(42) (a) Calculated with ^{19}F SCS data (CF$_3$CO$_2$H) from 6- and 7-substituted 2-fluoronaphthalenes[42b] and the respective DSP correlative equations in DMF for these two dispositions.[42b] The σ_R^0 values are -0.26 ($^+$NH$_3$,CF$_3$CO$_2$H) and -0.26 ($^+$NMe$_3$,CF$_3$CO$_2$H). (b) W. Adcock, J. Alste, S. Q. A. Rizvi, and M. Aurangzeb, *J. Am. Chem. Soc.*, **98**, 1701 (1976).
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(46) The ^{19}F SCS for **1** and **2** (Table III) as well as the ^{13}C SCS for system **4** (C-4, Table II) indicate that the inductive parameter (σ_I) for Me[16] and Me$_3$Sn attached to an sp^3-hybridized carbon is *zero*.
(47) The ^{19}F probe in **3** is probably very sensitive to any changes in the spatial proximity of the adjacent hydrogens in the bicyclooctyl group. In this connection, it is of interest to note that long-range "direct" coupling to these hydrogens is apparent from the very broad and ill-defined resonance pattern that is observed for the proton-coupled ^{19}F NMR spectra of system **3**. The corresponding resonance patterns for **1** and **2** were quite sharp.
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(65) NOTE ADDED IN PROOF. The ^{19}F SCS listed in parentheses (accurate to ±0.01) in Table III for systems **1** (except alkyl groups, Ph, SnMe$_3$) and **2** (except alkyl groups) were obtained after the acceptance of this manuscript for publication. Additional results (^{19}F SCS, ppm) for system **2** obtained under proton-decoupled conditions are for the *iodo* substituent: 0.29 (DMF), 0.45 (MeOH), 0.34 (C$_6$H$_6$), 0.53 (CH$_2$Cl$_2$), 0.68 (c-C$_6$H$_{12}$).

Iterative Force-Field Calculations of Cycloundecane, Cyclotridecane, and Cyclopentadecane

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Abstract: The conformations of cycloundecane, cyclotridecane, and cyclopentadecane have been investigated by iterative force-field calculations. Transition states linking the energy-minimum conformations were calculated for cycloundecane only. The known dynamic ^{1}H and ^{13}C NMR spectra of cycloundecane were analyzed in terms of the results of the force-field calculations of this hydrocarbon.

In recent years, X-ray diffraction studies, NMR spectroscopy, and strain energy calculations have provided considerable knowledge about the conformational properties of medium and large cycloalkanes and their derivatives. However, this knowledge is largely restricted to even-membered rings and rather little structural information is available for odd-membered saturated rings above cyclononane.

In this paper we present force-field calculations on the 11-, 13-, and 15-membered cycloalkanes. There is no direct structural information on these compounds, although the structure of cycloundecanone has been determined by X-ray diffraction methods.[1] NMR data[2,3] on the three hydrocarbons show that dynamic NMR effects occur at temperatures somewhat lower than -140 °C. Therefore, conformational barriers of the order of 6 kcal/mol must exist in these compounds. However, the low-temperature ^{1}H and ^{13}C NMR spectra are complex and cannot be interpreted in the absence of additional information, such as provided by force-field calculations.

Some force-field calculations have already been carried out on the 11-, 13-, and 15-membered cycloalkanes. Dale[4,5] has used a simple procedure to explore qualitatively or semi-quantitatively the energy-minimum conformations, as well as the interconversion paths linking these conformations in medium- and large-ring cycloalkanes. Although refined force-field calculations have been carried out on one or two conformations of cycloundecane,[6,7] this technique has not been applied in a systematic fashion to the ring systems discussed in the present work.

Results and Discussion

Strain energy (force-field or molecular mechanics) calculations were carried out with Boyd's iterative program MOLBUILD.[8] This program was modified to allow conformational changes to occur by driving the appropriate torsional angles as described by Wiberg and Boyd.[9] Approximate coordinates for trial geometries were calculated by means of the program COORD[10] with torsional angles obtained from Dreiding-Fieser molecular models. The exploration of pseudorotation paths involves the migration of a specific carbon atom (Figure 1) from a corner to an adjacent noncorner position (an elementary process[4,5]), or sequences of such migrations. As a result of an elementary process, three torsional angles change by about 120°: ±60 to ∓60, ±60 to 180, and 180 to ±60, respectively.[11] One torsional angle passes through 0° and the other two pass through 120°, in a sequential rather than simultaneous fashion.
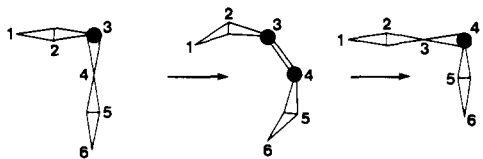
Figure 1. Migration of a carbon atom from a corner (black circle) to an adjacent noncorner position, in an elementary process.
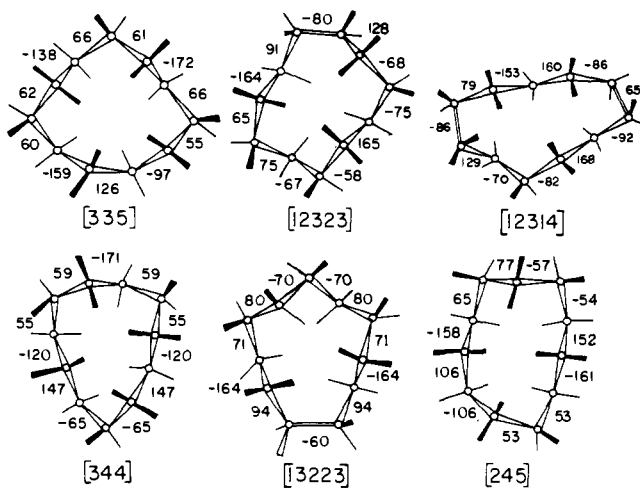

Figure 2. Calculated torsional angles in various conformations of cycloundecane.

Figure 3. Calculated torsional angles in various transition states of cycloundecane.

The strain energies reported in this study correspond to molecules in a hypothetical motionless state at 0 K. However, zero-point energy and vibrational enthalpy effects are expected to be similar for the different conformations of a given cycloalkane. All conformations reported in the present work (Table I) are true local energy minima, as evidenced by the fact that they all are calculated to have $3N - 6$ real vibrational frequencies.

Transition states for conformational interconversions were investigated only for cycloundecane, since the number of calculations required for cyclotridecane and cyclopentadecane are very large.

Dale's "wedge" system[4,5] has been adopted by us to represent the three-dimensional molecular conformations. The magnitude and sign of each torsional angle are indicated alongside the respective carbon–carbon bond. Generally, in order to achieve the least possible deformation at the corners, odd-membered compounds are expected to exist as three- or five-cornered conformations designated as "triangular" and "quinquangular" respectively.[4,5] A triangular conformation is represented by three numbers within square brackets, each denoting the number of bonds on consecutive sides of the conformation, starting with the shortest. Hence, the sum of the three numbers signify the ring size. Similarly, a quinquangular conformation is represented by five numbers.

Cycloundecane. (A) Conformations. For cycloundecane the strain energy calculations indicate the existence of six low-energy conformations which are shown in Figure 2. Contributions to the total strain energy of each conformation are listed in Table I. The lowest energy conformations are calculated to be the [335] and [12323], both of which have virtually the same energy. The next three conformations in order of increasing energy are the [12314], [344], and [13223]. The [344] conformation lies in a relatively flat-bottomed energy well since distorting some of its torsional angles by as much as 27° results in a mere 0.4 kcal/mol increase in energy.[13]

As Dale[4] has already pointed out, the low-energy [335] conformation of cycloundecane can be considered as formally derived from the square [3333] conformation of cyclododecane
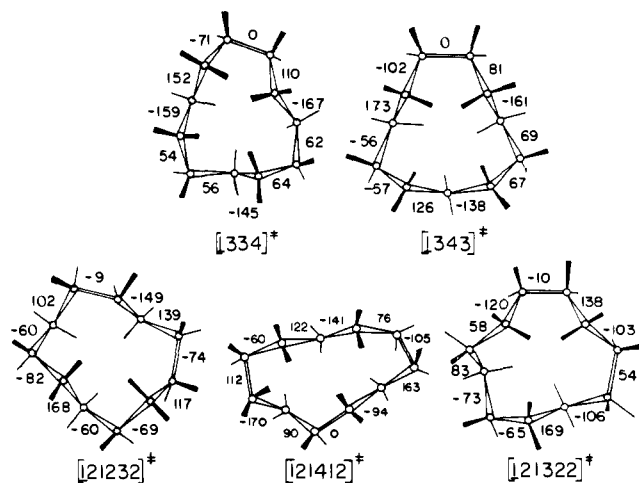
by ring contraction, whereas the [12323] is derivable from the [2323] conformation of cyclodecane by ring expansion. The [12314] conformation of cycloundecane,[12] which was not considered by Dale, is a crown-like conformation, and is derivable by ring expansion of the [1414] conformation of cyclodecane.

Considering the approximations made in Dale's calculations, there is a general agreement between the [335], [344], [12323], and [13223] conformations obtained by us and those reported by Dale.[4,5] The strain energies in the two studies agree to within ±1 kcal/mol (Table I), whereas the torsional angles generally agree to within ±20°. Dale investigated only a symmetrical [335] conformation (Table I). We find that a [335] structure with C_2 symmetry[14] is a transition state which is 2 kcal/mol less stable than the best unsymmetrical [335] conformation. Bixon and Lifson[6] have considered only a [344] conformation in cycloundecane.[15] Schleyer[7] has calculated the strain energies of [344] and [12314] conformations[15] and reported the [12314] to be preferred over the [344] by 2.8 kcal/mol. As shown in Table I, these two conformations have virtually the same energy in our calculations and are less stable than the [335] and [12323].

Groth[1] has determined the structure of cycloundecanone by X-ray. This compound exists as a [335] conformation with the carbonyl group unsymmetrically located near the middle of the long side of this triangular conformation. The reported geometry of cycloundecanone is in good agreement[16] with that of the [335] conformation of cycloundecane (Figure 1), the biggest discrepancy in the corresponding torsional angles of the two systems being only 2°.

(B) Conformational Interconversions. A scheme for the interconversions of cycloundecane conformations (except the [12314]) has been proposed by Dale.[4,5] We have used this as a basis for iterative force-field calculations on the transition states[17] for these interconversions. Our results are given in Figure 3 and Table II. The strain energies of the transition states shown in this table are relative to the strain energy of the [335] (or [12323]) conformation.

The low-energy [335] conformation pseudorotates via the [344] as an intermediate and pseudorotation partner (Figure 4). This facile process involves the [*1*334]‡ transition state, and has a barrier of 4.2 kcal/mol. The [344] conformation can alternatively pseudorotate via the [*1*343]‡ transition state without involving the [335] conformation, but this pseudorotation is calculated to be more difficult (Table II) than that involving the [335] and is therefore unimportant. The pseudorotation of the [335] conformation causes the mutual exchange of all the different carbons on the one hand, and all the

Table I. Calculated Strain Energies[a] (in kcal/mol) of Various Energy-Minimum Conformations of Cycloundecane, Cyclotridecane, and Cyclopentadecane

compd	conformation[b]	E_r	E_Θ	E_ϕ	E_{nb}	E_T	E_Δ	$E_\Delta{}^c$
cycloundecane	[12323]	0.83	4.21	5.53	5.63	16.2	0.0	0.3
	[335]	0.80	3.13	6.42	5.86	16.2	0.0	0.2[d]
	[12314]	0.77	2.83	8.38	5.37	17.4	1.2	
	[344]	0.80	2.90	7.52	6.18	17.4	1.2[d]	0.0[d]
	[13223]	0.89	5.75	5.34	5.70	17.7	1.5[d]	0.6[d]
	[245]	0.94	4.56	6.83	6.57	18.9	2.7	2.3
cyclotridecane	[13333]	0.73	2.00	4.49	5.01	12.2	0.0	1.1[d]
	[12433]	0.77	2.26	5.15	5.38	13.6	1.4	0.0
	[346]	0.76	2.06	5.67	5.32	13.8	1.6	4.4
	[445]	0.85	2.65	5.26	6.35	15.1	2.9	1.7[d]
	[355]	0.83	2.86	6.12	5.72	15.5	3.3	2.2[d]
cyclopentadecane	[33333]	0.67	1.75	3.45	4.72	10.6	0.0[e]	0.0[e]
	[13443]	0.67	2.15	3.59	4.73	11.1	0.5[d]	1.5[d]
	[13434]	0.67	2.34	4.44	4.28	11.7	1.1	2.7
	[14334]	0.69	2.54	3.99	4.70	11.9	1.3[d]	1.2[d]
	[13353]	0.73	2.01	3.99	5.27	12.0	1.4	2.5

[a] The following symbols are used: E_r, bond length strain; E_Θ, angle strain; E_ϕ, torsional strain; E_{nb}, nonbonded interaction strain. Total strain energy, $E_T = E_r + E_\Theta + E_\phi + E_{nb}$. E_Δ, strain energy relative to best conformation of the same cycloalkane. [b] All conformations have C_1 symmetry, except where otherwise stated. [c] Strain energy obtained by Dale,[4,5] relative to best conformation of the same cycloalkane. [d] For a conformation with C_2 symmetry. [e] For a conformation with D_5 symmetry.

Table II. Calculated Strain Energies[a] (in kcal/mol) of Various Transition States of Cycloundecane

transition state[b]	E_r	E_Θ	E_ϕ	E_{nb}	E_T	E_Δ	$E_\Delta{}^c$
[*1*334]‡	0.95	4.25	8.01	7.21	20.4	4.2	3.5
[*1*343]‡	0.88	4.67	9.56	6.75	21.9	5.7	5.7[d]
[*1*21232]‡	1.10	4.69	10.43	7.96	24.2	8.0	
[*1*21412]‡	0.82	4.27	13.8	6.56	25.4	9.2	
[*1*21322]‡	1.03	6.51	11.22	7.63	26.4	10.2	11.9

[a] See Table I for meaning of symbols. [b] All transition states have C_1 symmetry, except where otherwise indicated. [c] Strain energy obtained by Dale,[4,5] relative to the lowest energy conformation in cycloundecane, which is the [344] in Dale's calculations. [d] For a transition state with C_s symmetry.
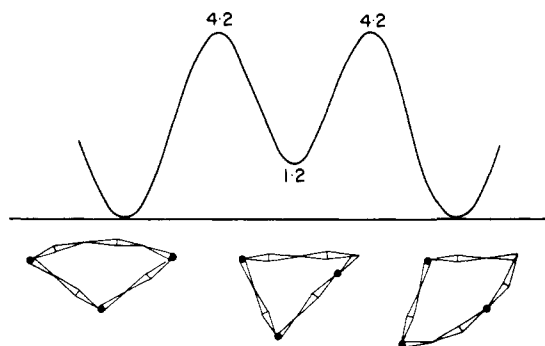
Figure 4. Pseudorotation itinerary for the [335] conformation of cycloundecane. Black circles are carbon labels.

different hydrogens on the other, resulting in a D_{11h} time-averaged symmetry.

The interconversion of the lower energy quinquangular conformation, [12323], with the triangular [335] involves the [*1*21232]‡ transition state and has a barrier of 8.0 kcal/mol. Dale[4,5] proposed that this interconversion proceeds via a [*1*235]‡ transition state, which we find to be at least 2.5 kcal/mol more strained than the [*1*21232]‡. Actually, the latter transition state is a sexangular partner of the quadrangular [*1*235]‡ and thus the two paths are closely related.

The higher energy quinquangular conformation, [13223], cannot interconvert with the triangular [335] directly, but it can do so indirectly via the [12323] conformation. The interconversion of the two quinquangular conformations involves the [*1*21322]‡ transition state and has a barrier of 10.2 kcal/mol, which therefore is also the barrier separating the

higher energy [13223] quinquangular conformation from the [335].

The crown-like [12314] conformation[12] is isolated from the [335] and [12323] by transition states calculated to have relative strain energies greater than 10.5 kcal/mol. The [12314] conformation pseudorotates via the [*1*21412]‡ transition state[12] and this process has a barrier of 9.2 kcal/mol.

(C) NMR Spectra. The 251-MHz ¹H and 63.1-MHz ¹³C NMR spectra of cycloundecane from −5 to −170 °C have been reported.[2,3] The ¹H NMR spectrum consists of a single absorption above about −140 °C. Below this temperature the resonance line broadens, and at −152 °C the line shape is approximately Lorentzian with a width of ca. 50 Hz. At −164 °C the spectrum consists of a relatively sharp absorption (width ≃ 50 Hz) on top of an unsymmetrical broad base (width ≃ 200 Hz). The ¹³C NMR spectrum of cycloundecane consists of a single relatively sharp line above about −140 °C. Below this temperature the resonance line broadens appreciably, reaching maximum broadening (width ≃ 200 Hz) at ca. −157 °C, and then sharpens again (width ≃ 125 Hz) with no observable new peaks at −164 °C. This behavior is indicative of exchange between two conformations with rather different populations.

The NMR spectral behavior of cycloundecane can be interpreted in terms of the force-field calculations given in the preceding sections. At low temperatures, only the [12323] and the [335] conformations should be significantly populated, as shown by the relative strain energies given in Table I. The interconversion of the [335] and [12323] should be rapid on the NMR time scale above −140 °C, and this should result in a single line with a time-averaged chemical shift of the two conformations. The dynamic NMR effect observed in cy-
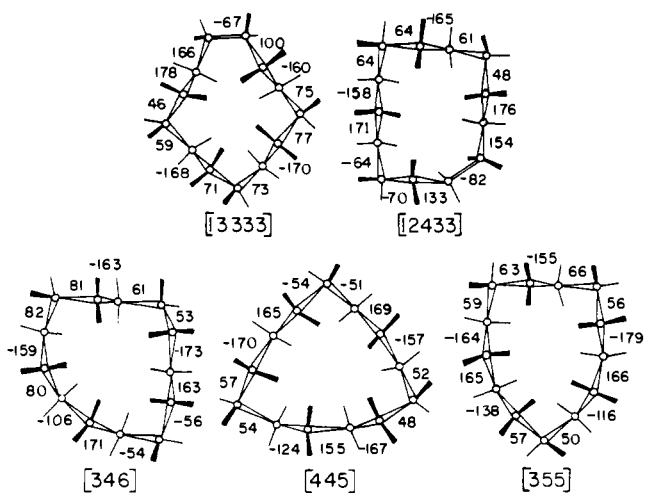
Figure 5. Calculated torsional angles in various conformations of cyclotridecane.

Figure 6. Calculated torsional angles in various conformations of cyclopentadecane.

cloundecane at low temperature is ascribed to the separation of the [12323] (about 15–30% at −150 °C) from the major [335] conformation. The relatively sharp absorption in the ^{13}C NMR spectrum at −164 °C is assigned to the rapidly pseudorotating [335] conformation. The [12323] conformation is not observable in the low temperature ^{13}C NMR spectrum because of its relatively low population and the presence of eleven different chemical shifts. This analysis is reinforced by the ^{1}H NMR spectrum: the relatively sharp signal and the broad base observed at −164 °C can be assigned to the major triangular and minor quinguangular conformations, respectively.

Our interpretation of the spectral behavior of cycloundecane requires that the free-energy difference ($\Delta G°$) between the major [335] and minor [12323] conformations be ca. 0.2 to 0.4 kcal/mol, and this is in good agreement with the force-field calculations which show that these two conformations have the same strain energies. The calculated (strain energy) barrier for the interconversion of the [335] and [12323] conformations of cycloundecane is 8 kcal/mol, in fair agreement[18] with the experimental (free energy) barrier which is of the order of 6 kcal/mol.

Cyclotridecane Conformations. For cyclotridecane the strain energy calculations indicate the existence of five low-energy conformations (see Table I and Figure 5). The [13333] conformation is of lowest energy, followed in order by [12433], [346], [445], and [355]. These results show substantial deviations from Dale's[4,5] semiquantitative calculations. The order of the two lowest energy conformations is reversed in the more accurate iterative calculations from that found by Dale. There are also substantial differences in the calculated strain energies of the other conformations (Table I).

Dale[4,5] considered only symmetrical conformations whenever symmetry was possible. The present calculations show that all the cyclotridecane conformations are unsymmetrical. For example, the symmetrical (C_2) structure having the [445] skeleton[19] is calculated to be 0.2 kcal/mol less stable than the best unsymmetrical [445] conformation.

Cyclopentadecane Conformations. For cyclopentadecane, the strain energy calculations indicate the existence of five low-energy conformations, all of which are quinquangular, as shown in Figure 6. Contributions to the total strain energy of each conformation are listed in Table I.

The results of the present calculations are similar to those of Dale[4,5] except for the [12534] conformation.[20] Both calculations show that the highly symmetrical [33333] is of lowest energy, but as pointed out by Dale, this conformation has a low entropy and is probably not favored at room temperature. It
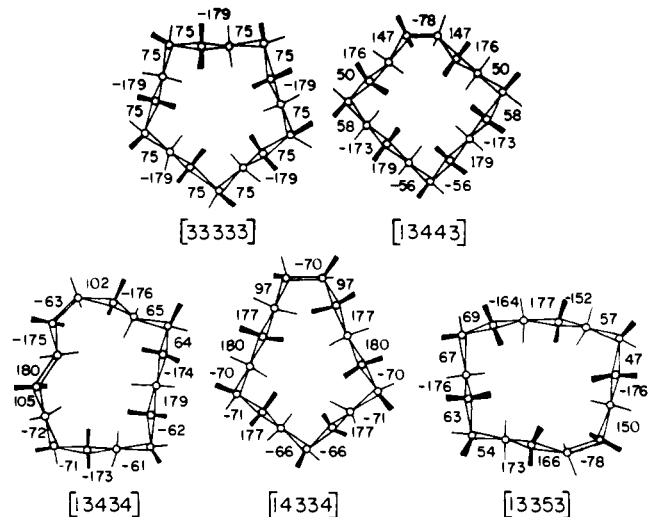
is apparent that cyclopentadecane should exist at room temperature as a mixture of five different conformations.[21]

Conclusions. Cycloundecane at about −150 °C is probably a mixture of the [12323] and [335] conformations with the latter predominating; at room temperature, several other conformations may also be significantly populated. Cyclotridecane is predicted to exist mainly but not exclusively in the [13333] conformation. Cyclopentadecane is most likely a mixture of several conformations; the highly symmetrical [33333] conformation has both a low entropy and enthalpy and may be the preferred conformation at very low temperatures.

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(11) These values are approximate and may vary by 10° or more in particular cases.
(12) There is a problem with the classification of the crown-like conformation denoted as [12314]. The projection of this conformation on the general plane of the ring looks quinquangular and is arbitrarily assigned the shorthand notation above. However, the [12314] conformation can alternatively be designated as [(11)] (eleven). Similarly the [121412]$^{\pm}$ transition state which is required for the pseudorotation of the [12314] can be designated as [1̄(10)]$^{\pm}$.
(13) A symmetrical [344] structure (torsional angles: −48, 148, −147, 57, 58, −155, 58, 57, −147, 148, and −48°) has a strain energy of 1.6 kcal/mol (E_r = 0.93, E_Θ = 2.88, E_ϕ = 6.51, E_{nb} = 7.51, and E_T = 17.8) relative to that of the [335] (or [12323]) conformation.
(14) A symmetrical [335] structure (torsional angles: 60, −155, 68, 71, −132, 111, −132, 71, 68, −155, and 60°) has a strain energy of 2.0 kcal/mol (E_r = 0.82, E_Θ = 2.20, E_ϕ = 8.50, E_{nb} = 6.69, and E_T = 18.2) relative to that of the [335] (or [12323]) conformation.
(15) The [344] conformation calculated by Bixon and Lifson has C_1 symmetry. The [344] and [12314] conformations reported by Schleyer have C_1 and C_2 symmetry, respectively.

(16) In general, the replacement of a methylene by a CO group in medium and large cycloalkanes is not expected to lead to significant conformational changes [see F. A. L. Anet, M. St. Jacques, P. Henrichs, A. Cheng, J. Krane, and L. Wong, *Tetrahedron*, **30**, 1629 (1974)].

(17) In a transition state of an elementary process the bond between the old and new corner atoms becomes eclipsed (Figure 1). This one-side bond is marked in italics in the name notation (underlined in Figure 3) and is associated with a torsional angle of $0°$. This value is approximate and may vary by as much as $15°$ in particular cases.

(18) Our experience with the iterative force-field calculations of medium and large cycloalkanes (*e.g.*, $n = 10$, 12, 14, and 16) is that the (strain energy) barriers are generally ca. 1 kcal/mol higher than the experimental (free energy) barriers [F. A. L. Anet and T. N. Rawdah, *J. Am. Chem. Soc.*, in press; F. A. L. Anet and A. K. Cheng, *ibid.*, **97**, 2420 (1975)].

(19) A symmetrical [445] structure (torsional angles: -53, 171, -161, 49, 53, -148, 160, -148, 53, 49, -161, 171, and $-53°$) has a strain energy of

3.1 kcal/mol ($E_r = 0.90$, $E_\Theta = 2.45$, $E_\phi = 6.03$, $E_{nb} = 6.93$, and $E_T = 15.3$) relative to that of the [13333] conformation.

(20) A [12534] conformation of cyclopentadecane (torsional angles: -57, 169, -176, 154, -72, -79, 139, -85, 139, 173, 153, -74, -71, 171, and $-58°$) has a strain energy of 5.2 kcal/mol ($E_r = 0.73$, $E_\Theta = 1.81$, $E_\phi = 7.82$, $E_{nb} = 5.39$, and $E_T = 15.8$) relative to that of the [33333]. In Dale's calculations the [12534] conformation has a relative strain energy of 2.6 kcal/mol.

(21) The [33333] conformation has a symmetry number of 10 compared to only 2 for the [13443] and [14334], and 1 for the [13434] and [13353]. Therefore at 25 °C the conformations of cyclopentadecane with C_1 and C_2 symmetries are favored by entropy terms of ca. 1.4 and 1.0 kcal/mol, respectively, over the [33333] conformation with D_5 symmetry. These entropy terms result in relative free energy of 0.0, 0.2, 0.5, 0.5, and 0.8 kcal/mol for the [13443], [13434], [33333], [13353], and [14334] conformations, respectively.

Conformations of *cis,cis*-1,3-Cyclooctadiene and Its Epoxides. Dynamic Nuclear Magnetic Resonance Spectroscopy and Iterative Force-Field Calculations

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Abstract: The 251-MHz ^{1}H and the natural-abundance 63.1-MHz ^{13}C NMR spectra of *cis,cis*-1,3-cyclooctadiene (I), *cis,cis*-1,3-cyclooctadiene monoepoxide (II), and *cis,cis*-1,3-cyclooctadiene *trans*-diepoxide (III) have been investigated over the temperature range of -10 to -170 °C. Compound I exists in solution as a nearly equal mixture of a symmetrical (C_2) twist-boat-chair (I-TBC) and an unsymmetrical twist-boat (I-TB) conformation. Two conformational processes affect the ^{13}C NMR spectrum of I and the free-energy barriers are 7.2 and 9.0 kcal/mol. The lower energy process is a ring pseudorotation of the twist-boat and leads to a C_2 time-averaged symmetry, whereas the higher energy process is the interconversion of the two conformations. The ^{1}H NMR spectra of I show complex and continuous changes from about -50 to -120 °C, and provide an upper limit of about 10 kcal/mol for the free-energy barrier for a third process which is required for I to achieve its maximum molecular symmetry of C_{2v}. Iterative force-field calculations on the conformations and conformational interconversion paths of I give results consistent with the NMR findings and define the conformations found experimentally. The ^{13}C NMR spectra of II reveal that all three exo epoxides formally derived from the two conformations of I are present in solution. Two conformational processes, with free-energy barriers of 7.2 and 9.5 kcal/mol, occur in II. The lower energy process interconverts the two exo epoxides derived from the twist-boat, while the higher energy process is the interconversion of the twist-boat with the twist-boat-chair. The ^{13}C NMR spectrum of III is found to be temperature independent and therefore a twist-boat-chair conformation with C_2 symmetry, similar to that of I-TBC, is proposed for this compound. The quite unequal populations of the two twist-boats of II and the absence of twist-boats of III is explained. Conformational implications of the current results for substituted derivatives of I and analogues of II and III are discussed.

Introduction

cis,cis-1,3-Cyclooctadiene (I), which is the most stable cyclooctadiene isomer, can be obtained readily by isomerization of 1,5-cyclooctadiene.[1] On the basis of ultraviolet spectroscopy and the examination of molecular models, Braude[2] deduced that the diene system in 1 must be nonplanar with a torsional angle of about 40–45°; the conformation depicted in his paper corresponds to a twist-boat-chair in our nomenclature. Traetteberg has investigated the structure of 1 in the gas phase by electron diffraction and has reported[3] that the conformation is a twist-boat with a diene twist angle of 38°. Photoelectron spectroscopy on 1 has revealed a torsional angle of 59°.[4]

Early low-temperature 60-MHz ^{1}H NMR spectra of 1 revealed the existence of a dynamic NMR effect at about -100 °C, but the complexity of the spectrum prevented a detailed analysis.[5] The olefinic proton coupling constants in I at room temperature correspond to a nonplanar diene moiety.[6]

Noniterative force-field calculations have been reported[7] for the twist-boat-chair, boat, and half-chair conformations of 1. An iterative force-field calculation on the twist-boat-chair and twist-boat conformations of I has also been carried out,

and a comparison of the calculated and observed energy differences between I and its 1,4 and 1,5 isomers has been made.[8] No force-field calculations of the interconversion paths of the twist-boat and twist-boat-chair have been published.

Epoxidation of 1 gives a monoepoxide (II)[9] and, stereospecifically, a trans diepoxide (III).[10]

I   II   III
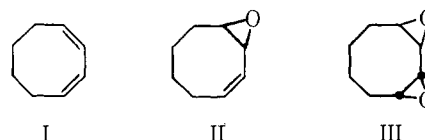
We now report ^{1}H and ^{13}C NMR data[11] and extensive force-field calculations on I and we show that the conformations of II and III can be deduced from their ^{13}C NMR spectra and a consideration of the conformational relationships of II and III to I.

Experimental Section

cis,cis-1,3-Cyclooctadiene[1] and its epoxides[9,10] were prepared by known procedures and the purity of the samples was checked by ^{1}H and ^{13}C NMR.