Dynamics of Cyclic Allenes. Conformational Properties of 1,2-Cyclononadiene, 1,2,6-Cyclononatriene, and 1,2,6,7-Cyclodecatetraene. Dynamic Nuclear Magnetic Resonance Spectroscopy and Iterative Force-Field Calculations†

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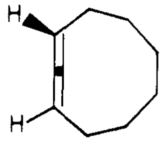
Abstract: The natural-abundance ^{13}C NMR spectra of 1,2-cyclononadiene (I), 1,2,6-cyclononatriene (II), and *meso*-1,2,6,7-cyclodecatetraene (III) have been studied over the temperature range of +60 to −180 °C. Compound I exists in solution as a mixture of two conformations (one symmetrical and one unsymmetrical) having a free-energy difference of 0.18 kcal/mol. Two conformational processes are found in I and the free-energy barriers are 7.3 and 6.0 kcal/mol. The lower energy process is a ring pseudorotation of the major (unsymmetrical) conformation leading to a time-averaged C_2 symmetry, whereas the higher energy process is the interconversion of the major conformation with the minor (symmetrical) conformation. Iterative force-field calculations on I give results consistent with the NMR findings and define the conformations found experimentally in structural terms. Compound II is found to exist in solution as an unsymmetrical conformation that can undergo a strongly hindered ring pseudorotation ($\Delta G^{\ddagger}$ = 13.1 kcal/mol) to achieve a C_2 time-averaged symmetry. Iterative force-field calculations indicates that the best path for this symmetrization process involves an axial-symmetrical form as intermediate. The lowest energy conformation of III has C_i symmetry. Symmetrization of this conformation results in a C_{2h} time-averaged symmetry and has a calculated strain-energy barrier of 6.8 kcal/mol. An experimental determination of this barrier by DNMR spectroscopy gives a $\Delta G^{\ddagger}$ of 7.1 kcal/mol. The ground-state conformation of *dl*-1,2,6,7-cyclodecatetraene (IV) is found by force-field calculations to have a "nonintersecting" twofold axis of symmetry. The lowest calculated strain-energy path for conformational interconversions in IV does not maintain the nonintersecting C_2 axis and is found to have a calculated strain-energy barrier of 9 kcal/mol. Based on the results of NMR experiments and force-field calculations, a mechanism for the stereospecific formation of III from the bis adduct of dibromocarbene to 1,5-cyclooctadiene is presented.

Cyclic medium-ring allenes and diallenes are strained compounds,[1] whose detailed structural and dynamic features are largely unexplored, despite some recent spectroscopic investigations.[2-4] The cyclic allenes, 1,2-cyclononadiene[5] (I), 1,2,6-cyclononatriene[6] (II), and *meso*-1,2,6,7-cyclodecatetraene[6] (III) are available via dibromocarbene adducts of cyclooctene or 1,5-cyclooctadiene. Compounds I and II can exist as racemic mixtures owing to the presence of chiral axes.[7] Resolution of racemic I has been achieved by means of platinum complexes.[8] Simple monocyclic diallenes possess two chiral centers and should exist in two diastereomeric forms, one diastereomer being racemic and the other a meso compound. Such isomers have been isolated in the case of the 12-membered diallene, 3,4,9,10-cyclododecatetraene-1,7-dione,[9] and the 14-membered diallene, 3,4,10,11-cyclotetradecatetraene-1,8-dione.[9] On the other hand, the 10-membered diallene, 1,2,6,7-cyclodecatetraene, has only been obtained as a single diastereomer,[6,10] which has recently been shown by x-ray diffraction[11] to be the meso isomer III. The racemic isomer (IV) of this compound is not presently known.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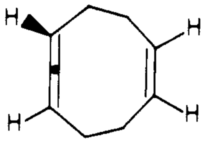
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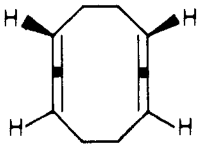
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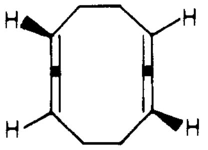
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We now report an investigation of the dynamic NMR behavior of I, II, and III in solution, as well as the results of iterative force-field calculations of the conformations and conformational interconversions that occur in compounds I-IV.

Force-Field Calculations and Parameters. Empirical force-field (strain-energy or molecular mechanics) calculations[12] were carried out on compounds I-IV with Boyd's iterative computer program.[13] The parameters for torsional and out-of-plane bending about an olefinic double bond were those of Ermer and Lifson.[14] Other force-field parameters, except those for the allenic moiety, were obtained from Boyd. Allenes have not previously been investigated by empirical force-field calculations, and thus parameters have not been established for cumulated double bonds. The vibrational frequencies of allene and its deuterated derivatives have been extensively investigated,[15] and it was our original intention to try to fit these frequencies with force-field parameters. However, the algorithm used by Boyd to calculate the angle bending contribution to the strain energy fails for an angle of 180° as occurs for the carbon skeleton in allene, and thus Boyd's program, in its current form, cannot be used for allene itself. In cyclic allenes, the C═C═C bond angle is bent and no difficulty arises.

The force-field parameters that we have chosen for the allene unit together with parameters for other groups are given in Table I. The torsional potential for the allene unit is analogous to that used by Ermer and Lifson[14] for double bonds. A twofold torsional potential was used for the cumulated double bonds between C(1) and C(3) with the energy minimum set at 90°. This potential was applied to both the C-C_{sp^2}-C_{sp^2}-C and the H-C_{sp^2}-C_{sp^2}-H arrangements in an allene unit. The internal-angle bending and the out-of-plane bending of the allenic sp^2-hybridized carbon atoms were chosen to have the

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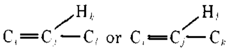
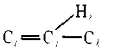
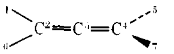
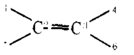
† Dedicated to Professor Thomas L. Jacobs on the anniversary of his 70th birthday.

Table I. Force-Field Parameters

Strain-energy terms[a]	Unstrained values of angles or distances	Force constants	Strain-energy terms[a]		Unstrained values of angles or distances	Force constants
Bond stretching[b]	r	K_r	Bond-angle bending[c]		θ	K_θ
$C_{sp^3}{-}H$	1.090	4.550	$H{-}C_{sp^3}{-}H$		107.9	0.508
$C_{sp^2}{-}H$	1.070	5.080	$H{-}C_{sp^3}{-}C_{sp^2}$ or $H{-}C_{sp^3}{-}C_{sp^3}$		109.5	0.608
$C_{sp}{-}C_{sp^2}$	1.310	6.800	$H{-}C_{sp^2}{-}C_{sp^3}$		119.5	0.350
$C_{sp^2}{-}C_{sp^3}$	1.500	5.100	$H{-}C_{sp^2}{-}C_{sp}$ or $H{-}C_{sp^2}{-}C_{sp^2}$		120.5	0.605
$C_{sp^3}{-}C_{sp^3}$	1.530	4.400	$C_{sp^3}{-}C_{sp^2}{-}C_{sp^2}$ or $C_{sp^3}{-}C_{sp^2}{-}C_{sp}$		124.7	0.620
$C_{sp^2}{-}C_{sp^2}$	1.330	6.800	$C_{sp^3}{-}C_{sp^3}{-}C_{sp^3}$ or $C_{sp^3}{-}C_{sp^3}{-}C_{sp^2}$		111.0	0.800
			$C_{sp^2}{-}C_{sp}{-}C_{sp^2}$		180.0	0.300
Out-of-plane bending[d]	δ	K_δ				
 $C_i{=}C_j(H_k){-}C_l$ or $C_i{=}C_j(H_l){-}C_k$	0	0.080				
 $C_i{=}C_j(H_k){-}C_l$	0	0.280				
Torsional strain[e]			ϕ	K_ϕ	B	C
$C{-}C_{sp^3}{-}C_{sp^3}{-}C$			±60 or 180	0.0158	1	3
$C{-}C_{sp^3}{-}C_{sp^2}{-}C$			±120 or 0	−0.0133	−1	3
	1–2–4–5 6–2–4–7		±90 ±90	0.0600 0.0600	1 1	2 2
	1–2–3–4 5–2–3–6		0 0	−0.1135 −0.1135	−1 −1	2 2
Nonbonded interactions[f]				A	B	C
C · · · C				4.45	104.0	3.090
C · · · H				0.96	30.0	3.415
H · · · H				0.19	18.4	3.750

[a] Energies are in units of 10^{-11} erg/molecule; r in angstroms; θ, ϕ, δ in degrees. To convert 10^{-11} erg/molecule to kilocalories/mole, multiply by 144. [b] $E(r) = \frac{1}{2}K_r(r - r_0)$. [c] $E(\theta) = \frac{1}{2}K_\theta\ (\theta - \theta_0)^2$, angles to be reduced to radians for use. [d] $E(\delta) = \frac{1}{2}K_\delta(\delta)^2$, where $(\pi - \delta)$ is the angle between the normal to the ijk plane and the vector from j to l. Atom l is the out-of-plane atom. [e] $E(\phi) = \frac{1}{2}K_\phi(B + \cos C\phi)$. [f] $E^{\mathrm{nb}}(r) = A/r^6 + B\exp(-Cr)$.

same numerical constants as those for the ethylenic sp^2-carbon atoms (Table I). The force constant for angle bending at the central sp-hybridized allenic carbon was taken to be 0.30 mdyn/rad^2, a value that is a little lower than that used by Allinger and Meyer[16] for an acetylenic carbon (0.38 mdyn/rad^2).

Calculations based on the Newton-Raphson procedure, as in the present instance, can converge to either an energy maximum or an energy minimum with respect to distortions corresponding to a normal mode of vibration. Ermer[17] has recently stressed the desirability of determining whether a given geometry obtained in a force-field calculation is a true (local) energy minimum with respect to any small distortion of the molecule. A test for such an energy minimum can be made if the vibrational frequencies of the conformation are calculated, as all vibrational frequencies should be real for a true minimum. Since Boyd's program provides the vibrational frequencies as an optional feature, we have checked that all the energy-minimum conformations obtained in our force-field calculations have $3N - 6$ real vibrational frequencies. For transition-state geometries, on the other hand, the criterion that must hold is that *one* and *only one* vibrational frequency be imaginary, and such a test has been applied to each conformational transition state in our calculations.

Approximate coordinates for trial geometries were calculated by means of the program COORD[18a] with torsional angles estimated from Dreiding-Fieser molecular models.[18b] The conformational energy surface was explored by "driving"[19] a torsional angle (or in some cases two torsional angles) by steps of 10–15°.

Experimental Section

1,2-Cyclononadiene, 1,2,6-cyclononatriene, and *meso*-1,2,6,7-cyclodecatetraene were prepared by known procedures.[5,6]

All NMR spectra were obtained on a superconducting solenoid spectrometer operating at 59 kG.[20] Protons were noise decoupled and the ^{13}C NMR spectra are Fourier transforms of accumulated free-induction decays and were obtained in 10-mm tubes under the following conditions: 45° pulse angle, 8K data points, 14286-Hz spectrum width, and an exponential broadening function corresponding to 4-Hz broadening. The solvent for 1,2-cyclononadiene was an ~1:3 mixture of $CHFCl_2$ and CHF_2Cl. For 1,2,6-cyclononatriene and for *meso*-1,2,6,7-cyclodecatetraene $CDCl_3$ and $CHFCl_2$ were used, respectively. A fluorine line of the solvent was employed as a lock. For the $CDCl_3$ solutions the fluorine signal of internal C_6F_6 was used for lock purposes. Tetramethylsilane was used as an internal reference. All temperatures were measured with a copper-constantan thermocouple situated in the probe a few centimeters below the sample.

Free energies of activation[21] were calculated from rate constants by the absolute rate theory.[22] The rate constants were obtained near the coalescence temperatures by fitting the ^{13}C NMR spectra with line shapes calculated with a Fortran program on the Nova (Data General Corp.) computer of the NMR spectrometer. Force-field calculations were carried out on an IBM-360/91 computer at the Campus Computer Network of UCLA.

Results and Discussion

^{13}C NMR Spectra of 1,2-Cyclononadiene (I). ^{13}C NMR spectra of I have been obtained over the temperature range of −10 to −180 °C, and typical spectra are displayed in Figure 1. Above about −50 °C, the spectrum shows five resonances with the chemical shifts and partial assignments given in Table II. All the carbon resonances of I broaden below −100 °C and rather complex but understandable spectral changes occur in the region of −100 to −180 °C. The behavior of the quaternary allenic carbon resonance is the easiest to interpret. At −140 °C, this carbon gives rise to two lines in the ratio of ~2:1 and thus I must exist in two different conformations, labeled I-A and I-B, respectively,[23] whose populations are also in the ratio of 2:1. The intensity of the smaller line of the quaternary carbon suddenly becomes small below about −170 °C and varies from experiment to experiment. The large change in the intensity of this line takes place without line broadening and is

Table II. ^{13}C NMR Chemical Shifts in Cyclic Allenes

			^{13}C chemical shifts[a]					
Compd	Temp, °C	Symmetry	CH_2			=C=	CH (allenic)	CH (olefinic)
I	-50	$C_2{}^b$	25.3	27.6	28.3	205.6	93.1	
	-130	C_2	25.3	26.9	26.9	206.4	92.6	
	-170	$C_2{}^b$	~25.2	28.1	~29.1	205.1	94.5	
		C_2	25.2	26.8	26.8	206.2	92.5	
		C_1	20.3	28.0	25.6	205.0	93.6;	
			30.1	28.0	32.6		95.5	
II	50	$C_2{}^b$	27.1	28.9		205.2	90.3	130.4
	-30	C_1	24.7, 29.1, 26.7, 30.9			205.2	87.3, 93.4	129.5, 131.2
III	-20	$C_{2h}{}^b$	26.2			208.2	90.6	
	-130	C_i	24.2, 28.2			208.2	89.5, 91.6	

[a] In parts per million downfield from internal tetramethylsilane. [b] Time-averaged symmetry.

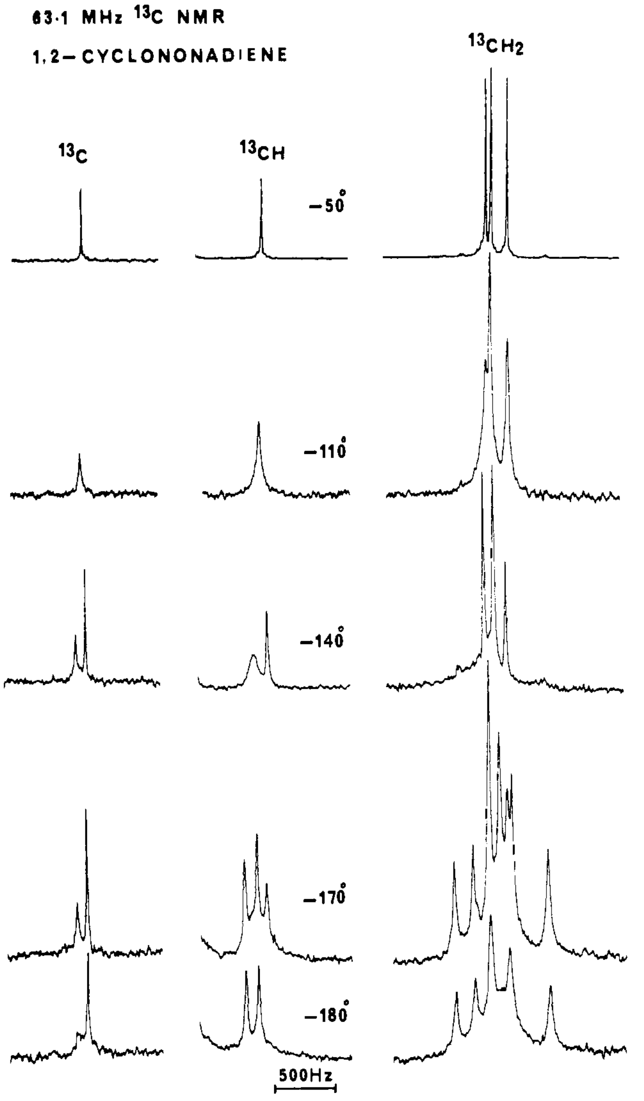


Figure 1. ^{13}C NMR spectra (63.1 MHz) of 1,2-cyclononadiene at various temperatures.

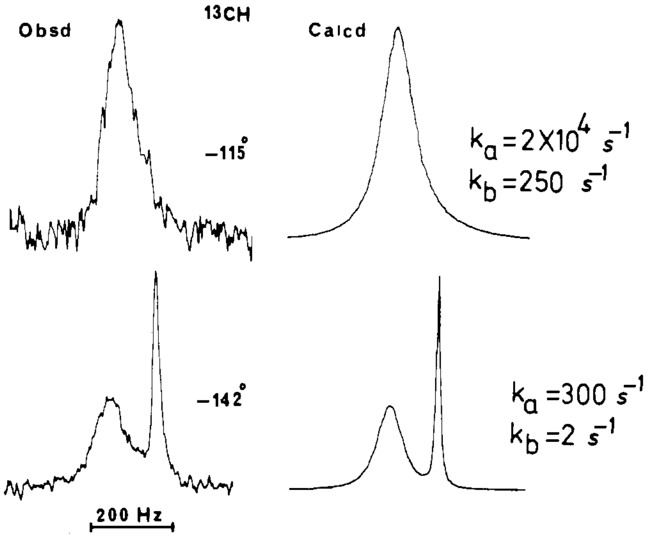


Figure 2. Experimental (left) and calculated (right) ^{13}C NMR spectra of the methine-carbon region of 1,2-cyclononadiene. The first-order exchange rate constants, k_a and k_b, correspond to conformational processes A and B, respectively.

accompanied by the appearance of crystals in the NMR sample tube. It is apparent that one conformation (the minor one, I-B) is rather insoluble and crystallizes out at very low temperatures. It also follows that the rate of interconversion of the two conformations below −170 °C is slow over the time required to measure a few spectra (~30 min).

The allenic methine carbons show spectral changes similar to those of the quaternary carbon, but with one additional feature. At −140 °C, the spectrum is a doublet with one sharp and one broad component. The sharp component has one half the area of the broad component, and thus must belong to the minor conformation, I-B. This conclusion is supported by the observation that the component which is sharp at −140 °C suddenly disappears below −175 °C as a result of crystallization, in agreement with the behavior of the quaternary allenic carbon. The broad component given by the allenic methine carbons at − 140 °C changes into a sharp 1:1 doublet below −160 °C. This second DNMR effect is best explained by assuming that the major conformation (I-A) lacks symmetry. Thus the two allenic methine carbons of this conformation are in different environments and have different chemical shifts. At −180 °C, only this doublet is observed in the spectrum, as I-B is no longer in solution. The presence of a single line for the methine carbons in I-B implies the presence of symmetry or time-averaged symmetry in that conformation.

The remaining portion of the spectrum of I arises from methylene carbons of I-A and I-B (Table II). Only the lines of the major conformation are visible at −180 °C (Figure 1); there are five lines instead of six because of a coincidence. The minor conformation, I-B, also has a chemical shift coincidence at low temperatures and thus shows two lines rather than three at −170 °C. The spectrum of the methylene carbons of I at −140 °C consists of three sharp lines and some very broad and overlapping bands. The two higher field sharp lines belong to

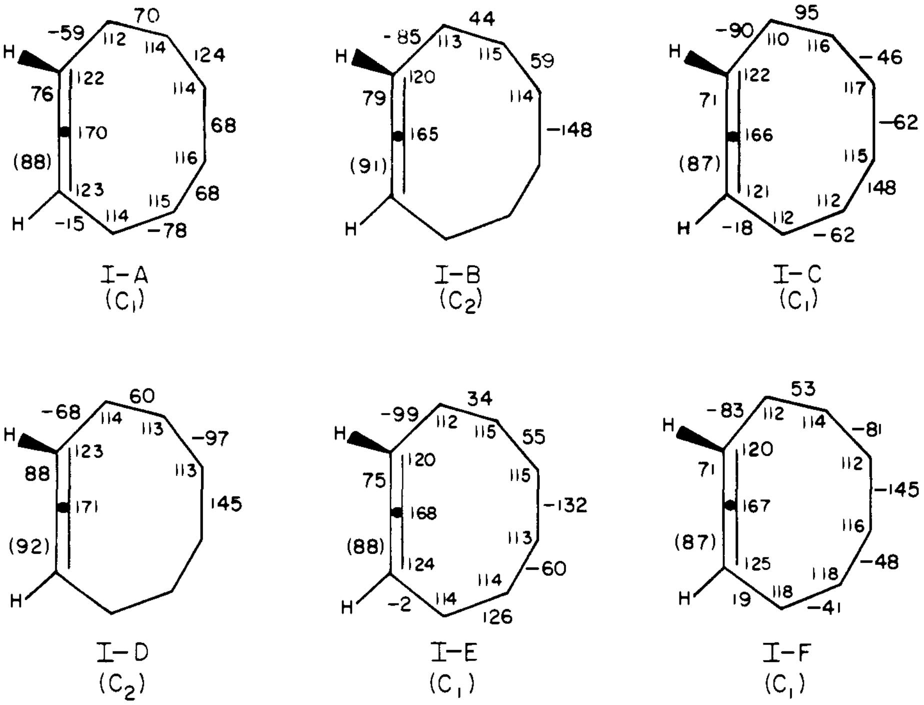


Figure 3. Calculated torsional and internal angles in various energy-minima conformations of 1,2-cyclononadiene (1). The torsional angles shown in parentheses belong to the allenic H-C_{sp^2}-C_{sp^2}-H arrangement.

Table III. Comparison of the Experimental and Theoretical Relative Energies[a] in 1,2-Cyclononadiene (I)

Conformation	Symmetry	Exptl	Calcd
I-A	C_1	0.00	0.00
I-B	C_2	0.18	0.10
$(\text{I-A} \rightleftharpoons \text{I-B})^{\ddagger}$	C_1	7.3	8.7
$(\text{I-A} \rightleftharpoons \text{I-A}')^{\ddagger}$	C_1	6.0	7.0

[a] In units of kilocalories/mole, relative to I-A.

I-B and the lower field sharp line arises from the previously mentioned coincident pair of lines of I-A. The remaining methylene resonances of I-A are very broad at this temperature and are scarcely visible in the spectrum.

Two conformational processes are evident in 1,2-cyclononadiene (I) from the variable temperature ^{13}C NMR data: (a) a degenerate interconversion of the unsymmetrical major conformation I-A with itself to give a C_2 time-averaged symmetry (process A); (b) an interconversion of I-A with I-B (process B). Process A is mainly responsible for line-shape changes between −130 and −170 °C; process B gives rise to spectral changes mainly between −110 and −140 °C.

The DNMR picture of I presented above is confirmed by line-shape calculations of the allenic methine carbon resonances at −115 and −142 °C (Figure 2). The rate constants were obtained with the constraint that the $\Delta G^{\ddagger}$s for the two processes (Table III) are temperature independent, at least over this 27 °C range. The line broadening observed at −142 °C is essentially determined by k_a of process A. At −115 °C, process A is very rapid and the line width is largely dependent on k_b of process B.

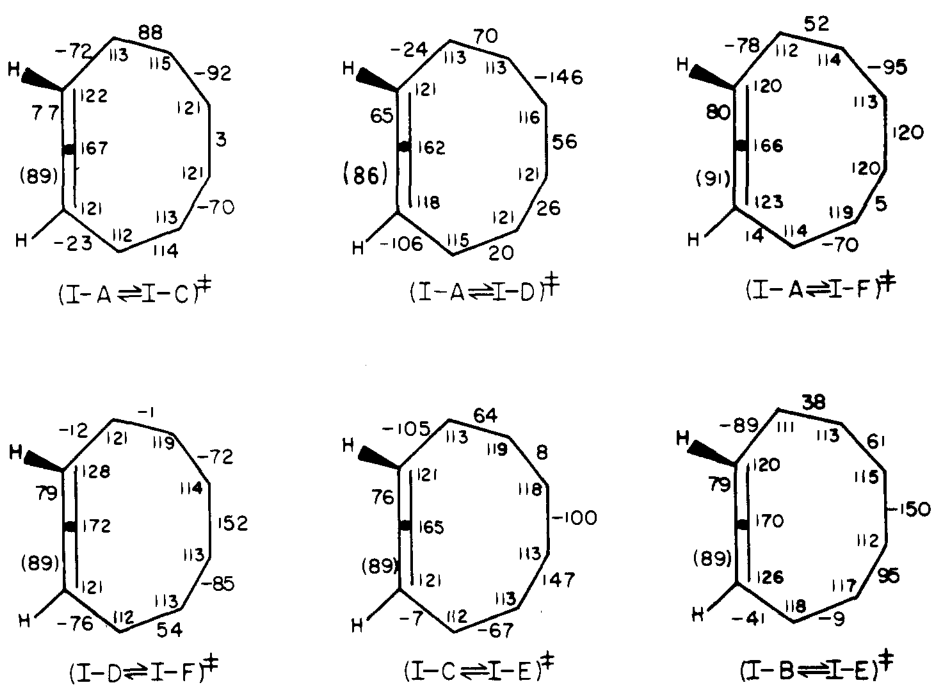
Force-Field Calculations on 1,2-Cyclononadiene (I). Altogether 11 geometries were found important for a description of the conformational features of I. Six correspond to energy minima (Figure 3), and five to one-dimensional energy maxima (saddle points or transition states) as shown in Figure 4. Calculated strain-energy paths for conformational interconversions of the various forms of I are shown in Figures 5 and 6. The starting conformation for these calculations was I-A. By driving the torsional angle ϕ_{5678} of I-A, a smooth conformational change occurred leading to a transition state, $(\text{I-A} \rightleftharpoons \text{I-C})^{\ddagger}$. Upon further driving of the same torsional angle, an energy minimum, namely I-C (C_1), was obtained, which is 0.6 kcal/mol above I-A. The calculated strain energy for $(\text{I-A} \rightleftharpoons \text{I-C})^{\ddagger}$ is 8.7 kcal/mol higher than that of I-A (Figure 5).

By driving ϕ_{4567} in the I-C conformation from −46 to +8°, another transition state was found which had a calculated strain energy of 4.0 kcal/mol above that of I-A. Further driving of this torsional angle to ~55° leads to yet another energy-minimum conformation (I-E, C_1), which is 1.9 kcal/mol above I-A. Finally, the torsional angle, ϕ_{6789}, of I-E can be driven from −60 to +59°, and this results in a conformation, I-B (C_2), which has virtually the same strain energy as does I-A. Conformations I-A and I-B are important, as will be shown below, because they are significantly populated under the conditions of our NMR experiments. From Figure 5, it is clear that the interconversion of I-A with I-B by the path shown has a strain-energy barrier of 8.7 kcal/mol. This path has the lowest energy of several paths which we investigated. Conformation I-A′ is a pseudorotated form of I-A, i.e., it is identical with I-A in the absence of labeling.

Although I-B is an intermediate in the interconversion of I-A with I-A′ by the processes shown in Figure 5, there exists a second and lower energy path to achieve this interconversion, and this does not involve I-B as an intermediate. It should be noticed that the interconversion of I-A with any conformation or transition state having C_2 symmetry is automatically a mechanism for the interconversion of I-A with I-A′.

The best path for interconverting I-A with I-A′ proceeds via the relatively low-energy intermediate I-D having C_2 symmetry, as shown in Figure 6. For the calculation of the transition state for this process, we can first drive ϕ_{6789} of I-A, thus obtaining a high-energy intermediate (I-F), which upon subsequent driving of ϕ_{3456} gives I-D (see Figures 4 and 6). The strain-energy barrier separating I-A from I-A′ by this mechanism is 7.0 kcal/mol (Figure 6) and is thus distinctly lower than that of the mechanism shown in Figure 5.

Contributions to the strain energies in various conformations and transition states of I are given in Tables IV and V, re-



(I-A⇌I-C)‡ (I-A⇌I-D)‡ (I-A⇌I-F)‡

(I-D⇌I-F)‡ (I-C⇌I-E)‡ (I-B⇌I-E)‡

Figure 4. Calculated torsional and internal angles in various energy-maxima geometries of 1,2-cyclononadiene (I). The torsional angles shown in parentheses belong to the allenic H-C_{sp^2}-C_{sp^2}-H arrangement.

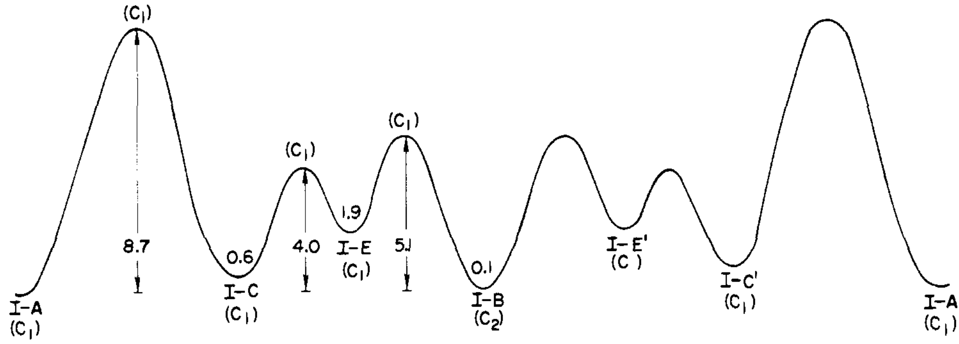


Figure 5. Calculated strain-energy profile for the degenerate interconversion of I-A with I-A′ via I-B.

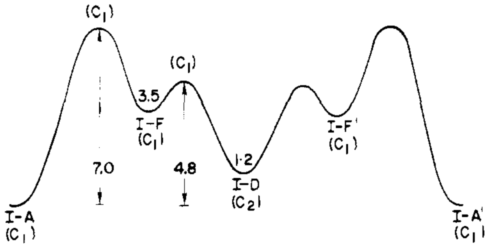


Figure 6. Calculated strain-energy profile for the degenerate interconversion of I-A with I-A′ via I-D.

Table IV. Calculated Strain Energies in Different Energy-Minima Conformations of 1,2-Cyclononadiene (I)

	Strain-energy contributions, kcal/mol					
	I-A (C_1)	I-B (C_2)	I-C (C_1)	I-D (C_2)	I-E (C_1)	I-F (C_1)
Bond stretching	0.49	0.53	0.51	0.39	0.55	0.63
Bond-angle bending	2.50	3.26	3.23	1.54	2.60	4.66
Out-of-plane bending	0.02	0.00	0.05	0.01	0.02	0.04
Torsional strain	5.79	4.71	5.31	8.21	6.28	5.52
Nonbonded interactions	3.39	3.83	3.72	3.23	4.63	4.86
Total strain energy	12.19	12.33	12.82	13.38	14.08	15.71

spectively. The bond stretching and out-of-plane bending terms are small in all geometries. Transition states usually have higher bond-angle bending terms than the energy-minima conformations. The other strain-energy contributions are substantial and vary over a relatively wide range of values.

Interpretation of the NMR Data in Light of the Force-Field Calculations. The major and minor conformations of I detected by NMR have already been labeled I-A and I-B, respectively, in anticipation of the force-field calculations just discussed. This assignment is supported by the following: (a) I-A and I-B are the two lowest energy conformations and their energies are similar; (b) the symmetries of I-A and I-B are correct; (c) the calculated (strain-energy) barriers involving interconversions of I-A, I-A′, and I-B agree with experimentally determined (free-energy) barriers as shown in Table III.

The assignment of I-A to the major conformation seems to be unambiguous, whereas that of I-B to the minor conformation is not quite so certain. Figure 5 shows that I-C is 0.5 kcal/mol above I-B, but it is conceivable that this order is an

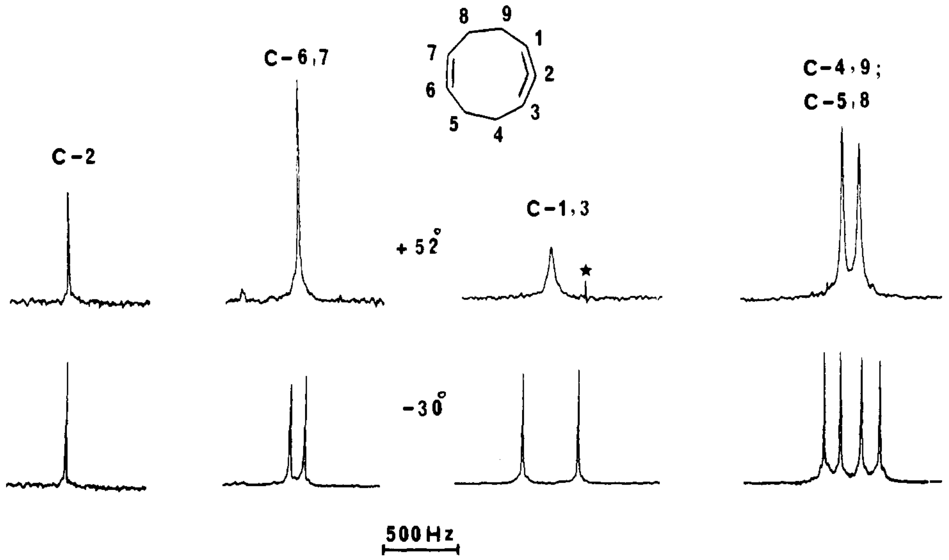


Figure 7. 63.1-MHz ^{13}C NMR spectra of 1,2,6-cyclononatriene (II) in the region of rapid and slow exchange. The line marked with a star is a beat.

Table V. Calculated Strain Energies in Different Energy-Maxima Geometries of 1,2-Cyclononadiene (I)

	Strain-energy contributions, kcal/mol				
	(I-A ⇌ I-C)‡ (C_1)	(I-C ⇌ I-E)‡ (C_1)	(I-B ⇌ I-E)‡ (C_1)	(I-A ⇌ I-F)‡ (C_1)	(I-D ⇌ I-F)‡ (C_1)
Bond stretching	0.69	0.64	0.60	0.70	0.63
Bond-angle bending	6.31	4.77	3.59	5.62	4.90
Out-of-plane bending	0.01	0.01	0.01	0.00	0.01
Torsional strain	9.75	6.20	8.24	8.20	6.43
Nonbonded interactions	4.14	4.57	4.84	4.67	5.04
Total strain energy	20.90	16.19	17.28	17.01	17.01

artifact of the calculations and that I-C is actually slightly more stable than is I-B. It is true that I-C does not have the correct symmetry, but this objection can be overcome by claiming that the barrier separating I-C from I-B (and thus from I-C′) is somewhat overestimated by the force-field calculations and therefore the time-averaged symmetry is correct.[24] Overall, however, the assignment of I-C to the minor conformation appears much less probable than that of I-B.

The detection of two conformations of I at low temperatures implies that these conformations also will be substantially populated at room temperature. It is also possible that conformations such as I-C and I-D, which have not been observed in the low temperature NMR work, may be populated to as much as 10% at room temperature.

^{13}C NMR Spectra of 1,2,6-Cyclononatriene (II). The ^{13}C NMR spectrum of II in $CDCl_3$ at room temperature (25 °C) shows broadening of some of the methylene and methine resonances. At ~50 °C the broad lines become sharper and the spectrum (Figure 7) consists of five resonances with chemical shifts and partial assignments given in Table II. Decreasing the temperature below room temperature results in the splitting of the methylene and methine resonances into doublets with an intensity ratio of 1:1 (coalescence temperature, 18 ± 2 °C). The quaternary allenic carbon resonance remains sharp at all temperatures. No further DNMR effect was observed down to −170 °C.

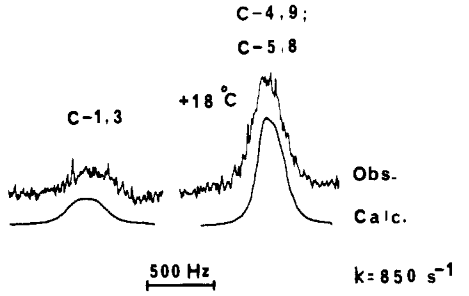


Figure 8. Experimental (top) and calculated (bottom) ^{13}C NMR spectra of the methylene and allenic methine resonances of 1,2,6-cyclononatriene.

The presence of nine chemical shifts for II at −30 °C and below is consistent with a single conformation which lacks symmetry. The ^{13}C NMR spectrum at 18 °C was fitted by a line-shape calculation for the methylene and the allenic methine resonances with $k = 850\ s^{-1}$ (Figure 8). From the absolute rate theory, a free-energy of activation ($\Delta G^{\ddagger}$) of 13.1 ± 0.2 kcal/mol can be calculated.[21]

Force-Field Calculations on 1,2,6-Cyclononatriene (II). Four geometries (two energy minima and two conformational transition states) were found relevant for a description of the conformational properties of II (Figures 9 and 10). An unsymmetrical conformation (II-A) has the lowest calculated strain energy.

Two different processes exist for the introduction of a time-averaged C_2 axis into II (Figure 10). The first, and lower energy, process has a barrier of 15.1 kcal/mol and involves an intermediate (II-B), which has C_2 symmetry, and two unsymmetrical transition states. The second process has a slightly higher calculated strain-energy barrier (16.6 kcal/mol) and has a single transition state, which is of C_2 symmetry. The force-field calculations are probably not accurate enough to establish unambiguously which of these two paths is actually preferred. In our preliminary communication[4] on the conformation of II we reported that Dreiding molecular models appeared to indicate that the lowest energy path for the symmetrization of II-A took place better via II-C than via II-B. Both II-B and II-C were considered as intermediates, whereas

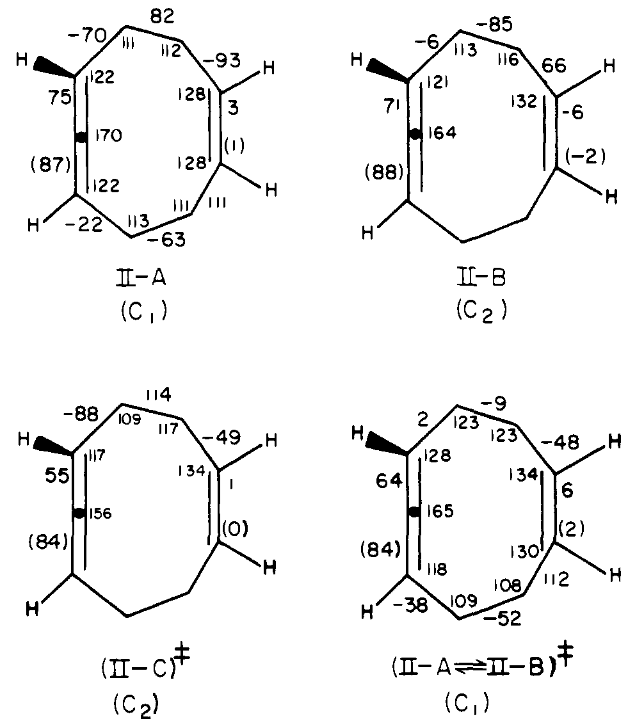


Figure 9. Calculated torsional and internal angles in different geometries of 1,2,6-cyclononatriene. The torsional angles shown in parentheses belong to the allenic and olefinic H-C_{sp^2}-C_{sp^2}-H arrangements.

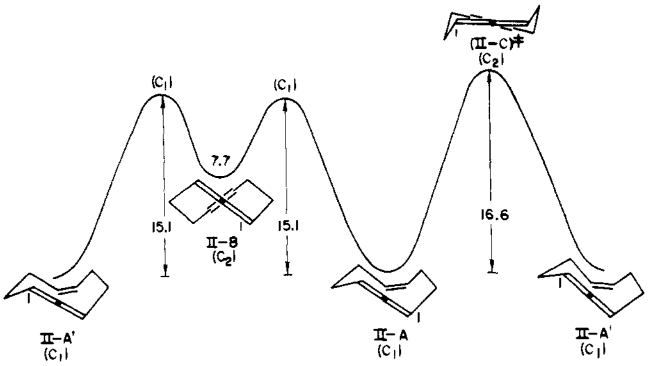


Figure 10. Calculated strain-energy profile for pseudorotation of II-A.

the present force-field calculations clearly reveal that only II-B is an intermediate, II-C being an energy maximum, i.e., a transition state. On the whole, however, the deductions made previously[4] on the basis of molecular models agree qualitatively with the results of the force-field calculations.

Contributions to the overall strain energies in different geometries of II are given in Table VI. The four calculated geometries are characterized by different contributions of bond-angle bending and torsional strain; other strain-energy terms are less pronounced.

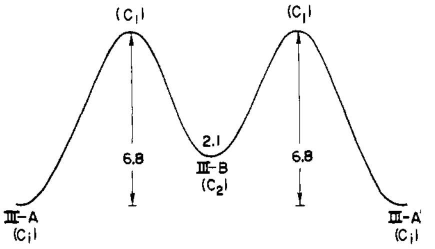


Figure 12. Calculated strain-energy profile for pseudorotation of III-A.

Table VI. Calculated Strain Energies in Different Energy-Minima and Energy-Maxima Geometries of 1,2,6-Cyclononatriene (II)

	Strain-energy contributions, kcal/mol			
	II-A (C_1)	II-B (C_2)	(II-A ⇌ II-B)‡ (C_1)	(II-C)‡ (C_2)
Bond stretching	0.28	0.42	0.53	0.42
Bond-angle bending	2.06	6.33	12.16	10.98
Out-of-plane bending	0.04	0.05	0.20	0.24
Torsional strain	4.63	6.64	7.37	13.06
Nonbonded interactions	2.20	3.45	4.08	1.14
Total strain energy	9.21	16.89	24.34	25.84

In summary, the NMR and force-field calculations on II are in satisfactory agreement: there is a single low-energy conformation, which is unsymmetrical, and the barrier to ring pseudorotation is 13.1 kcal/mol (experimental) or 15.1 kcal/mol (theoretical).

^{13}C NMR Spectra of *meso*-1,2,6,7-Cyclodecatetraene (III). ^{13}C NMR spectra of III have been investigated from −10 to −140 °C. At the upper end of this temperature range the spectrum consists of three singlets with the chemical shifts and assignments shown in Table II, in agreement with previous room-temperature measurements.[3] The methylene and methine resonances broaden below about −90 °C and give rise to 1:1 doublets at about −120 °C. The quaternary allenic carbon resonance remains sharp at all temperatures. The NMR data is consistent with a single conformation having either C_2 or C_i symmetry, and it rigorously excludes a single conformation with C_{2h} symmetry.

The ^{13}C NMR spectrum at −114 °C is well fitted by a line-shape calculation for a degenerate two-site exchange process with $k = 600\ s^{-1}$. From the absolute rate theory, a

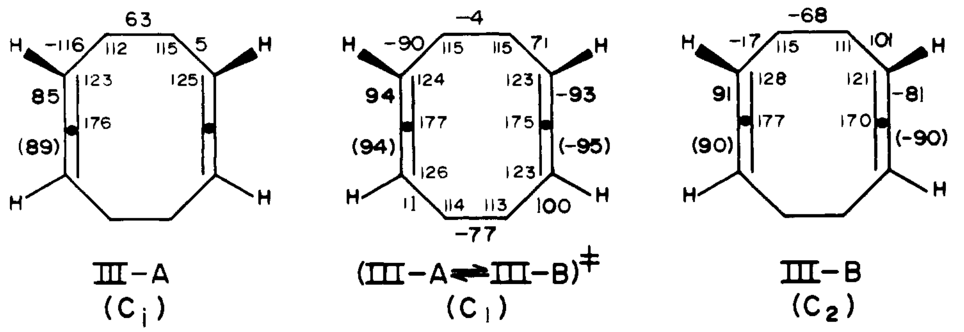


Figure 11. Calculated torsional and internal angles in different geometries of the meso isomer, III. The torsional angles shown in parentheses belong to the allenic H-C_{sp^2}-C_{sp^2}-H arrangement.

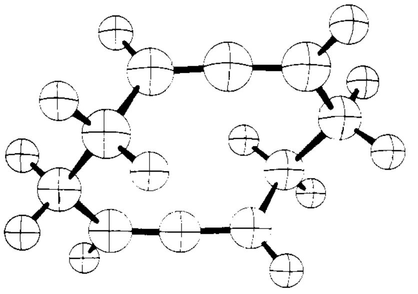


Figure 13. An ORTEP perspective representation of the centrosymmetric conformation, III-A.

$\Delta G^{\ddagger}$ of 7.1 ± 0.2 kcal/mol can be calculated for this process.[21]

Force-Field Calculations on *meso*-1,2,6,7-Cyclodecatetraene (III). Three geometries (two energy minima and a transition state) were found to be necessary in a description of the conformational features of this compound. The most stable conformation of the meso isomer III is found to be III-A, in agreement with x-ray diffraction results.[11] The calculated torsional and internal angles of III-A are given in Figure 11; an ORTEP[25] perspective representation of this centrosymmetric conformation is shown in Figure 12. The torsional and internal angles given by the force-field calculation are in excellent

Table VII. Calculated Strain Energies in Different Energy-Minima and Energy-Maxima Geometries of *meso*-1,2,6,7-Cyclodecatetraene (III)

	Strain-energy contributions, kcal/mol		
	III-A (C_i)	(III-A ⇌ III-B)‡ (C_1)	III-B (C_2)
Bond stretching	0.22	0.25	0.23
Bond-angle bending	1.27	1.80	2.44
Out-of-plane bending	0.01	0.05	0.00
Torsional strain	0.28	6.14	2.06
Nonbonded interactions	1.51	1.51	0.70
Total strain energy	3.29	10.10	5.43

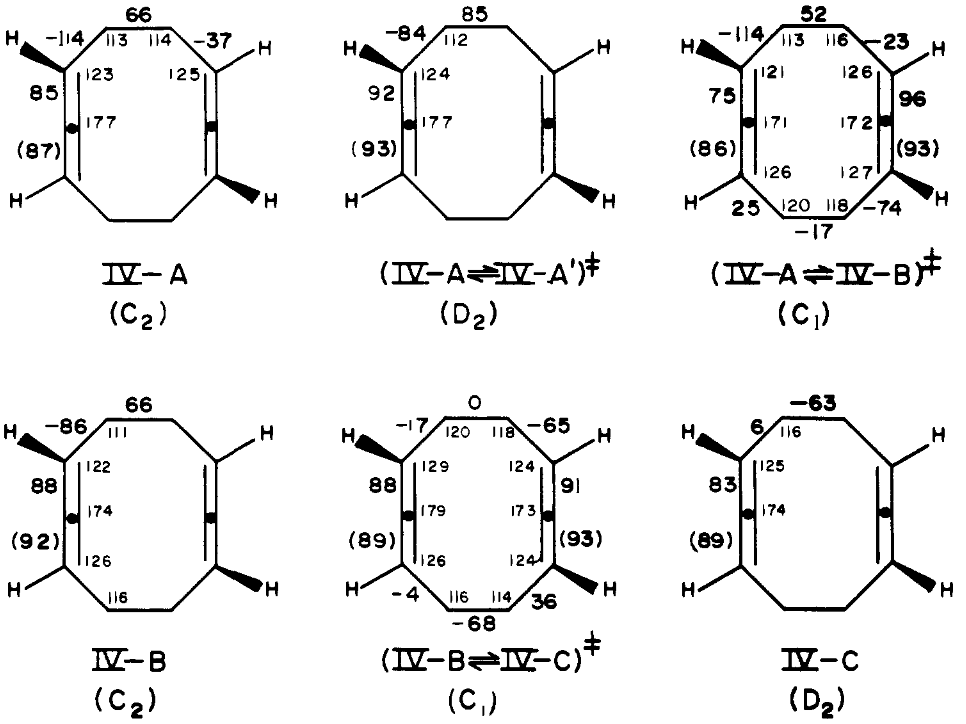


Figure 14. Calculated torsional and internal angles in different geometries of the *dl* isomer, IV. The torsional angles shown in parentheses belong to the allenic H-C_{sp^2}-C_{sp^2}-H arrangement.

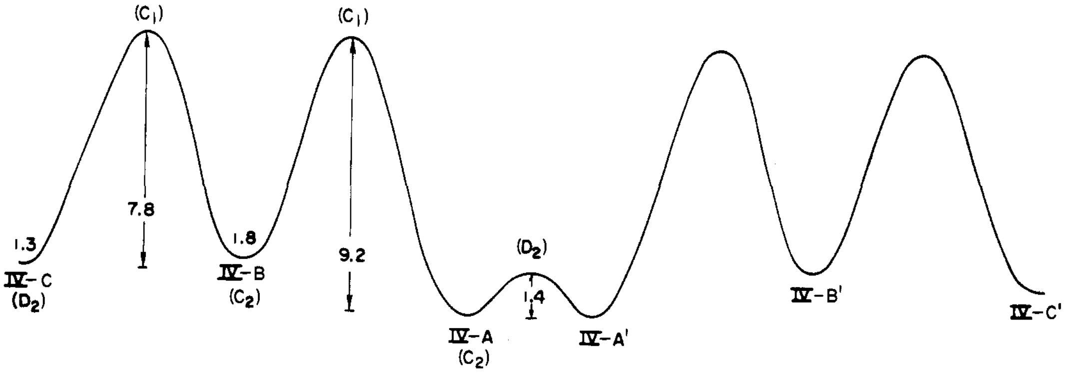


Figure 15. Calculated strain-energy profile for the conformational interconversion in the *dl* isomer, IV.

Table VIII. Calculated Strain Energies in Different Energy-Minima and Energy-Maxima Geometries of *dl*-1,2,6,7-Cyclodecatetraene (**IV**)

	Strain-energy contributions, kcal/mol					
	IV-A (C_2)	(IV-A $\rightleftharpoons$ IV-A′)‡ (D_2)	(IV-A $\rightleftharpoons$ IV-B)‡ (C_1)	IV-B (C_2)	(IV-B $\rightleftharpoons$ IV-C)‡ (C_1)	IV-C (D_2)
Bond stretching	0.24	0.12	0.40	0.24	0.44	0.40
Bond-angle bending	1.21	0.61	5.27	2.37	4.95	2.95
Out-of-plane bending	0.02	0.03	0.06	0.01	0.02	0.01
Torsional strain	2.79	6.65	5.79	3.84	5.96	0.51
Nonbonded interactions	1.55	−0.22	3.48	1.17	3.58	3.21
Total strain energy	5.81	7.19	15.00	7.63	14.95	7.08

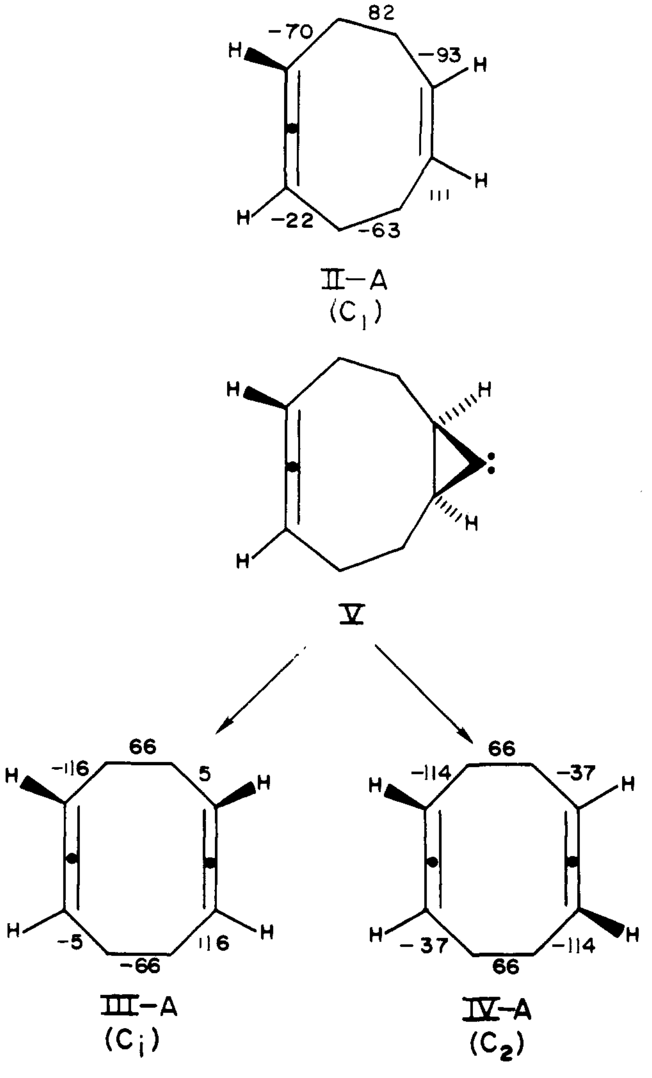


Figure 16. Formation of the meso and *dl* isomers of 1,2,6,7-cyclodecatetraene from the allenocarbene, V. The torsional angles in the allenocarbene are expected to be similar to those calculated for the ground-state conformation of 1,2,6-cyclononatriene.

agreement with the x-ray structural data,[11] the average deviation being <1°.

A second conformation, III-B (Figures 11 and 13), can be obtained by driving *one* of the two C-CH_2-CH_2-C torsional angles in III-A. In this process, the second (undriven) C-CH_2-CH_2-C torsional angle does not change appreciably. Since III-B is 2.3 kcal/mol above III-A, it is not expected to be populated in the temperature range investigated,[26] unless the calculations are rather seriously in error.

From Figure 13 it can be seen that III-B is an intermediate in the ring pseudorotation of III-A, i.e., in the interconversion of III-A and III-A′. Kinetically, the pseudorotation in III-A has the features of a degenerate reaction with a single high-energy intermediate and two equal-energy transition states. The value of $\Delta G^{\ddagger}$ for an overall reaction of this type differs from that for the half reaction—in the present case the III-A to III-B process—by $RT \ln 2$. However, $\Delta H^{\ddagger}$ is the same for both the overall and the half reaction. At the temperature of our NMR measurements, $RT \ln 2$ amounts to only 0.2 kcal/mol, and this is not a significant quantity when comparing the experimental data to the results of force-field calculations. Thus, the calculated strain-energy barrier of 6.8 kcal/mol is in excellent agreement with the experimental free-energy barrier of 7.1 kcal/mol.

Another possible mode for the conformational conversion of III-A to III-A′ involves driving *both* of the C-CH_2-CH_2-C torsional angles so as to maintain a center of symmetry. This process does not give rise to an intermediate conformation, and proceeds via a highly symmetrical (C_{2h}) transition state, which is calculated to be about 15 kcal/mol higher than III-A. Thus, this one-step interconversion mode contributes negligibly compared to that which involves III-B as an intermediate.

Force-Field Calculations on *dl*-1,2,6,7-Cyclodecatetraene (IV). Although the *dl* isomer IV is not presently known, its conformation is of interest for comparison with that of the meso isomer III. Altogether three energy-minimum and three energy-maximum geometries (Figure 14) were found relevant for a description of the conformational features of IV. The most stable conformation (IV-A) has a "nonintersecting" twofold axis of symmetry[27] (Figure 14). According to the analytical geometry reasoning of Dunitz and Waser,[27] the Dreiding molecular model of IV-A should be perfectly flexible when distorted so as to maintain the nonintersecting C_2 axis.

The force-field calculations show that IV-A does have a low-energy path for a limited pseudorotation into IV-A′ via a transition state with D_2 symmetry (Figure 15). However, pseudorotation of IV-A into IV-C (or IV-C′) is very difficult when a nonintersecting C_2 axis is maintained, the calculated barrier being ~16 kcal/mol. A better process for interconverting IV-A with IV-C is shown in Figure 15, which proceeds via an intermediate (IV-B)[28] and two unsymmetrical transition states. This process, which does not maintain a nonintersecting C_2 axis, has a barrier of ~9 kcal/mol. Thus, even this unsymmetrical process is quite hindered.

Contributions to the overall strain energies in the three geometries of the *meso*-diallene III and in the six geometries of the *dl*-diallene IV are given in Tables VII and VIII, respectively. The bond-stretching and out-of-plane bending terms are always small, but the other strain-energy contributions are substantial.

Mechanism of Formation of *meso*-1,2,6,7-Cyclodecatetraene (III). The synthesis of III proceeds via the bis adduct of dibromocarbene to *cis,cis*-1,5-cyclooctadiene. The adduct is a mixture of syn and anti isomers in the ratio of 5:1 and upon treatment with alkyllithium both isomers yield only the meso isomer of 1,2,6,7-cyclodecatetraene.[10] It is likely that the bis adduct first leads to an allenocarbene (V), which upon rearrangement gives the *meso*-diallene (Figure 16). The ring expansion reaction presumably has a low activation energy and takes place very rapidly. Therefore, the rearrangement may occur before a conformational change takes place, especially if the conformational barrier is high. The discussion given below, which is based on the results of NMR experiments and force-field calculations, provides an explanation for the formation of the meso isomer.

The intermediate allenocarbene V should have torsional angles very similar to those of the cyclic alleno olefin II (Figure 16), whose conformation is known. Conversion of the allenocarbene V to the meso and to the *dl* isomer of the diallene involves changes in the two C-CH_2-CH_2-C torsional angles. One of these angles has very similar values in III, IV, and V, while the other torsional angle has an opposite sign in IV from that in V. The conversion of the allenocarbene V to the meso isomer of the diallene does not require any change in the signs of the torsional angles in the two C-CH_2-CH_2-C moieties. On the other hand, the formation of the *dl* isomer of the diallene requires a sign change in one of these torsional angles.

An estimation of the energy involved in eclipsing this torsional angle can be obtained from the pseudorotation in the alleno olefin II, because the latter process involves changes in torsional angles that are very similar to those required to convert the allenocarbene to the *dl* isomer of the diallene. Since the pseudorotation barrier in the alleno olefin II is $\sim$13 kcal/mol, the conformational change required to give the *dl* isomer is expected to be very slow and the rearrangement should give essentially none of this isomer.

Conclusion

DNMR spectroscopy and iterative force-field calculations are powerful tools for investigating the conformational features of cyclic medium-ring allenes. These techniques probably can be applied to larger membered cyclic allenes.

Two of the compounds investigated in this research are liquids at room temperature, and thus x-ray diffraction studies would be difficult to carry out because they would have to be done at low temperatures. Since the compounds are volatile, electron diffraction can be applied, but the number of atoms is sufficiently large that reliable structural conclusions probably can be obtained only when a single conformation is populated. Thus, I is not suitable for an electron diffraction study, whereas II is well suited.

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(23) These labels anticipate an assignment of conformations made on the basis of force-field calculations, to be presented in a subsequent section.
(24) It is also conceivable that the minor conformation is rapidly interconverting mixture of I-B, I-C, and I-C′, although the constancy of the chemical shifts of the minor form observed between −130 and −170 °C (Table II) does not provide any evidence for this assignment. The minor conformation is very unlikely to be I-D, as this requires substantial errors in the calculated energies of both I-B and I-D, as well as requiring a change in the process assigned to the degenerate interconversion of the major conformation (a process that does not involve the minor conformation), leading to a very poor agreement of the calculated and experimental barriers.
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