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FORCE-FIELD CALCULATIONS FOR SOME UNSATURATED CYCLIC HYDROCARBONS†

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Abstract—Boyd's iterative force-field computer program, with modified parameters, has been used to calculate strain energies in the following molecules: *trans*-cyclooctene, cyclohexene, methylenecyclohexane, 1,3,5- and 1,3,6-cyclooctatriene, and cyclononyne. Both static and dynamic aspects of the conformational properties of these molecules have been investigated in detail, and the results are discussed in conjunction with extant experimental data and previous force-field calculations.

Empirical force-field (strain-energy or molecular mechanics) calculations, with geometrical optimization by means of iterative computer procedures, can be carried out easily and cheaply, even on relatively large organic molecules.[1] Such calculations, especially when combined with NMR and direct structural data, are very valuable and can provide a deep understanding of the conformational properties of cyclic molecules.[2] In this paper, we present calculations on a variety of cyclic unsaturated hydrocarbons carried out by means of the procedure and computer program developed by Boyd.[3,4] The parameters of the force field used by this author for saturated hydrocarbons have been found to be very satisfactory for cycloalkanes.[2,5] However, the parameters for the ethylenic group in Boyd's program are less satisfactory, in our opinion, especially when a twisted double bond is present, as is sometimes the case in medium rings. For example, *trans*-cyclooctene, although admittedly a very strained and twisted olefin, cannot be satisfactorily treated with Boyd's parameters.[6] Allinger and Sprague[7] and Ermer and Lifson[8] have employed torsional and out-of-plane parameters that do reproduce the geometry of *trans*-cyclooctene.

Force-field calculations. The force-field used by Ermer and Lifson[8] is more complicated than Boyd's, and contains a number of bilinear cross terms, which were introduced mainly to improve the calculated vibrational frequencies, but the cross terms have apparently little effect on the strain energy, or on the calculated thermodynamic properties.

Allinger and Sprague[7] have reported calculations of the conformations and energies of a series of olefins and their force field reproduces correctly the geometry of *trans*-cyclooctene. The procedure used by these authors gives rise to certain problems when the symmetry is constrained or when conformational transition states are examined. Ermer[9] 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 distorsion of the molecule. A test for a true (local) 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. For transition state geometries, on the other hand, the criterion that must hold is that *one* and *only one* vibrational frequency be imaginary. For example, the boat conformation[10] of *cis,cis*-1,5-cyclooctadiene is actually a conformational transition state.[11,12]

The modified Newton–Raphson iteration procedures used by Ermer and Lifson[8] as well as by Boyd[3] lead to straightforward calculations of the vibrational frequencies, and are therefore particularly suitable for examining conformational transition states. Paths linking conformations can be investigated with force-field calculations by "driving" a torsional angle or in some cases more than one torsional angle.[13] In this procedure, the torsional potential is changed to force the desired geometric change, but the energy is calculated with the normal torsional potential. Once a geometry close to the transition state is obtained, the calculations can be carried out in a normal manner, since convergence to an energy maximum takes place equally well as to an energy minimum in the modified Newton–Raphson procedure.

Force-field parameters. Empirical force-field parameters for the strain-energy calculations are shown in Table 1 and are the same as those used by Boyd[3] with the following exceptions: (a) torsional and out-of-plane parameters for double bonds, (b) a conjugation energy term in the form of a two-fold torsional potential for single bonds flanked by two double bonds, and (c) parameters for the acetylenic moiety.

The double bond parameters are very similar to those of Ermer and Lifson.[8] The out-of-plane angle, however, is defined as in Boyd's original program (Table 1) and thus the force constant is different from that of Ermer and Lifson; the energy required for a given small out-of-plane distorsion, however, are very similar.

The conjugation energy terms for the cyclooctatrienes was obtained from the torsional angle of single bonds flanked by two double bonds. A two-fold potential with a stabilization (negative strain energy) of 4.25 kcal/mol for the planar (0° or 180° angle) arrangement was chosen, since this reproduces the barrier to rotation in 1,3-butadiene.[14] Although this treatment is not as general as that used by Allinger,[15] it is much simpler, and should be adequate for cyclic dienes and trienes.

The main parameter of interest for acetylenes is angle bending. The force constant which we have used for

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C≡C–C bending is the same as that used by Allinger and Meyer.[16]

Approximate coordinates for trial geometries of the six molecules presented in this paper were calculated by means of the program COORD[17] with torsional angles estimated from Dreiding–Fieser molecular models. The calculations were carried out on an IBM-360/91 computer at the Campus Computing Network of UCLA.†

trans-*Cyclooctene.* The conformation of *trans*-cyclooctene has been determined by electron-diffraction measurements[18] to be a twist-chair-chair. Similar conformations occur in various *trans*-cyclooctene metal complexes[19] and in *trans*-2-cyclooctenyl dinitrobenzoate.[20] The twist-chair-chair conformation actually was predicted correctly by empirical force-field calculations.[7,8] The geometry obtained with the parameters given in Table 1 is in good agreement with previous calculations and with the experimental data (Table 2). The ring torsional angle of the double bond in *trans*-cyclooctene is about 136°, indicating a highly twisted double bond. Thus, this molecule serves as an excellent test of force field parameters for the double bond.

Cyclohexene. The chiral half-chair proposed in 1937,[21] has been found to be the conformation of cyclohexene by electron-diffraction measurements.[22] Similar conclusions were reached by IR and Raman studies[23] and from X-ray diffraction measurements of substituted cyclohexenes.[24] Ring inversion in cyclohexene and in some of its derivatives have been investigated by dynamic NMR spectroscopy,[25] and has been the subject of a number of studies. Thermodynamic measurements[26] on cyclohexene have been interpreted in terms of a mixture of half-chair and boat conformations where the former is the predominant conformation and is more stable than the boat by 2.7 kcal/mol. Since the free-energy barrier to ring inversion in cyclohexene is about 5.3 kcal/mol,[27,28] it appeared that the boat was an intermediate in the ring inversion of the half-chair.[27] However, force-field results[7,29,30] and general considerations[28] show that the boat is actually a transition state and is 6.1[7] or 6.9[30] kcal/mol higher in energy than the half-chair. The experimental free-energy barrier (ΔG^{+}) for ring inversion in partially deuterated cyclohexenes is 5.2[27] or 5.4[28] kcal/mol. On the assumption that the only contribution to ΔS^{+} arises from reaction pathway multiplicity and is therefore $R \ln 2$, and that the isotope effects are negligible, a ΔH^{+} of 5.5 kcal/mol has been estimated[28] for the ring inversion barrier in cyclohexene, since $\Delta G^{+} = \Delta H^{+} - T\Delta S^{+}$. However, this analysis neglects the fact that the half-chair is chiral and exists as a mixture of two mirror-image conformations, whereas the boat is achiral. The entropy of mixing contribution is

Table 1. Force-field parameters

Strain-Energy Terms[a]	Unstrained Values of Angles or Distances	Force Constants
Bond Stretching[b]	$\underline{r}$	$\underline{K_r}$
C_{sp^2}-H	1.070	5.080
C_{sp^3}-H (allylic -CH_2-)	1.090	4.550
C_{sp^3}-H (non-allylic -CH_2-)	1.090	4.450
C_{sp}-C_{sp}	1.212	10.000
C_{sp}-C_{sp^3}	1.466	5.200
C_{sp^2}-C_{sp^2} (single bond)	1.460	5.800
C_{sp^2}-C_{sp^2} (double bond)	1.330	6.800
C_{sp^2}-C_{sp^3}	1.500	5.100
C_{sp^3}-C_{sp^3}	1.530	4.400
Bond-Angle Bending[c]	$\underline{\theta}$	$\underline{K_\theta}$
H-C_{sp^2}-H	118.9	0.290
H-C_{sp^3}-H	107.9	0.508
H-C_{sp^3}-C_{sp} or H-C_{sp^3}-C_{sp^2} or H-C_{sp^3}-C_{sp^3}	109.5	0.608
H-C_{sp^2}-C_{sp^2}	120.5	0.605
H-C_{sp^2}-C_{sp^3}	119.5	0.350
C_{sp}-C_{sp}-C_{sp^3}	180.0	0.380
C_{sp}-C_{sp^3}-C_{sp^3} or C_{sp^2}-C_{sp^3}-C_{sp^2} or C_{sp^2}-C_{sp^3}-C_{sp^3} or C_{sp^3}-C_{sp^3}-C_{sp^3}	111.0	0.800
C_{sp^2}-C_{sp^2}-C_{sp^2} or C_{sp^2}-C_{sp^2}-C_{sp^3}	124.7	0.620
C_{sp^3}-C_{sp^2}-C_{sp^3}	119.0	0.650

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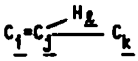
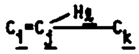
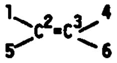
†Calculated atomic coordinates for conformations discussed in paper are available from the authors on request.

Table 1. (*Contd*)

Strain-Energy Terms[a]	Unstrained Values of Angles or Distances	Force Constants		
Out-of-Plane Bending[d]	$\underline{\delta}$	$\underline{K_\delta}$		
 or 	0	0.080		
	0	0.280		
Torsional Strain[e]	$\underline{\phi}$	$\underline{K_\phi}$	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
$C=C_{sp^2}-C_{sp^2}=C$	0 or 180	-0.0295	1	2
 1-2-3-4	0	-0.1135	-1	2
5-2-3-6	0	-0.1135	-1	2
Non-bonded 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

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[a] Energies are in units of 10^{-11} erg/molecule; $\underline{r}$ in Ångstroms; $\underline{\theta}$, $\underline{\phi}$, $\underline{\delta}$ in degrees. To convert 10^{-11} erg/molecule to kcal/mol, multiply by 144.

[b] $\underline{E}(\underline{r}) = \frac{1}{2}\underline{K_r}(\underline{r} - \underline{r}_\circ)$.

[c] $\underline{E}(\underline{\theta}) = \frac{1}{2}\underline{K_\theta}(\underline{\theta}-\underline{\theta})^2$, angles to be reduced to radians for use.

[d] $\underline{E}(\underline{\delta}) = \frac{1}{2}\underline{K_\delta}(\underline{\delta})^2$, where$(\pi/2-\underline{\delta})$ is the angle between the normal to the plane $\underline{ijk}$ and the vector from $\underline{j}$ to $\underline{\ell}$. Atom $\underline{\ell}$ is the out-of-plane atom.

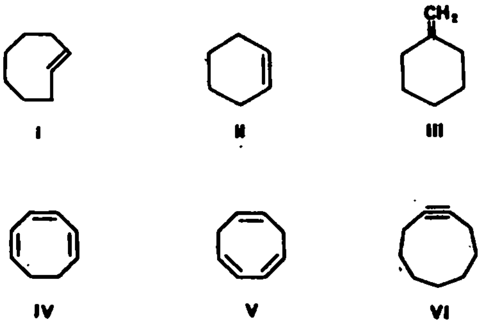
[e] $\underline{E}(\phi) = \frac{1}{2}\underline{K_\phi}(B + \cos C\underline{\phi})$.

[f] $\underline{E}^{nb}(\underline{r}) = A/\underline{r}^6 + B\exp(-C\underline{r})$.

$-R\ln 2$ and cancels the path multiplicity effect and thus the value of $\Delta H^{\ddagger}$ should be 5.3 kcal/mol. The path multiplicity effect which is clearly evident in deuterium labelled species, can alternatively be formulated in terms of symmetry numbers (valid for unlabelled species). The half-chair, with a C_2 axis has $\sigma = 2$, whereas the boat, which lacks C_2 axes, has $\sigma = 1$. This difference in symmetry numbers is of course offset by the chirality effect previously mentioned.

Using the force-field parameters given in Table 1, we find that the strain energy of cyclohexene is a minimum for the half-chair conformation, and that the boat is a true energy maximum (transition state or saddle point) separating enantiomeric half-chairs (Fig. 1), in agreement with other recent force-field calculations.[7,30] However, the strain energy is a fairly flat function of the 3456 torsional angle near the energy maximum ($\omega = -20$ to $+20$). Structural parameters and contributions to the total strain energy in different forms of cyclohexene are given in Fig. 2 and Table 3 respectively.

Methylenecyclohexane. The barrier to ring inversion in methylenecyclohexane(III) has been determined by dynamic ^{1}H NMR spectroscopy.[31,32] It is higher than the barrier in cyclohexanone ($\Delta G^{\ddagger} = 4.0$ kcal/mol),[33] but still substantially lower than the barrier in cyclohexane ($\Delta G^{\ddagger}$ 10.1 kcal/mol).[34] Since calculations of the barrier to ring inversion in methylenecyclohexane(III) have not



Formula 1.

Table 2. Comparison of the experimental and calculated data for the structure of *trans*-cyclooctene (I). The numbers in brackets are standard deviations

	Strain-Energy Calculations			Electron Diffraction
	This Study	E[a]	A[b]	T[c]
Bond Lengths (Å)				
1-2	1.324	1.338	1.338	1.332
2-3	1.492	1.504	1.499	1.499
3-4	1.547	1.541	1.546	1.549
4-5	1.557			
5-6	1.559			
Bond Angles (°)				
1-2-3	119.1	117.9	118.9	121.9 (0.4)
2-3-4	107.9	106.4	104.0	104.6 (0.2)
3-4-5	114.7	115.0	116.5	113.8 (0.2)
4-5-6	116.0	117.0	119.7	118.8 (0.3)
C=C-H	120.5	121.9	120.5	118.4 (1.0)
Dihedral Angles (°)				
1-2-3-4	-86.5	-87.0	-92.6	-91.1 (0.4)
2-3-4-5	50.7	50.0	46.4	54.2 (0.5)
3-4-5-6	-81.0	-80.6	-76.7	-82.8 (0.3)
4-5-6-7	114.4	114.8	110.9	111.8 (0.6)
C-C=C-C	135.4	138.0	145.0	136.0 (0.2)
H-C=C-H	172.0	177.6	170.4	177.5 (5.6)

[a] O. Ermer and S. Lifson, J. Am. Chem. Soc., 95, 4121 (1973).

[b] N. L. Allinger and J. T. Sprague, ibid., 94, 5734 (1972).

[c] M. Traetteberg, Acta Chem. Scand., Ser. B, 29, 29 (1975).

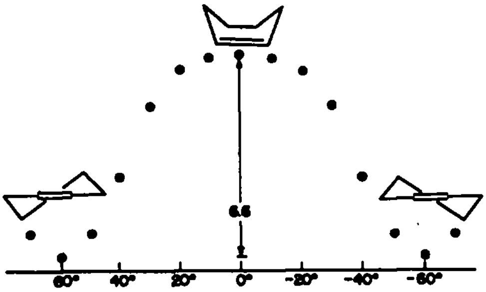


Fig. 1. Calculated strain-energy profile for ring inversion in cyclohexene (II).

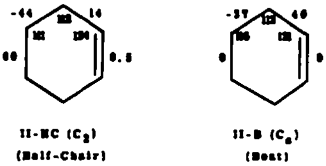


Fig. 2. Calculated torsional and internal angles in half-chair and boat forms of cyclohexene (II).

been reported, we have investigated this molecule by the force-field method. Ring inversion in 6-membered rings usually proceed via intermediate boat conformations.[35] In the present case we have examined seven different ways of converting the chair form to a boat form (Table 4). The paths correspond to driving either a single torsional angle (ω_1, ω_2 or ω_3) or two adjacent torsional angles. The lowest barrier is obtained by driving ω_1, the torsional angle adjacent to the methylene group. Driving ω_2 or ω_1 and ω_6 is almost as favorable but the other paths are substantially higher in energy. The calculated strain-energy barrier is 8.1 kcal/mol, which compares well with the observed free-energy barrier (8.4±0.1 kcal/mol).[31] The various boat and twist-boat conformations of methylenecyclohexane are of similar energies, and are 5 to 6 kcal/mol higher in energy than the chair.

1,3,5- and 1,3,6-Cyclooctatrienes. We have already reported preliminary results of force-field calculations on these two trienes.[2b] For the 1,3,5-isomer (IV), there is only one energy minimum (Fig. 4), and this corresponds to a twist-boat (IV-TB) with a CH_2–CH_2 torsional angle of 63°, in contrast to the boat conformation ($\omega = 0$) generally depicted in the literature. The boat is the conformation which is obtained with molecular models and twisting the boat appears to require energy. However, the torsional energy is greatly reduced upon twisting, and this more than makes up the concomitant increase in the internal angle strain (Fig. 5, Table 4). The torsional energy difference between the boat and the twist-boat arises from both conjugation and eclipsing effects.

The twist-boat lacks symmetry and can undergo two distinct processes. The lower-energy process, which can

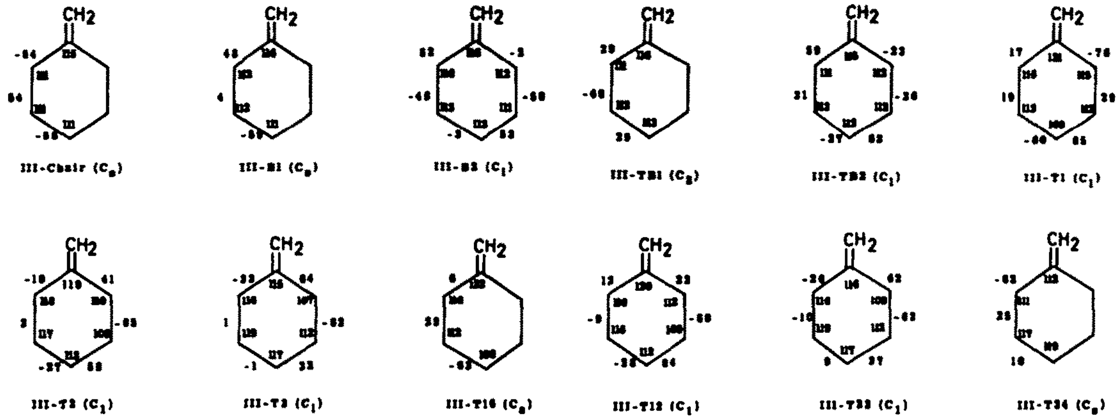


Fig. 3. Calculated torsional and internal angles in various energy-minima and energy-maxima geometries of methylenecyclohexane (III). Only ring torsional angles are given.

Table 3. Calculated strain energies (kcal/mol) in various geometries of cyclohexene (II)

Strain-Energy Contributions	Half-Chair (II-HC, C_2) $\omega_4 = 60°$	$\omega_4 = 50°$	$\omega_4 = 40°$	$\omega_4 = 30°$	$\omega_4 = 20°$	$\omega_4 = 10°$	Boat (II-B, C_s) $\omega_4 = 0°$
Bond Stretching	0.14	0.14	0.17	0.21	0.23	0.23	0.23
Bond-Angle Bending	0.21	0.53	1.25	1.60	1.18	1.10	1.08
Out-of Plane Bending	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Torsional Strain	1.24	1.94	3.04	4.77	6.10	6.46	6.54
Non-bonded Interactions	3.29	3.03	3.01	3.22	3.51	3.63	3.67
Total Strain Energy	4.88	5.64	7.47	9.80	11.02	11.42	11.52

Table 4. Calculated strain energies (kcal/mol) in various conformations of methylenecyclohexane (III)

Strain-Energy Contributions	Chair (III-C, C_s)	Boat-1 (III-B1, C_s)	Boat-2 (III-B2, C_1)	Twist-Boat-1 (III-TB1, C_2)	Twist-Boat-2 (III-TB2, C_1)
Bond Stretching	0.18	0.25	0.24	0.24	0.25
Bond-Angle Bending	0.44	0.53	0.56	0.46	0.50
Torsional Strain	0.23	4.80	4.65	4.35	4.38
Out-of-Plane Bending	0.01	0.05	0.02	0.00	0.04
Non-bonded Interactions	2.87	4.31	3.95	3.86	4.05
Total Strain Energy	3.73	9.94	9.42	8.91	9.22

be called a pseudorotation, has the plane symmetrical boat (IV-B) as a transition state. The higher-energy process is a ring inversion and its transition state, the "half-chair" (IV-HC), has C_2 symmetry. The two processes are depicted in Fig. 4. Experimental free-energy barriers corresponding to these two processes have been determined by dynamic NMR spectroscopy[2b,36,37] and are in good agreement with the calculated strain-energy barriers (Table 7).

Two energy minima were found for 1,3,6-cyclooctatriene (V). The lower-energy conformation is the twist-boat-chair (V-TBC) and has C_2 symmetry. The higher-energy conformation (the half-chair, V-HC) has C_s symmetry and is an intermediate in the ring inversion of the twist-boat-chair (Fig. 6). The two conformations of V have very different internal and torsional strains, but unlike the situation in the 1,3,5-isomer, the conformational ground state, V-TBC, has a relatively high torsional strain but low internal angle strain (Table 6).

The present data strongly indicate that 1,3,5-cyclooctatriene (IV) is conformationally homogeneous at room temperature. This feature should facilitate a struc-

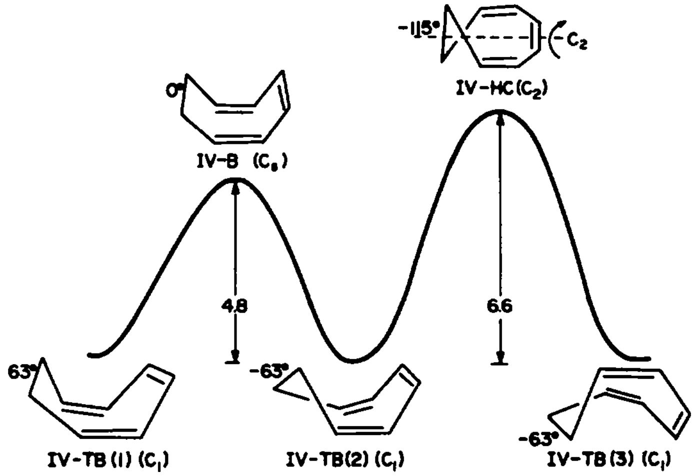


Fig. 4. Calculated strain-energy profile for ring inversion and pseudorotation of twist-boat conformation of 1,3,5-cyclooctatriene (IV).

Table 5. Calculated strain energies (kcal/mol) of various transition-state geometries for the interconversion of "chair" and "boat" families in methylenecyclohexane (III)

Strain-Energy Contributions	Driven Angle(s)						
	ω_1	ω_2	ω_3	ω_1 and ω_6	ω_1 and ω_2	ω_2 and ω_3	ω_3 and ω_4
	II-T1	III-T2	III-T3	III-T16	III-T12	III-T23	III-T34
Bond Stretching	0.24	0.28	0.34	0.23	0.26	0.33	0.36
Bond-Angle Bending	1.95	2.59	3.13	2.20	2.31	2.96	3.43
Torsional Strain	6.10	5.64	6.33	6.05	6.39	6.65	7.16
Out-of-Plane Bending	0.04	0.09	0.02	0.10	0.06	0.02	0.00
Non-bonded Interactions	3.46	3.36	3.51	3.25	3.39	3.57	3.84
Total Strain Energy	11.79	11.96	13.33	11.83	12.41	13.53	14.79

Table 6. Calculated strain energies (kcal/mol) in various energy-minima and energy-maxima geometries of 1,3,5- and 1,3,6-cyclooctatriene

Strain-Energy Contributions	1,3,5-Cyclooctatriene (IV)			1,3,6-Cyclooctatriene (V)		
	Twist-Boat (IV-TB, C_1)	Boat (IV-B, C_s)	Half-Chair (IV-HC, C_2)	Twist-Boat-Chair (V-TBC, C_2)	Half-Chair (V-HC, C_s)	Transition State (V-T)
Bond Stretching	0.24	0.24	0.45	0.20	0.26	0.40
Bond-Angle Bending	5.20	2.54	11.15	2.14	6.84	9.13
Out-of-Plane Bending	0.19	0.22	0.55	0.10	0.00	0.20
Torsional Strain	-2.16	4.80	-2.14	4.90	2.10	1.80
Non-Bonded Interactions	2.86	3.46	2.95	2.94	2.87	2.87
Total Strain Energy	6.61	11.26	13.24	10.28	12.07	14.40

ture determination of IV in the gas phase by electron diffraction. It would be valuable, of course, to have direct structural data on IV for comparison with the results of the force-field calculations.

Cyclononyne. Allinger and Meyer[16] have published force-field calculations for cyclononyne. They apparently only investigated one conformation, which has approximately C_s symmetry.

We have carried out an extensive force-field study on the conformations and conformational interconversions of cyclononyne (VI) (Table 8, Figs. 7 and 8). The lowest-energy conformation, VI-A, was found to be unsym-

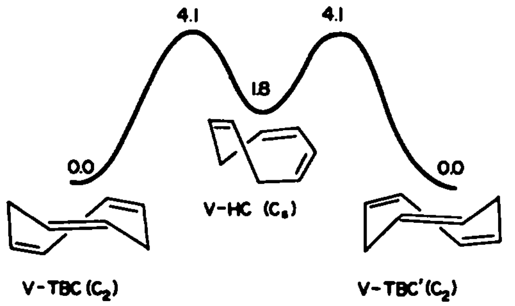


Fig. 5. Calculated torsional and internal angles in various energy-minima and energy-maxima geometries of 1,3,5- and 1,3,6-cyclooctatriene.

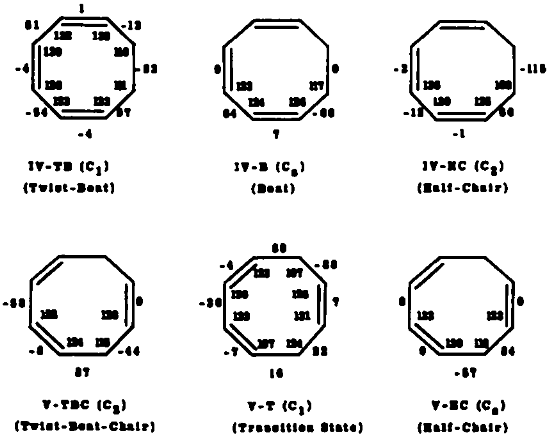


Fig. 6. Calculated strain-energy profile for ring inversion in 1,3,6-cyclooctatriene (V).

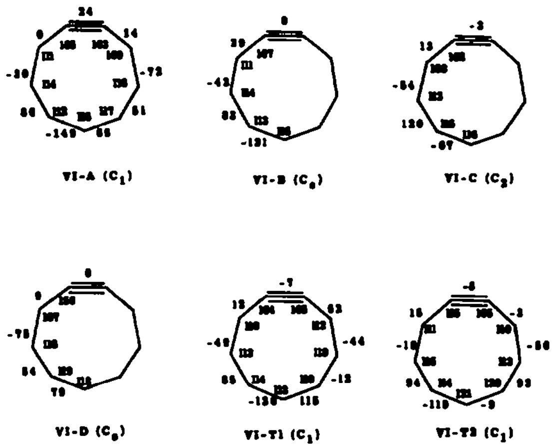


Fig. 7. Calculated torsional and internal angles in various energy-minima and energy-maxima geometries of cyclononyne (VI).

metrical. By driving ϕ_{3456} of this conformation from 51 to −86° another energy-minimum geometry, VI-B (C_s), which is 0.4 kcal/mol less stable than VI-A, was obtained. The transition state (VI-T1) separating VI-A from VI-B was found to be 6.4 kcal/mol above VI-A. Conformation VI-A can be converted to yet another energy-minimum conformation, VI-C, by driving ϕ_{4567}. This latter conformation has a two-fold axis of symmetry and its strain energy is 0.7 kcal/mol above that of VI-A. The energy barrier for interconversion of VI-A with VI-C is calculated to be 9.0 kcal/mol. Thus there are three relatively low-energy conformations for cyclononyne.

Table 7. Experimental and calculated relative energies[a] in 1,3,5-cyclooctatriene (IV)

Conformation	Symmetry	Exptl. Free Energy	Calcd. Strain Energy
Twist-Boat (IV-TB)	$\underline{C}_1$	0.0	0.0
Boat (IV-B)	$\underline{C}_s$	4.3	4.8
Half-Chair (IV-HC)	$\underline{C}_2$	6.2 ± 0.5[b]	6.6
		6.7 ± 0.2[c]	

[a] In units of kcal/mol, relative to twist-boat.

[b] Ref. 36.

[c] Ref. 37.

Table 8. Calculated strain energies (kcal/mol) in various energy-minima and energy-maxima geometries of cyclononyne (VI)

Strain-Energy Contributions	VI-A	VI-B	VI-C	VI-D	VI-T1	VI-T2
Bond Stretching	0.88	0.63	0.66	0.82	0.88	0.96
Bond-Angle Bending	6.31	3.59	7.05	13.23	7.40	8.62
Torsional Strain	3.58	6.49	4.82	1.76	7.62	8.93
Non-bonded Interactions	4.42	4.92	3.40	3.26	5.66	5.71
Total Strain Energy	15.19	15.63	15.93	19.07	21.56	24.22

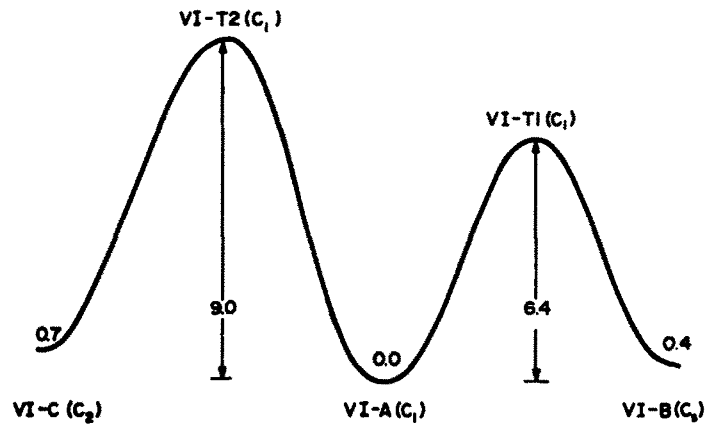


Fig. 8. Calculated strain-energy profile for interconversion of various conformations of cyclononyne (VI).

CONCLUSIONS

Boyd's force-field parameters, as modified and extended in the present paper, satisfactorily reproduce the geometries and conformational energies of representative unsaturated cyclic hydrocarbons. Predictions are made concerning the conformations of cyclononyne.

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