF of the secondary H of propane and combine it with the FF of ethylene to get the EIE_β in eq 1. The EIE_α between a secondary C–D adjacent to oxygen and a vinyl C–D in eq 2 is assumed to be equal to the EIE/D in eq 3.[17,21] From the EIE's in eqs 1 and 2, we may estimate that at 25 °C,[22] the value of α for complete rehybridization is 1.32/D while the maximum β value is 1.19/D. These data lead to the conclusion that product-determining cleavage of **3** → **5** is unlikely as the measured KIE assuming this mechanism of 1.64 is far higher than the EIE_α of 1.32. In fact, the transition state for deoxygenation is expected to be early, and complete rehybridization at the carbons undergoing cleavage is unlikely.

If we take the 3-21G geometry of **TS3-4** in Figure 1 as approximating that of the transition state for 3-bond cleavage, we see that breaking C–O bonds have increased from 1.46 to 1.82 Å while the C–C bond increases from 1.54 to 1.64 Å. Thus, cleavage of the C–O bond has progressed further than that of the C–C bond and α should be greater than β. Gajewski[17] has postulated a linear free energy relationship between KIE and EIE such that KIE = $(EIE)^i$ where i is the range of 0.0 to 1.0 and is a measure of the degree of change in σ bonding at the site undergoing rehybridization. In the present case, we have used the 3-21G geometries of **3** and **TS3-4** to determine the change in p character in the developing π bonds of ethylene as the transition state is reached. Using the methodology of Haddon,[23] we calculate fractional increases in percent p of 0.67 at C_α and 0.12 at C_β in going to the transition state for 3-bond cleavage.[24] If we set these values equal to Gajewski's i, and use the equations $\ln \alpha/\ln EIE_\alpha = 0.67$ and $\ln \beta/\ln EIE_\beta = 0.12$, α and β values of 1.22 and 1.03 are calculated. These values lead to a mean KIE = $(\alpha\beta)^{1/2}$ = 1.12 in good agreement with the experimental value of 1.13 obtained assuming concerted 3-bond cleavage.



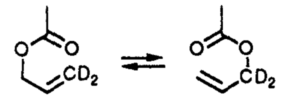
(1)

$K_{eq} = EIE_\beta = 1.19$



(2)

$K_{eq} = EIE_\alpha = 1.32$



(3)

$(K_{eq})^{1/2}$ = EIE = 1.32/D

It is clear from the above analysis of the degree of bond breaking in the 3-21G transition state for 3-bond cleavage that this process, while concerted, is highly nonsynchronous[25] and approaches the limiting case in which **2** is an intermediate. Indeed the high degree of nonsynchronous bond breaking and consequent minimal rehybridization at C_2 and C_3 in the transition state makes it impossible to unequivocally distinguish this mechanism from one involving the intermediacy of **2** through the use of isotope effects. The observed KIE is also consistent with the intermediacy of **2** if a bit more rehybridization at C_1 and C_4 is assumed. Thus, product-determining formation of **2** would have an EIE of 1.32 which, when combined with the observed KIE of 1.28, leads to an i of 0.89 requiring almost complete breaking of the C–O bonds in going to the transition state. An examination of the deoxygenation of **1**-*2,2,3,3*-d_4 by C will probably not solve this problem as the degree of rehybridization at C_2,C_3 is small in the 3-bond cleavage mechanism and its associated KIE may be indistinguishable from the βKIE for the formation of **2**.[26] Since cyclobutane is not observed in this system, we feel that the intermediacy of **2** is unlikely. The fact that **2** is not an intermediate in this highly exothermic reaction is not surprising as recent thermochemical[27] and molecular orbital[28,29] calculations have indicated that the barriers to reaction in **2** are small and may only be entropic. The observed KIE's also do not rule out product-determining cleavage to **4** + **6**, which has a calculated mean EIE of $(EIE_\beta{}^2EIE_\alpha)^{1/3}$ = 1.23/D. Since the mean KIE measured assuming this mechanism is 1.18/D, the average fraction of σ bond cleavage is 0.76 and

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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.

Acknowledgment. M.L.M. thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. P.B.S. is grateful to the National Science Foundation for financial support. Computer time for this study was donated by the Auburn University Computer Center and the Alabama Supercomputer network.

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

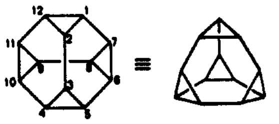
Raymond L. Disch and Jerome M. Schulman*

Contribution from the Department of Chemistry, Queens College, City University of New York, Flushing, New York 11367. *Received August 7, 1989*

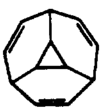
Abstract: We show by ab initio calculations at the 6-31G* SCF level that the $(CH)_{12}$ hydrocarbon **1** is kinetically stable in T_d symmetry. The calculated vibrational frequencies of **1** and of cubane, which serves as a model, are given. The lowest frequency of **1**, 375 cm^{-1}, is found for 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.

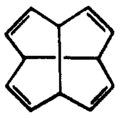
The subject of this paper is compound **1**, whose presumed T_d symmetry derives from a carbon skeleton that is a tetratruncated tetrahedrane containing planar, saturated six-membered rings.[5]



1



2



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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[5] Compound **1** is named heptacyclo[5.5.0.0^{2,12}.0^{3,5}.0^{4,10}.0^{6,8}.0^{9,11}]dodecane in the systematic nomenclature. We propose the nonsystematic name "truncane" to indicate its status as the simplest hydrocarbon having the structure of a truncated solid of cubic or higher symmetry.

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