calculated barrier heights for the twist of the double bond (see eq 6) and the barrier heights for the actual shift (eq 4). The same proviso, however, has to be made for the classical reaction rates. Additionally it was assumed that the vibrational mode F behaves harmonically. For the lowest bound state, this approximation is fairly reasonable, but for the higher bound states, deviations will become more important. Generally, the anharmonicity will lead to a lower tunneling rate ω_n. This will be partly cancelled by an increasing population f_n of the upper vibrational levels so that the overall effect upon the VAT rate k_t is indistinct. As we have obtained the classical reaction rates and the KIE within the harmonic oscillator approximation, it is merely a matter of self-consistency to use this approximation also to calculate the tunneling rates. A further remark must be made about the validity of the one-dimensional approach. In the derivation of the equations, it was assumed that all vibrations (except ν_F) attribute adiabatically to the tunneling rate. As discussed earlier, this approximation becomes less reliable for a large reaction path curvature.[22a] It is to be expected that a more realistic multidimensional model will lead to lower tunneling rates.[31] In view of these facts, it is clear that we must interpret the absolute values with care. However, it was only our intention to calculate within a consistent model whether the tunneling mechanism might play a role in the [1,5]-shift in *cis*-1,3-pentadiene and, if so, via which TS the reaction is most likely to proceed.

Conclusions

The 3-21G calculations strongly support Dewar's suggestion[8] that tunneling from a twisted form of the reactant should play an important role in the mechanism of the thermal [1,5]-H shift in *cis*-1,3-pentadiene. The reaction is found most likely to proceed via the TS of C_{2v} symmetry. Both optimized TSs have an acute angle at the migrating hydrogen atom, which contradicts the suggestion of Kwart et al.[3] that the TS should have a collinear geometry. The calculated KIEs are found to be temperature dependent, thus confirming recent model studies where it was found that not only a linear but also a bent TS should exhibit a temperature-dependent KIE. The mechanism of VAT also shows a temperature dependence which arises from an essentially different origin than the one for the classical reaction kinetics. Arrhenius extrapolation of the results of Roth and König to room temperature and conclusions based thereupon are therefore not justified.

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Registry No. 1, 1574-41-0; deuterium, 7782-39-0.

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Ab Initio Heats of Formation of Medium-Sized Hydrocarbons. 5. A $(CH)_{12}$ Structure Related to the Truncated Tetrahedron[1]

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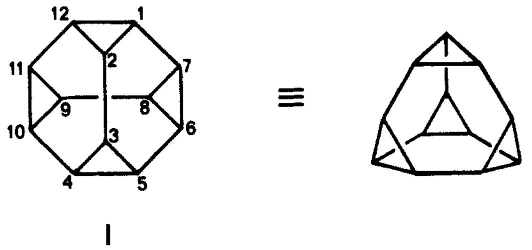
Abstract: The geometry and energy of the $C_{12}H_{12}$ hydrocarbon I, whose carbon framework closely approximates a truncated tetrahedron, was studied by ab initio SCF calculation. Two possible precursors of I are also examined: the triene II, which is more stable than I by ca. 16 kcal/mol, and the tetraene III, which is less stable than I by ca. 24 kcal/mol. The standard heat of formation of I is found to be ca. 91 kcal/mol.

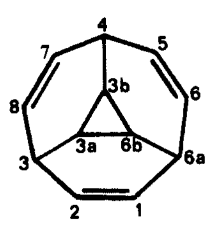
I. Introduction

A curious and as yet unknown $C_{12}H_{12}$ hydrocarbon is the dodecane I, whose carbon framework consists of four planar cyclohexanes and four cyclopropanes. It is formally derived from tetrahedrane by successive replacement of CH apical units with C_3H_3 moieties (truncation[2]), leading via prismane,[3] cuneane,[4] and diademane[5] (all known) to the fourfold trishomobenzene I.[6]

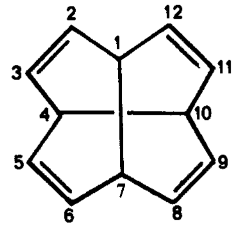
Woodward and Hoffmann[7] pointed out that the tetraene III is a potential photochemical precursor of I by a totally antarafacial $[2_a + 2_a + 2_a + 2_a]$ cycloaddition; no attempt to prepare III has yet succeeded.[8] Similarly, the triene II, a potential precursor



I



II



III

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(2) The process of truncation can of course be applied to other cyclic and acyclic hydrocarbons containing methine groups. Truncation applied to tetrahedrane, cubane, and dodecahedrane produces C_{12}, C_{24}, and C_{60} frameworks in the form of semiregular convex polyhedra whose faces are regular polygons, namely, the truncated tetrahedron, truncated cube, and truncated dodecahedron. See, for example; Lyusternik, L. A. *Convex Figures and Polyhedra*; Dover Publications: New York, 1963.

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(6) I = heptacyclo[$5.5.0.0^{2,12}.0^{3,5}.0^{4,10}.0^{6,8}.0^{9,11}$]dodecane. II = 3,3a,3b,4,6a,6b-hexahydro-3,4-ethenocyclopropa[*d*,*e*]naphthalene. III = tricyclo[$5.5.0.0^{4,10}$]dodeca-2,5,8,11-tetraene. The 357 valence isomers of formula $(CH)_{12}$ have been tabulated, see the following: Banciu, M.; Popa, C.; Balaban, A. T. *Chem. Scr.* **1984**, *24*, 28.

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Table I. Geometrical Parameters of I, II, and III[a]

I		II				III	
			Bond Lengths (Å)				
C_1C_2	1.512 (1.505)	C_1C_2	1.309	C_1H_1	1.083	C_1C_2	1.537
C_1C_7	1.513 (1.500)	C_2C_3	1.535	C_3H_3	1.090	C_2C_3	1.311
C_1H_1	1.081 (1.076)	C_3C_{3a}	1.537	$C_{3a}H_{3a}$	1.082	C_1C_7	1.598
		$C_{3a}C_{3b}$	1.505			C_1H_1	1.088
						C_2H_2	1.083
			Bond Angles (deg)				
$C_1C_2C_{12}$[b]	60.0 (60.0)	$C_{3a}C_{3b}C_{6b}$	60.0	$C_3C_{3a}C_{3b}$	119.1	$C_1C_2C_3$	120.6
$C_1C_2C_3$[b]	120.0 (120.0)	$C_2C_3C_{3a}$	113.3	$H_1C_1C_{6a}$	115.9	$C_1C_7C_6$	115.7
$H_1C_1C_2$	116.3 (116.2)	$H_{3a}C_{3a}C_{3b}$	116.8	$H_3C_3C_{3a}$	108.5	$H_1C_1C_7$	106.5
$H_1C_1C_7$	113.9 (114.1)					$H_2C_2C_1$	117.1
			Dihedral Angles (deg)				
$C_1C_2C_3C_5$[b]	0.0 (0.0)	$C_3C_2C_1C_{6a}$	0.0	$H_8C_8C_3C_{3a}$	−153.9	$C_3C_2C_1C_7$	56.5
$C_2C_3C_4C_5$[b]	109.5 (109.5)	$C_{3b}C_{3a}C_3C_8$	−26.4	$H_8C_8C_7H_7$	0.0	$C_1C_2C_3C_4$	−13.0
						$C_2C_3C_4C_5$	−69.8
						$H_1C_1C_7H_7$	0.0
						$H_2C_2C_3H_3$	+2.7

[a] Optimized in the STO-3G basis assuming T_d, C_{3v}, and D_{2d} symmetries, respectively; 6-31G* values for I are in parentheses. [b] Symmetry-determined parameter.

of I by a thermally allowed $[2_s + 2_s + 2_s]$ cycloaddition, has resisted several attempts at synthesis.[9] The present work considers the structures and energies of I–III.

II. Methods

Geometries of I, II, and III, assuming T_d, C_{3v}, and D_{2d} symmetries, respectively, were optimized at the STO-3G level.[10] For comparison, I was optimized at the 6-31G* level. The 6-31G*(SCF) energies at the STO-3G geometries were then calculated, and the heats of formation were obtained by using homodesmic reactions, as described previously.[11] Heats of formation of I–III were also calculated from the 6-31G*(SCF) energies by using the group equivalents of Wiberg[12] and the atom equivalents of Ibrahim and Schleyer.[13] All ab initio calculations were carried out with optimized programs developed by us. The three molecules were also studied by the molecular mechanics method, MM2.[14]

III. Results

We find no negative eigenvalues of the STO-3G force-constant matrix for I; thus, it is a local minimum on that $C_{12}H_{12}$ potential energy surface. Although we have not performed full vibrational analyses for II and III, there are, of course, no negative eigenvalues of the STO-3G force-constant matrix in the subspace of totally symmetric distortions. The fact that MM2 calculations lead to C_{3v} and D_{2d} geometries for II and III, respectively, provides strong indication that they are also local minima.

Table I contains the STO-3G geometrical parameters of the three structures and for comparison the 6-31G* parameters of I. The $C_1C_2C_3$ and $H_1C_1C_2$ angles of I, 120.0° and 116.3°, respectively, are not far from the HCC angle in cyclopropane, 117.6°; thus, it is not surprising to find that much of the strain energy of I is contained in its four cyclopropanes. In the tetraene III the double bonds are twisted by 13°, a result of the strained conformation into which the cycloheptadienes are locked. This perhaps accounts for the long C_1C_7 bond, 1.598 Å.

The geometric parameters of I change only slightly upon passing from the STO-3G to the 6-31G* basis. The fact that its C_1C_2 and C_1C_7 lengths are almost identical in the two bases indicates that the planar cyclohexane rings differ negligibly from regular hexagons and thus the carbon framework of I is very nearly a truncated tetrahedron. There is good agreement between the STO-3G parameters given in Table I and the corresponding MM2 values (not tabulated); in particular, the bond angles and dihedral angles are in agreement to ca. 1°. MM2 calculations suggest that C_1C_7 is longer than C_1C_2 by 0.014 Å; however, recent work by Osawa et al.[15] indicates that CC bonds between cyclopropanes, as in I and bicyclopropyl, may require a unique MM2 parameter which would shorten them somewhat. The MM2 double bonds are 0.03 Å longer than their STO-3G counterparts, while the STO-3G lengths between singly bonded sp^2 and sp^3 carbons are longer by ca. 0.02 Å.

The 6-31G*(SCF) energies at the STO-3G-optimized geometries are (in au) the following: II, −461.3168; I, −461.2915; and III, −461.2609. The heats of formation of II and III can be calculated by using the homodesmic reactions

$$6\text{propene} + 6\text{isobutane} \rightarrow \text{II} + 3\text{ethylene} + 12\text{ethane} \quad (1)$$

$$8\text{propene} + 4\text{isobutane} \rightarrow \text{III} + 4\text{ethylene} + 10\text{ethane} \quad (2)$$

The zero-point energies of I–III are estimated to be 126 kcal/mol from an empirical formula for hydrocarbons.[11b] The enthalpy corrections from 0 to 298 K for the three isomers, estimated from suitable model compounds, are each ca. 5 kcal/mol. The heats of reactions 1 and 2, corrected for the zero-point and thermal effects, are 36 and 54 kcal/mol, respectively; they are estimates of the strain energies of II and III. Using the known heats of formation of isobutane, propylene, ethylene, and ethane, we obtain 75 and 115 kcal/mol for the heats of formation of II and III, respectively.

For I, we use the reaction

$$12\text{isobutane} \rightarrow \text{I} + 18\text{ethane} \quad (3)$$

The heat of reaction calculated at the 6-31G*(SCF) level, 104 kcal/mol, is undoubtedly too low since, as we have found for both cubane[11] and triprismane,[16] such highly angle-strained hydrocarbons require the inclusion of the effects of electron correlation, e.g., 6-31G*(RMP2) energies. The heats of reaction for these molecules at the SCF level are too low by 15 and 11 kcal/mol, respectively. For I, whose carbons are presumably less strained than those of cubane, a correction of ca. 12 kcal/mol to the calculated heat of reaction 3 seems appropriate, giving 116 kcal/mol as the heat of reaction (equivalently, the strain energy

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Table II. Heats of Formation of I, II, and III

		ΔH_f(298 K)		
molecule	6-31G*(SCF) energy (au)	method A[a]	method B[b]	method C[c]
II	-461.3168	75	75	79
I	-461.2915 (-461.2925)[d]	91	89	94
III	-461.2609	115	110	115

[a] Obtained by using homodesmic reactions 1-3 as described in the text. [b] From the 6-31G*(SCF) energies and the group equivalents of ref 12. [c] From the 6-31G*(SCF) energies and the atom equivalents of ref 13. [d] Energies are calculated at the STO-3G geometries, except for the value of I given in parentheses, calculated at the 6-31G* geometry.

Table III. Orbital Energies of I (au) and Approximate Photoelectron Ionization Energies (ev)

orbital	orbital energy[a]	vertical ionization potential[b]
$2a_1$	-1.2104	27.8
$3t_2$	-1.1122	25.7
2e	-0.8887	21.0
$4t_2$	-0.8412	20.0
$3a_1$	-0.7236	17.6
$2t_1$	-0.6707	16.5
$4a_1$	-0.6479	16.0
$5t_2$	-0.6387	15.8
$6t_2$	-0.5058	13.0
$7t_2$	-0.4906	12.7
3e	-0.4838	12.6
$3t_1$	-0.3735	10.3
4e	-0.3358	9.5

[a] 6-31G* value calculated at the STO-3G geometry. The C_{1s} orbitals transform as a_1, e, $t_2(2)$, and t_1 with energies of ca. -11.22 au. [b] Obtained from the Wiberg formula: IP = 0.768 × (orbital energy) + 2.47 (in eV), ref 18.

of I). This leads to a ΔH_f of 91 kcal/mol. The 116-kcal/mol strain energy of I is not much greater than that of four cyclopropanes, 108 kcal/mol.

The heats of formation of I, II, and III predicted by the Wiberg group-equivalent scheme[12] are 89, 75, and 110 kcal/mol, respectively; the corresponding atom-equivalent values[13] are 94, 79, and 115 kcal/mol. Both sets are in good agreement with their counterparts obtained from the homodesmic reactions: 91, 75, and 115 kcal/mol. The MM2 values, 88, 83, and 107 kcal/mol, are similar, but the 5 kcal/mol energy difference between I and II seems too small. It is noteworthy that I at the 6-31G*(SCF) level is more stable than its homodesmer hexaprismane by some 60 kcal/mol.[17]

Table III contains the orbital energies of I in the 6-31G* basis and their conversion into vertical ionization potentials assuming Koopmans' theorem and using the least-squares fit of Wiberg et al.[18] The highest occupied orbital (4e) corresponds to an ionization energy of 9.5 eV; it lies more than 0.5 au below the first virtual orbital.

IV. Discussion

Thermal rearrangements which argue for the possible observability of I are the following: diademane to triquinacene and homodiademane to homotriquinacene,[19] with half-lives of 243 and 7.3 h, respectively, at 60 °C. We have attempted to locate the transition state for concerted interconversion of I and the triene by computing 4-31G(SCF) energies at a series of geometries linearly interpolated between those of I and II. A maximum in the energy occurs along this linear, synchronous pathway at ca. 36% of the distance from I to II. This provided the starting point for a gradient optimization in C_{3v} to the nearest extremum. A saddle point with one negative eigenvalue of the force-constant matrix was obtained. The 4-31G maximum energy relative to that of I (i.e., the activation energy) is quite large; when it is scaled by the ratio by which the 4-31G(SCF) activation energy for the tropilidene–norcaradiene rearrangement exceeds experiment, E_a for I → II is estimated to be 24 kcal/mol. While less than the values 31.6 and 28.3 kcal/mol of E_a for the decomposition of diamantane and homodiamantane, respectively, it is similar to that calculated for trishomobenzene, 24-26 kcal/mol.[19] Comparison of the rate of decomposition of I with those of the three other systems, however, requires an adverse statistical factor of four.

Table IV. Isomer Count for Selected Substitutional Isomers of I[a]

	number of isomers			
mol formula	N_{as}	N_{ep}	N_s	N_t
$C_{12}H_{11}X_1$	1	0	1	1
$C_{12}H_{10}(X_1)_2$	3	2	5	7
$C_{12}H_{10}X_1X_2$	1	5	6	11
$C_{12}H_9(X_1)_3$	5	8	13	21
$C_{12}H_9(X_1)_2X_2$	5	25	30	55
$C_{12}H_9X_1X_2X_3$	0	55	55	110
$C_{12}H_8(X_1)_4$	9	18	27	45
$C_{12}H_8(X_1)_3X_2$	5	80	85	165
$C_{12}H_8(X_1)_2(X_2)_2$	15	120	135	255
$C_{12}H_8(X_1)_2X_2X_3$	5	245	250	495
$C_{12}H_8X_1X_2X_3X_4$	0	495	495	990

[a] N_t and N_s are the total number of isomers and number of structural isomers, respectively, which are obtained from the cycle indices $Z(\mathrm{T})$ and $Z(\mathrm{T}_d)$. The number of enantiomeric pairs, $N_{ep} = N_t - N_s$, while the number of achiral isomers $N_{as} = 2N_s - N_t$.

In view of the possible existence of I, it seems useful to enumerate the substitutional isomers, as was done previously by us for dodecahedrane.[20] (Extension to up to four different substituents has been made by Paquette et al.[21]) The method relies upon Pólya's counting theorem[22] and requires the two cycle indices of I with respect to the group T_d and its subgroup T:

$$Z(T) = 1/12[f_1{}^2 + 8f_3{}^4 + 3f_2{}^6]$$

and

$$Z(\mathrm{T_d}) = 1/24[f_1{}^{12} + 8f_3{}^4 + 3f_3{}^6 + 6f_4{}^3 + 6f_1{}^2f_2{}^5]$$

The total number of isomers, N_t, equal to the number of achiral structural isomers, N_{as}, plus twice the number of enantiomeric pairs, N_{ep}, is obtained from the cycle index $Z(T)$ in the manner described previously.[20,21] The number of structural isomers, N_s, equal to $N_{as} + N_{ep}$ is obtained from $Z(T_d)$. Values for these isomer numbers, which increase rapidly with the number of substituents, are given in Table IV.

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