Table V

$9\text{-X-F} + Li^+\ 2,3\text{-BF}^- \rightleftharpoons Li^+\ 9\text{-X-F}^- + 2,3\text{-BF}$

X	$K_{20°}$	$\Delta H°$, cal/mol	$\Delta S°$, eu
H	4.1	−290 ± 60	1.8 ± 0.2
CH_3	3.74	−780 ± 50	0.0 ± 0.2
Et	1.57	−770 ± 40	−1.8 ± 0.2
i-Pr	0.26	180 ± 40	−2.1 ± 0.2
t-Bu	0.021	1140 ± 40	−3.8 ± 0.2

enthalpy term. As discussed above these equilibria involve contact ion pairs. We interpret the results with a model in which the cesium cation is located above and approximately at the center of the five-membered ring in the planar 9-alkylfluorenyl ions. In this location the cation is at the "center of gravity" of negative charge for best electrostatic attraction and does not interfere significantly with rotation of the alkyl group about its bond to the 9-carbon.

On the other hand, the equilibria in the Li case involve changes in both entropy and enthalpy. The ion pairs in this system are largely solvent separated; solvation of the small Li cation is an important component. In these ion pairs increased branching in the 9-alkyl group clearly produces increased steric interactions with solvent molecules solvating the Li cation. Such interactions can result in a progressive decrease in entropy by increased hindrance to rotation about the R–C-9 bond and/or by changes in the entropy of solvation of the Li cation by increased restrictions in the motion of solvating solvent close to the 9 substituent.

We conclude that all of the results on relative ion-pair acidities of 9-alkylfluorenes are completely consistent with the application of conventional physical organic inductive, field, and bond strength effects to contact and solvent-separated ion pairs and do not require such additional effects as anionic hyperconjugation and unusual dispersion interactions.

Conformational Analysis. LXXXIV. A Study of the Structures and Energies of Some Alkenes and Cycloalkenes by the Force Field Method[1,2]

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Abstract: Our earlier described force field has been extended to include compounds containing (nonconjugated) olefinic linkages. The structures and energies of small alkenes are adequately calculated. A number of conformational problems were studied: cyclopentene; the cis and trans isomers of cyclohexene, cycloheptene, cyclooctene, and cyclodecene; 1,4-cyclohexadiene; 1,5-cyclooctadiene; and some bicyclic olefins. The results are in general in good to fair agreement with the literature in cases where comparisons can be made. In cases where literature data do not exist for the structures or energies, predictions are made regarding these items.

In recent papers we have described the development of a force field method for the calculation of structures and energies of hydrocarbons[5a] and for ketones.[5b] In this paper will be described the extension of the same method in a compatible way to include alkenes and related compounds. An ordinary alkene can be treated by the methods of molecular mechanics just as a saturated hydrocarbon can; it is only necessary to know the values for the natural angles, force constants, etc., which are different in and about the double bond. For conjugated systems, or for systems that cannot be adequately described by a single Kekulé structure, more sophisticated methods are in general necessary. These will be the subject of a later paper. This paper will be concerned only with molecules containing isolated double bonds.

The force field and attendant parameters developed in earlier work for hydrocarbons and ketones carry over here.[6] It is only necessary to assign values to

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(1) Paper LXXXIII, M. T. Tribble and N. L. Allinger, *Tetrahedron*, 28, 2147 (1972).

(2) Supported in part by Grant No. GP-15263 from the National Science Foundation.

(3) Correspondence should be addressed to this author at the University of Georgia.

(4) National Science Foundation Predoctoral Fellow, 1969–1970.

(5) (a) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Amer. Chem. Soc.*, **93**, 1637 (1971); (b) N. L. Allinger, M. T. Tribble, and M. A. Miller, *Tetrahedron*, **28**, 1173 (1972).

(6) In our earlier paper, the stretch–bend interaction term was calculated by multiplying the amount of stretching in a bond by the absolute value of the angle bending for the angles at the ends of the bond. Such a term does not correspond to the kind of term one expects in a Taylor's expansion truncated at the quadratic approximation. While we recognize that there is no theoretical basis for such a term, it was used for the sake of expediency, because it was observed that when bond angles close down (as in cyclobutane) the bonds stretched, but when the bond angles were opened up (as in hexamethylethane) the bonds were also stretched. At the urging of Professor L. S. Bartell, to whom we are indebted for his persistent concern, we have looked into this matter and find now that results very similar to those obtained before can be obtained by the use of a stretch–bend interaction term in which the absolute value of the angle bendings is replaced by a signed quantity, and the signs are chosen such that the bonds are stretched when the angle closes (as in cyclobutane). In order to prevent the bond lengths from contracting in a molecule such as hexamethylethane, it is necessary to add a cubic term to the bond stretching. Evidence indicating that this is an appropriate addition has been given by H. B. Burgi and L. S. Bartell, private communication, and we have used a value for the cubic constant as they have recommended ($a = 2\ \text{Å}^{-1}$). A rough reoptimization of the various parameters entering into the calculations was then carried out, and it

Table I. Force Field Parameters

van der Waals Constants

	r^*, Å	ϵ, kcal/mol
C_{sp^2}	1.85	0.033
H	1.50	0.060

Natural Bond Lengths and Stretching Force Constants

Bond	l_0, A	k_l, mdyn/Å
$C_{sp^3}–C_{sp^2}$	1.496	4.4
$C_{sp^2}=C_{sp^2}$	1.332	9.6
$C_{sp^2}–H$	1.090	4.6

Natural Bond Angles and Bending Force Constants

Angle[a]	Type[b]	θ_0, deg	k_θ, mdyn Å/rad²
$H–C_{sp^2}–H$		122.2	0.20
$C_{sp^3}–C_{sp^2}–H$		117.9	0.24
$C_{sp^2}–C_{sp^2}–H$	1°	118.9	0.24
$C_{sp^2}–C_{sp^2}–H$	2°	119.9	0.24
$C_{sp^3}–C_{sp^2}–C_{sp^3}$		116.6	0.40
$C_{sp^3}–C_{sp^2}–C_{sp^2}$	2°	122.2	0.40
$C_{sp^3}–C_{sp^2}–C_{sp^2}$	3°	121.7	0.40
$C–C_{sp^3}–C_{sp^3}$		*a*, *e*	*a*, *e*
$C–C_{sp^3}–H$		*a*, *e*	*a*, *e*

Cubic bending constant (k_{θ^3}) = 0.007

Torsional Constants

Angle[a]	k_ω	k'_ω
$C–C_{sp^3}–C_{sp^3}–C$	0.50	
$C–C_{sp^3}–C_{sp^3}–H$	0.50	
$C–C_{sp^3}–C_{sp^2}–C_{sp^3}$	2.10	
$H–C_{sp^3}–C_{sp^2}–C_{sp^3}$	2.10	
$C–C_{sp^3}–C_{sp^2}–H$	1.90	
$H–C_{sp^3}–C_{sp^2}–H$	1.90	
$C–C_{sp^3}–C_{sp^2}=C_{sp^2}$	0.0[c]	
$H–C_{sp^3}–C_{sp^2}=C_{sp^2}$	0.0[c]	
$C_{sp3}–C_{sp^2}=C_{sp^2}–C_{sp^3}$	13.55[d]	−0.68
$H–C_{sp^2}=C_{sp^2}–C_{sp^3}$	13.55[d]	
$H–C_{sp^2}=C_{sp^2}–H$	13.55[d]	

Stretch–Bend Constants[a]

$k_{l\theta}(C–C_{sp^3}–C) = -0.09$ mdyn/rad

$k_{l\theta}(C–C_{sp^3}–H) = -0.04$ mdyn/rad

[a] Where carbon hybridization is not specified, the parameters apply to both C_{sp^3} and C_{sp^2}. [b] The type refers to the degree of substitution of the central atom (*i.e.*, primary, secondary, tertiary, or quaternary). [c] Small negative values would improve the fit to experiment in certain cases, but others would get worse. In the absence of convincing data, the value zero has been used. [d] There are four torsional energies to be summed across a double bond *ab* C=C *cd:* these are *ac*, *ad*, *bc*, and *bd*, Each of these has the value zero when $\omega = 0$, and 13.55 when $\omega = 90°$, which approximately accounts for the torsional barrier in ethylene: J. E. Douglas, B. S. Rabinowitch, and S. F. Looney, *J. Chem. Phys.*, **23**, 315 (1955). [e] See ref 5 for numerical values.

the new parameters which are peculiar to the double bond. The parameters settled upon are given in Table I.

These parameters were evaluated by fitting to the structures of the simple molecules ethylene,[7] propene,[8] and isobutene,[9] (see Table II).

In dealing with experimental structural data, the bond lengths obtained by different methods are not exactly comparable. Diffraction (r_g) values seem to be best suited for comparing distances measured in different laboratories. However, the same value measured by different groups may vary by up to 0.01 Å.[10] The most reliable spectroscopic distances which can be obtained by complete isotopic substitution (r_s) are in general 0.005–0.010 Å shorter than their diffraction counterparts for first-row atoms.[10] Since only diffraction methods are well suited for determining the structures of large molecules (more than say 15 atoms), we are trying to duplicate r_g values in the present calculations; thus, where spectroscopic data are available, we have added 0.006 Å to the r_s distances to convert them to "experimental" r_g values.

The few simple molecules mentioned sufficed to assign most of the structural parameters necessary for the force field calculation of olefins, when combined with parameters already available for saturated hydrocarbons. An occasional additional value is necessary in special cases, and these will be commented on in passing as they occur.

The force constants were taken from measurements on alkenes, and some of the bending constants were empirically reduced so as to be more compatible with the values used for hydrocarbons. The force constants in the literature were inevitably assigned with the aid of a force field that differed substantially from that used in the present work; thus we feel that while the force constants should be of the same order of magnitude as the experimental values, there is no compelling reason to give them the same quantitative values. The force constants in the present work are chosen to fit to structure and enthalpy data, not to vibrational spectra.

Experimental barriers to rotation are available for propene[8] (1.98 kcal/mol) and for isobutene[9] (2.21 kcal/mol), and were used in assigning torsional constants. In the calculation of rotational barriers, a rigid-rotor approximation was used in the present work. It was felt that the rather large stretching and angular deformations which were found to occur if the eclipsed forms were allowed to relax do not very well approximate what occurs when the molecule undergoes a change in the normal coordinate assigned to rotation. Although the true situation is probably somewhere in between, the rigid-rotor approximation seems like the better choice.[5] Our calculated (rigid-rotor) values were 1.85 and 2.14 kcal/mol, respectively.

Heats of Formation. These are calculated by assigning enthalpy increments to the various bond types and structural features found in small molecules to duplicate the experimental $\Delta H_f°$ values. Increments

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was found that the results essentially duplicated the earlier results, with only three exceptions worth mentioning. It was found in cyclodecane that the bond lengths were on the average 0.006 Å shorter than previously, which is in better agreement with experiment. It was also found that for hexamethylethane, the central bond length was 0.007 Å shorter than previously, in poorer agreement with experiment, but the C–C–C angles that were opened out were calculated to have the value 112.6° instead of 113.1° (*vs.* 111.0 ± 0.4° experimental). Finally, over a list of 14 representative compounds, the standard deviation between the calculated and observed heats of formation was determined and found to be 0.50 kcal/mol, compared to 0.48 kcal/mol with our previous force field. In other words, the modified force field employing a signed stretch–bend interaction together with a cubic term in the stretching can be made to yield results which are for practical purposes indistinguishable from those calculated by our previously described force field. Because of the prohibitive amount of labor that would be involved, we have not repeated the calculations with the modified version of the force field, but add this comment only as a justification for the odd mathematical form of this interaction term in our earlier force field.

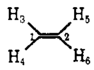
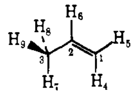
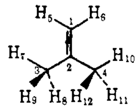
(7) L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitsu, and J. E. Young, Jr., *J. Chem. Phys.*, **42**, 2683 (1965).

(8) D. R. Lide, Jr., and D. Christensen, *ibid.*, **35**, 1374 (1961).

(9) L. H. Scharpen and V. W. Laurie, *ibid.*, **39**, 1732 (1963).

(10) (a) D. R. Lide, Jr., *Tetrahedron*, 17, 125 (1962); (b) B. P. Stoicheff, *ibid.*, 17, 135 (1962).

Table II. Geometries of Ethylene, Propene, and Isobutene

		Electron diffraction	Calcd
	$C_1{=}C_2$, Å	1.337 ± 0.001	1.337
	C_1–H_3, Å	1.103 ± 0.001	1.093
	$\angle C_1{=}C_2$–H_5, deg	121.4 ± 0.6	120.9
		Microwave[a]	Calcd
	$C_1{=}C_2$, Å	1.342 ± 0.004	1.338
	C_2–C_3, Å	1.507 ± 0.004	1.510
	$\angle C_1{=}C_2$–C_3, deg	124.3 ± 0.3	124.6
	$\angle C_1{=}C_2$–H_6, deg	119.0 ± 0.3	118.9
	$\angle C_2{=}C_1$–H_4, deg	120.5 ± 0.3	120.1
	$\angle C_2{=}C_1$–H_5, deg	121.5 ± 0.3	121.4
		Microwave[a]	Calcd
	$C_1{=}C_2$, Å	1.336 ± 0.004	1.338
	C_2–C_3, Å	1.513 ± 0.003	1.511
	$\angle C_3$–C_2–C_4, deg	115.3 ± 0.1	115.0
	$\angle H_5$–C_1–H_6, deg	118.5 ± 0.2	118.5

[a] 0.006 has been added to the reported bond lengths (see text).

for saturated hydrocarbons were developed previously, and are carried over here. The additional enthalpy increments necessary for calculation for the heats of formation of olefins as developed in the present work are given in Table III.

Table III. Bond Enthalpy Increments

C_{sp^3}–C_{sp^3}	2.97[a]	Iso (C_{sp^3})	−0.74[a]
C_{sp^3}–C_{sp^2}	−0.13[b]	Iso (C_{sp^2})	−0.17[b]
$C_{sp^2}{=}C_{sp^2}$	29.33[b]	Neo	−1.75[a]
C–H (all)	−4.47[a]	Methyl group	0.74[a]

[a] Obtained from ref 5. [b] Obtained from an optimization based on all compounds listed in Table IV where experimental $\Delta H_f°$ is reported to two decimal places.

In a preliminary calculation our model was found to exaggerate the heat of formation difference between *cis*- and *trans*-2-butene by about 1 kcal/mol. After numerous attempts to resolve this through parameter revisions, we decided to add a first-order harmonics term to the potential function for twofold barriers such that

$$E_\omega = {}^1/_2k_\omega(1 - \cos 2\omega) + {}^1/_2k'_\omega(1 + \cos \omega) \quad (1)$$

where k'_ω is the first-order constant. The use of multiple harmonics is commonly employed in determining torsional constants from experimental spectra. We initially used a k'_ω of −1.0 kcal/mol for the C_{sp^3}–$C_{sp^2}{=}C_{sp^2}$–C_{sp^3} interaction, but later settled on a value of −0.68 kcal/mol obtained by treating k'_ω as an adjustable parameter in the bond enthalpy optimization (*vide infra*) of our heat of formation calculations.

The quantities in Table III were evaluated from the available experimental data on the compounds given in Table IV[11,12] by a least-squares optimization of the appropriate parameters. The heat of formation is calculated by the equation

$$\Delta H_f° = E_s + \Delta H_{\mathrm{bond}} + \Delta H_{\mathrm{str}}$$

where E_s is the steric energy of the molecule calculated by our program, ΔH_{bond} is the sum of the bond enthalpy contributions, and ΔH_{str} is the sum of the structural enthalpy contributions.[13]

Table IV lists all of the compounds used in evaluating the enthalpy terms for the alkene study. It is somewhat limited, although it is representative of all of the good gas-phase data available. It might be noted that while experimental errors in heats of formation are typically reported of ±0.2–0.3 kcal/mol, results on the same compounds from different laboratories usually differ from one another by this amount or more. Therefore, the best experimental data (reported to two decimal places in Table IV) are probably only accurate to about ±0.3–0.5 kcal/mol. One way to compare the accuracy of the present calculations is to look at the root-mean-square deviation between the calculated and experimental values for all the compounds (reported to two decimals) in Table IV, which was 0.31 kcal/mol, and compare this value with the numbers given in the last sentence.

Having completed our parameterization, it was then desirable to first check that we could calculate adequately the structures and energies of a variety of simple olefins. Some of this work was done earlier with a relatively inadequate force field.[14] In general, the results were better with the present force field.

The gauche conformer of 1-butene was calculated to be more stable than the cis by 0.70 kcal/mol, which is not in very good agreement with the microwave value[15] of 0.15 ± 0.15 kcal/mol, or within nmr estimate of equal amounts of the three rotational forms.[16] Our geometries for both the gauche and cis forms agree with the microwave structures.

The calculated geometries for *cis*- and *trans*-2-butene are compared with the experimental structures[17,18]

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(11) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

(12) D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969, Chapter 14.

(13) After extensive calculations had been completed, a few small improvements in some of the numerical data in Table II were made. It was judged not to be worthwhile to repeat the least-squares optimization, however.

(14) N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *J. Amer. Chem. Soc.*, **90**, 5773 (1968).

(15) S. Kondo, E. Hirota, and Y. Morino, *J. Mol. Spectrosc.*, **28**, 471 (1968).

(16) A. A. Bothner-By, C. Naar-Colin, and H. Gunther, *J. Amer. Chem. Soc.*, **84**, 2748 (1962).

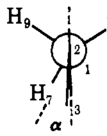
(17) A. Almeningen, I. M. Anfinsen, and A. Haaland, *Acta Chem. Scand.*, **24**, 43 (1970).

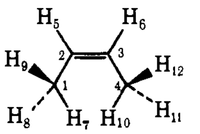
Table IV. Calculated Heats of Formation for Simple Olefins

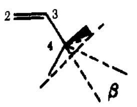
	E_s[c]	Bond enthalpy	Conformation enthalpy	$\Delta H_f°$ Calcd	$\Delta H_f°$ Expt[a]	Calcd − Expt
Ethylene	1.17	11.45		12.62	12.50	0.12
Propene	1.68	3.12		4.80	4.88	−0.08
1-Butene	3.24	−2.85	0.09	0.48	−0.03	0.51
cis-2-Butene	3.40	−5.21		−1.81	−1.67	−0.14
trans-2-Butene	2.24	−5.21		−2.97	−2.67	−0.30
Isobutene	1.08	−5.38		−4.30	−4.04	−0.26
cis-2-Pentene	4.66	−11.18	0.06	−6.46	−6.71	0.25
trans-2-Pentene	3.78	−11.18	0.09	−7.31	−7.59	0.28
2-Methyl-2-butene	3.19	−13.71		−10.52	−10.17	−0.35
2-Methyl-2-pentene	4.30	−19.68		−15.38	−15.98	0.60
2,3-Dimethyl-2-butene	5.37	−22.21	0.22	−16.62	−16.68	+0.06
Cyclopentene	9.06	−0.75		8.31	8.56	−0.25
Methylcyclopentene	8.11	−9.25		−1.14	−1.5[b]	0.4
Methylenecyclopentane	10.47	−6.89		3.58	2.4[b]	1.2[d]
Cyclohexene	5.52	−6.72		−1.20	−0.84	−0.36
Methylcyclohexene	4.92	−15.22	0.07	−10.23	−10.0[b]	−0.2
Methylenecyclohexane	5.34	−12.86		−7.52	−7.2[b]	−0.3
Cycloheptene	11.04	−12.69		−1.65	−1.8	0.2
cis-Cyclooctene	13.28	−18.66		−5.38	−6.2	0.8
trans-Cyclooctene	22.32	−18.66		3.66	4.1[b]	−0.4

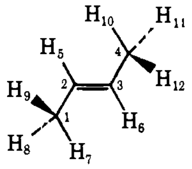
[a] All heat of formation data are taken from ref 11 (see also ref 12). Unless otherwise noted, measurements were taken in the gas phase. [b] The experimental $\Delta H_f°$ includes 1 kcal/mol added to correct for work done in solution. [c] E_s is the "steric energy" calculated by the program. [d] The bond energy scheme of ref 11 gives for this compound a heat of formation in good agreement with our calculated value, but in poor agreement with experiment, which suggests that the experimental value may be inaccurate.

Table V. Geometries of *cis*- and *trans*-2-Butene









	Cis Electron diffraction[a]	Cis Microwave[b]	Cis Calcd	Trans Electron diffraction[a]	Trans Calcd
$C_2{=}C_3$, Å	1.346 ± 0.003	1.350[c]	1.342	1.347 ± 0.003	1.339
C_1–C_2	1.506 ± 0.002	1.497	1.513	1.508 ± 0.002	1.511
$\angle C_1$–$C_2{=}C_3$	125.4 ± 0.4	126.7	127.9	123.8 ± 0.4°	125.1°
α, deg	9.0 ± 6.8		8.6		
β, deg	4.9 ± 2.0		3.6		

[a] Reference 17. [b] Reference 18. [c] Assumed value.

in Table V. The conspicuous disagreements appear to be our larger calculated C–C–C angle in the cis isomer, and smaller C=C length in the trans isomer. When compared with many other similar olefins, the experimental value for the double bond in the trans isomer seems out of line, and we feel our calculated value is better. Our calculated C–C–C angle in the cis isomer is probably 1 or 2° too large. After completion of this work and a good deal of additional calculational work on other structures, it appears that we have chosen the repulsive part of our van der Waals curve for hydrogens to be a little steeper than it should be, *i.e.*, the hydrogens are too "hard," and the bending deformations are too easy (force constants too small) in an attempt to compensate for that. The errors seem to be pretty small, however, and so we are ignoring them at this point.

Our calculations on *cis*-2-butene indicate that the methyl group is rotated from planarity and tilted, in good agreement with experimental data. The symmetry is C_2, not C_{2v} as might have been anticipated.

Although no experimental structural data are available, we felt that di-*tert*-butylethylene would be a good test of our model, since hydrogenation data[19] in acetic acid indicate about 9.7 kcal/mol of strain in the cis isomer as compared to the trans, which would correspond to 10.7 kcal/mol in the gas phase. Our calculations gave a value of 10.36 kcal/mol which is in good agreement. Of concern, however, is the fact that our calculated heats of hydrogenation for both isomers are significantly larger than experiment (trans, expt 26.9 kcal/mol (calcd 29.5 kcal/mol); cis, expt 36.2 kcal/mol (calcd 39.8 kcal/mol)). As will be seen, of all the olefins studied these results are the most anomalous and may be due to imperfections in our nonbonded potential or the absence of olefin stretch-bend participation. Without further collaborating evidence, however, we decided not to introduce new parameters to correct our force field since the experimental data may be in considerable error.

The low energy conformation of *cis*-di-*tert*-butylethylene has a C_2 symmetry, rather than C_{2v}, as does

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(18) S. Kondo, Y. Sakurai, E. Hirota, and Y. Morino, *J. Mol. Spectrosc.*, **34**, 231 (1970).

(19) R. B. Turner, D. E. Nettleton, Jr., and M. Perelman, *J. Amer. Chem. Soc.*, **80**, 1430 (1958).

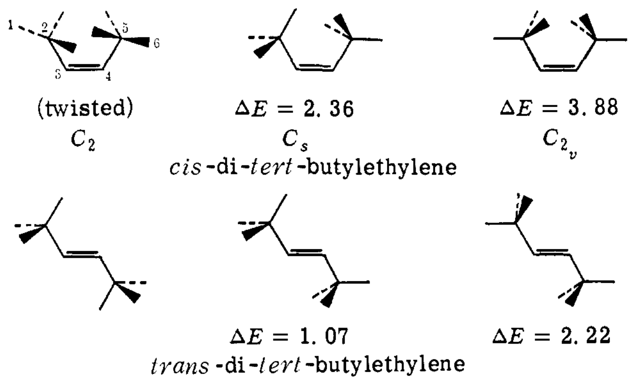
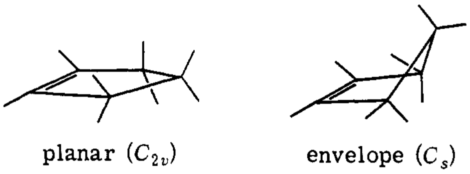


Figure 1. Conformations and relative energies (kcal/mol) for di-*tert*-butylethylene. For clarity, hydrogens are not shown. All methyl groups are staggered, or approximately so.

cis-2-butene, and for the same reason. If a plane containing carbons 3 and 4 is placed midway between atoms 2 and 5, these are respectively above and below the plane by 0.03 Å. Carbons 1 and 6 are respectively below and above the plane by 0.37 Å (see Figure 1).

Cyclopentene is the smallest cyclic olefin which we have studied. Its envelope form with a ring pucker of 19° is found favored over the planar form by 0.41 kcal/mol. This may be compared with an equilibrium angle of 23.3 ± 1° and a barrier opposing planarity of 0.663 ± 0.014 kcal/mol obtained by Lord[20] from the infrared spectrum. The heat of hydrogenation differs from the experimental value by −0.65 kcal/mol (see Table VI [21-26]).



The enthalpy difference between methylenecyclopentane and methylcyclopentene is calculated to be 4.72 kcal/mol in favor of the endo double bond, which agrees quite well with 4.79 kcal/mol deduced[14] from gas-phase measurements,[27] 3.87 kcal/mol from hydrogenations in acetic acid,[28] and 4.29 kcal/mol from an extended Hückel calculation.[29]

The potential function for the pseudorotation of cyclohexene has been calculated, and contrary to earlier calculations,[14] the boat form is found to be the transition state in the pseudorotation from one chair form to another with a $\Delta H^{\ddagger}$ of 6.39 kcal/mol. This result is in agreement with the recent study of Bucourt[30] which concluded that the boat is about 7 kcal/mol less stable than the chair and that they are not separated by an energy barrier. It may also be compared with the low-temperature nmr studies of Anet[31] which indicate the barrier between chair forms is 5.3 kcal/mol.

Table VI. Heats of Hydrogenation for Cyclic Olefins

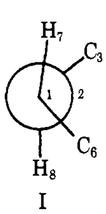
Alkane Heat of Formation Data			
Compound	Calcd[a] $\Delta H_f°$	Expt[b] $\Delta H_f°$	Calcd − expt
Cyclopentane	−17.96	−18.46	0.50
Cyclohexane	−29.88	−29.43	−0.45
Cycloheptane	−28.37	−28.34	−0.03
Cyclooctane	−29.07	−30.06	0.99
Cyclodecane	−35.66	−36.29	0.63

Alkene Heat of Formation Data			
Compound	Calcd $\Delta H_f°$	Expt[c] $\Delta H_f°$	Calcd − expt
Cyclopentene	8.31	8.56	−0.25
Cyclohexene	−1.20	−0.84	−0.36
Cycloheptene	−1.65	−1.8	0.2
cis-Cyclooctene	−5.38	−6.2	0.8
trans-Cyclooctene	3.66	4.1	−0.4
cis-Cyclodecene	−14.30		
trans-Cyclodecene	−12.94		

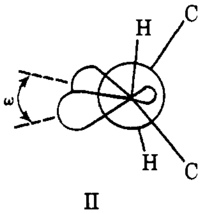
Heats of Hydrogenation					
Compound	Calcd $-\Delta H_H$	Gas phase $-\Delta H_H$	Solution $-\Delta H_H$	Calcd − expt	Ref
Cyclopentene	26.27	26.92	(25.7)	−0.65	21, 22
Cyclohexene	26.68	28.59	(27.10)	0.09	23, 24
Cycloheptene	26.72	26.52	(25.85)	0.20	25, 24
cis-Cyclooctene	23.69	23.53	(22.98)	0.16	25, 26
trans-Cyclooctene	32.73	(33.24)[d]	32.24	(−0.51)	26
cis-Cyclodecene	21.36	(21.67)[d]	20.67	(−0.31)	26
trans-Cyclodecene	22.72	(24.01)	24.01	(−1.29)	26

[a] Reference 5. [b] Reference 12. [c] Reference 11. [d] Gas-phase values for these compounds were estimated as being 1 kcal/mol larger than the reported solution values, because of dipole solvation.

The trans isomer of cyclohexene was also studied. Our calculations find it to be 42.4 kcal/mol less stable than the cis isomer, with a geometry indicating considerable distortion of the π bond (I). This geometry is interesting in that energetically the π bond is only half disrupted (30.9 kcal/mol torsional energy across $C_1{=}C_2$) even though the C-C=C-C dihedral angle

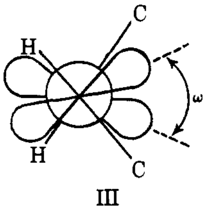


I



II

ω 6–1–2–3 = 85.1°
ω 7–1–2–8 = 166.6°



III

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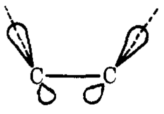
is 85°. The reason for this is that our model has simulated a rehybridization (II) rather than simple twisting (III) of the double bond. The preference for this type of distortion rather than twisting is illustrated in structure II. The overlap of the π-atomic orbitals (and thus the stability of the π bond) is a function, among other things, of the cosine of the angle between them. Locating the hydrogens in toward the ring carbon atoms (as in II), which constitutes a rehybridization of the olefinic carbons, reduces the angle between the atomic orbitals and thus increases the overlap. A limiting point is reached when the increase in overlap due to the smaller angle, ω, is offset by the decrease in overlap due to the orbitals being canted away from one another as in IV.

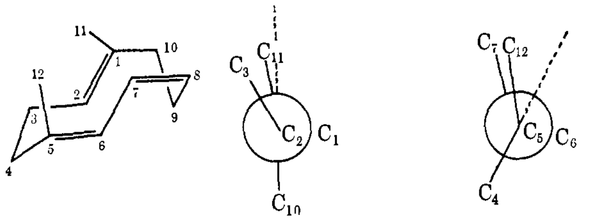


IV
(top view)

Evidence supporting this type of rehybridization is found in the 0.8 D dipole moment of *trans*-cyclooctene[32] as compared to the quite normal 0.4 D moment of the cis isomer. Infrared data for *trans*-cyclooctene have also been interpreted[32] in terms of increased p character in the C_{sp^2}–H bond. The recently reported[33] crystal structure of the pregeijerene silver nitrate adduct, shown in Figure 2, provides direct structural evidence. The methyl group (C_{11}) attached to C_1 is bent in toward the ring 4° from being coplanar with atoms C_1, C_2, and C_{10}, and the methyl group (C_{12}) attached to C_5 is bent 20° in toward the ring. Both of these distortions indicate some rehybridization of the unsaturated ring carbon atoms in order to relieve ring strain. The size of the distortion across the C_5–C_6 bond is probably influenced by the silver ion which is found to be complexed only with the diene linkage.

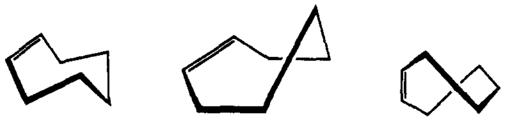
Although it would have been interesting to calculate the stability of *trans*-cyclohexene with respect to conversion to the cis isomer, we were unable to do so because a transition state could not be selected. The problem is that our computer program generates structures of minimum energy and, by definition, a transition state is a saddle point between the minimum energy forms. Often times the gross geometry of a transition state is obvious and we are able to find the saddle point by restricting atomic movement to certain planes or symmetry. This is not the case with the cyclohexene trans to cis conversion. A rather crude approximation can be made, however, by considering the reaction coordinate shown in Figure 3. Evaluating only the second-order torsional interactions across the C_1–C_2 bond (*i.e.*, ignoring the small first-order harmonics term of eq 1), the $\Delta H^{\ddagger}$ is 12.9 kcal/mol. Even though this is probably an upper limit (no attempt was made to optimize the pathway), the value is still low enough to indicate complete room temperature instability.

Cycloheptene has generally been assumed to exist in simple chair and boat conformations which would be unambiguously represented with models.[34–36] Theoretical calculations, however, have thus far been rather inconclusive as to which conformation is preferred. Using only a potential for nonbonded H···H interactions, Paunez and Ginsburg calculated the boat form to be the more stable of the two by 0.67 kcal/mol. Our earlier calculations, using the Westheimer method,[14] found the boat favored by 0.94 kcal/mol, while Favini, *et al.*,[37] in a similar calculation in which the twist form was also considered, found the chair favored over the boat by 1.19 kcal/mol and over the twist by 1.71 kcal/mol.

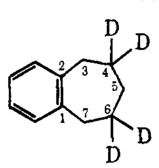


ω 10–1–2–3 = 165° ω 4–5–6–7 = 150°
ω 3–2–1–11 = 11° ω 12–5–6–7 = 10°

Figure 2. Pregeijerene geometry.



Experimental results for various cycloheptene derivatives are more nearly consistent with one another but provide little quantitative information for cycloheptene itself. The dipole moment of the benzene analog of 4-cyclohepten-1-one indicates a predominance of the chair form to the extent of about 95%.[35] The ^{19}F nmr spectrum of 5,5-difluorocycloheptene[38] shows a single AB system from −147° to the coalescence point of −92°, above which a single line appears, indicating that the molecule exists as a chair form and the fluorines become equivalent by a ring inversion similar to 1,1-difluorocyclohexane.[39] The calculated $\Delta H^{\ddagger}$ is 7.4 ± 0.1 kcal/mol. A similar conclusion was reached in an nmr study of 4,4,6,6-tetradeuterio-1,2-benzocycloheptene[40] (V). The lowest energy form, predominant to an extent of about 95%, was presumed to be a chair conformation on the basis of the equivalence of the C_3 and C_7 methylene groups along with the different chemical shifts of the C_5 protons. The $\Delta G^{\ddagger}$ was calculated to be 10.9 kcal/mol. The possibility of a



V

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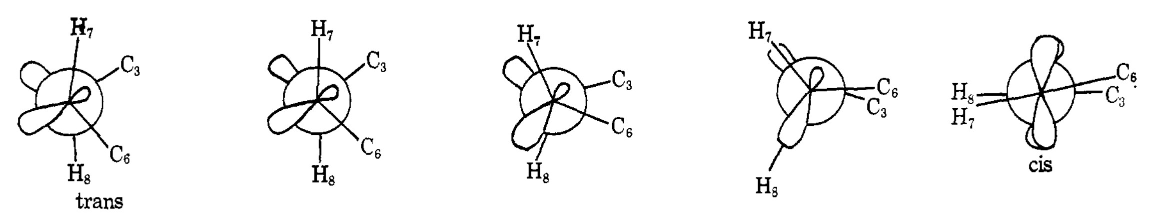


interaction	ω	E_ω	ω	E_ω	ω	E_ω	ω	E_ω	ω	E_ω
C_3/C_6	85°	16.1	72°	14.7	36°	5.6	0°	0	0°	0
C_3/H_7	41°	7.0	54°	10.6	90°	16.3	126°	10.6	180°	0
C_3/H_8	41°	7.0	54°	10.6	90°	16.3	126°	10.6	180°	0
H_7/H_8	167°	0.8	180°	0	144°	5.6	108°	14.7	0°	0
Σ		30.9		35.9		43.8		35.9		
ΔE_ω		0		5.0		12.9		5.0		

Figure 3. Possible π-bond reaction coordinate for the *trans*- to *cis*-cyclohexene conversion. E_ω is the second-order torsional interaction expressed in kcal/mol.

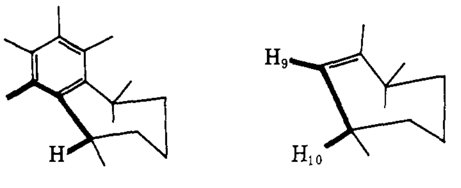
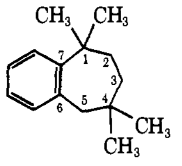


Figure 4.

boat form was eliminated on the basis of the small chemical shift difference between the axial and equatorial substituents on C_5. Similar studies on a number of di- and tetramethyl derivatives of benzocycloheptene have also found a predominance of the chair form with the $\Delta G^{\neq}$ to inversion ranging between 9.9 and 13.7 kcal/mol.[41] An nmr investigation of 1,1,4,4-tetramethyl-6,7-benzocycloheptene (VI) concluded that the



VI

chair and boat forms existed in a 2:1 equilibrium mixture,[42] but in this case the methyl groups have severe interactions in the "normal" ring conformations and the conformer which they assume to be a boat form is probably a pseudorotational isomer somewhere between the true boat and twist conformations.

The only reasonably direct evidence for the structure of cycloheptene itself is from a study of its Raman and infrared spectra.[43] Using a valence force field previously obtained from cyclohexene, the vibrational frequencies of cycloheptene chair, twist, and boat forms were calculated. Comparing these with the experimental values, it was concluded that the cycloheptene ring exists in the chair conformation in the crystal. In the liquid at room temperature additional bands, attributed to the boat form, were detected. It is difficult to assess the accuracy of the assignments, however, since force fields are not exactly transferable and since the rather crude cyclohexene molecular parameters were used in calculating the cycloheptene conformations.

From all of this one might conclude that cycloheptene probably exists predominantly as a chair form, being preferred by about 1–2 kcal/mol over the other conformations. Our calculations indicate the chair favored by 0.57 kcal/mol over the twist form and 3.37 kcal/mol over the boat. The calculated heat of hydrogenation of 26.72 kcal/mol, as compared to a 26.52 kcal/mol experimental gas-phase value,[25] helps substantiate our conclusions.

Before discussing the conformational mobility of the cycloheptene ring, we wish to point out that quite often conformational aspects of a parent molecule are analyzed on the basis of experimental data obtained for various derivatives without giving sufficient consideration to the fact that any conclusions properly refer to the derivatives and may really be poor approximations to the parent molecule. The mobility of the seven-member unsaturated ring, for example, has been discussed in a recent review article,[44] but the discussion is based to a large extent on the behavior of various benzocycloheptenes. Consequently we cannot apply the conclusions to cycloheptene itself without giving careful consideration to the differences between these two molecules. Probably the most important is that in benzocycloheptene the α hydrogens (Figure 4) have the possibility of C_{sp^2}/H eclipsing of the type encountered in toluene (0.5 ± 0.5 kcal/mol rotational barrier),[45] which by symmetry has a zero rotational barrier regardless of what constant we might use for the C_{sp^2}/H interaction. The α hydrogens of cycloheptene, however, can have H/H eclipsing of the type found in propene (1.98 kcal/mol rotational barrier).[8] As we have found, *vide infra*, the effects of this are quite significant.

Considering the chair, boat, and twist conformers of cycloheptene to all exist as pairs of equivalent forms, we studied in some detail the interconversion pathways (Figure 5) and possible transition states (Figure 6) between them. The interconversion of chair forms ($C_a \rightleftharpoons C_b$) is calculated to proceed most easily *via*

$$C_a \rightleftharpoons B_b \rightleftharpoons (T_a \text{ or } T_b) \rightleftharpoons B_a \rightleftharpoons C_b$$

with the potential function for this pathway shown in Figure 7. Alternate higher energy pathways *via* VII

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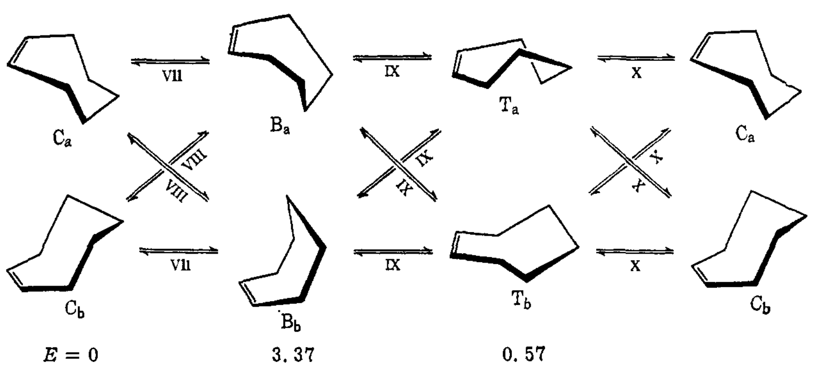

Figure 5. Interconversion pathways between various forms of cycloheptene. (Roman numerals refer to transition states of Figure 6.)

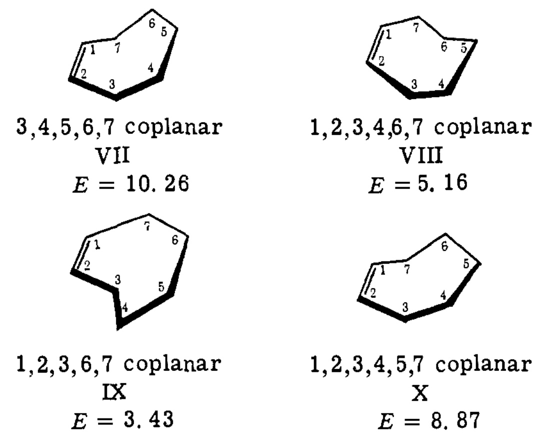

Figure 6. Cycloheptene transition states.

and X are also shown. The rate determining steps (neglecting entropy effects) are $C_a \rightleftharpoons B_b$ and $B_a \rightleftharpoons C_b$, and the $B \rightleftharpoons T$ interconversions are low-energy pseudorotations with the calculated potential function shown in Figure 8. The 5.16 kcal/mol calculated $\Delta H^{\ddagger}$ for the chair inversion is somewhat lower than the 7.4 ± 0.1 kcal/mol 5,5-difluorocycloheptene value, but this is not particularly disturbing since steric or electrostatic differences introduced by the fluorine atoms may easily account for the difference.

The considerably higher $\Delta G^{\ddagger}$ values (9.9–13.7 kcal/mol) for the benzocycloheptenes are consistent with our results if one takes into account the aforementioned H/H and C_{sp^2}/H eclipsing. The rate determining step in the chair inversion has a transition state (VIII) characterized by a relief of the H_9/H_{10} eclipsing (see Figure 4) of the chair form. This relief amounts to about 3.5 kcal/mol. Because of the zero torsional constant for the C_{sp^2}/H interaction in benzocycloheptene,[46] there is no torsional relief for this molecule in the $C_a \rightleftharpoons B_b$ transition state. Presuming benzocycloheptene to follow the same interconversion pathway as cycloheptene (as seems to be the case from a casual examination of the various transition states), the calculated $\Delta H^{\ddagger}$ would thus be in the range of 9–10 kcal/mol, which is in reasonable agreement with experimental values.

An independent study of cycloheptene inversion,[41] based on calculations from models, considered the same interconversions shown in Figure 5 and concluded that the most favorable pathway was

$$C_a \rightleftharpoons B_a \rightleftharpoons (T_a \text{ or } T_b) \rightleftharpoons B_b \rightleftharpoons C_b$$

with a $\Delta H^{\ddagger}$ for the rate determining step ($C_a \rightleftharpoons B_b$) of 14.6 kcal/mol. The $B \rightleftharpoons T$ pseudorotation was given a $\Delta H^{\ddagger}$ of 11.1 kcal/mol and the alternate pathways $C_a \rightleftharpoons B_b$ and $C \rightleftharpoons T$ were estimated to be 20-25 kcal/mol. Unfortunately, models represent a rather limited force field reflecting only ring angle deformations. Torsional and van der Waals considerations can be mentally added, but qualitative accuracy is achieved only in the simplest and most obvious interactions. Thus, while models indicate transition state VII to be more stable than VIII leading to the $C_a \rightleftharpoons B_b$ pathway shown above, our calculations find the reverse to be true, resulting in the previously mentioned $C_a \rightleftharpoons B_b$

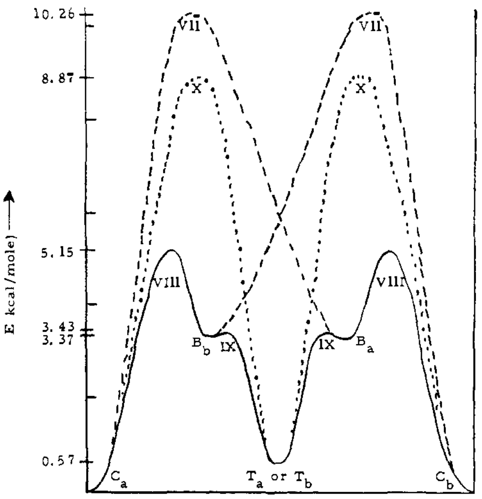

Figure 7. Interconversion of chair forms of cycloheptene.

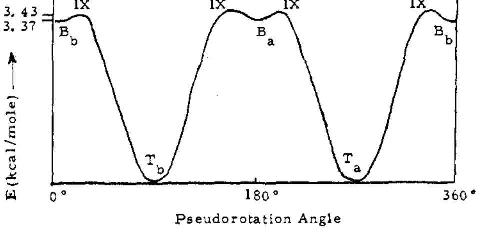

Figure 8. Pseudorotation of cyloheptene.

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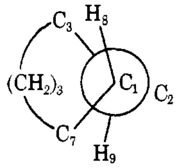
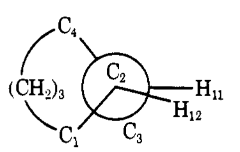
[46] Actually, the constant for the C_{sp^2}/H interaction need not be zero as long as that of the C_{sp^2}/C_{sp^3} interaction has a corresponding value. This will keep the sum of the torsional interactions across the $C_{(ar)}$–C_{sp^3} bond fairly constant regardless of the bond's rotation.

pathway being preferred. We feel, of course, that the above study of cycloheptene inversion, based on model calculations, is in considerable qualitative error.

Recently Corey, *et al.*,[47] reported obtaining the *trans*-cycloheptene adduct of 2,5-diphenyl-3,4-isobenzofuran in the reaction of *trans*-1,2-cycloheptene thiocarbonate with trimethyl phosphite. *trans*-Cycloheptene itself could not be isolated. Our calculations find *trans*-cycloheptene to be 20.32 kcal/mol less stable than the cis isomer. Our geometry about the trans double bond (XI) shows considerable rehybridization of the unsaturated carbon atoms in order to relieve ring angle strain. To estimate the $\Delta H^{\ddagger}$ for trans to cis conversion, a transition state with a 90° C–C=C–C dihedral angle (XII) was assumed. The energy of this form was found to be only 5.97 kcal/mol greater than for the trans isomer, indicating complete room temperature instability of the trans ring double bond. Because we cannot be certain that our 90° structure accurately represents the actual transition state, our calculated $\Delta H^{\ddagger}$ is only approximate.



ω 3–2–1–7 = 125°
ω 9–2–1–8 = 166°
XI

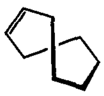


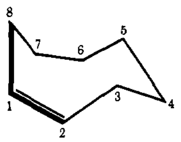
ω 10–2–3–11 = 4°
ω 1–2–3–4 = 90°
XII

The cis and trans isomers of cyclooctene are known and both are of conformational interest. A model of the cis isomer shows it to be quite flexible with no obvious preferred conformations. Pauncz and Ginsburg,[36] considering only the three regular conformations illustrated, calculated the chair form favored over the boat by 0.32 kcal/mol and over the twist by 12.58 kcal/mol. An examination of models shows these regular forms to suffer from ethane-type H/H torsional interactions as well as other nonbonded H···H interactions. Favini, *et al.*,[37] considered another form, described as an intermediate in a chair-to-boat inversion, and calculated it to be 7.9 kcal/mol less strained than either the chair or boat and 11.4 kcal/mol less strained than the twist. Our lowest energy conformation (XIII) is a similar or perhaps the same nondescript flexible form. Assuming what seems to be this same conformation, an nmr study of *cis*-cyclooctene found two averaging processes for the ring protons: a time average two-fold axis of symmetry through the C_1–C_2 and C_5–C_6 bonds ($\Delta G^{\ddagger}$ = 5.8 kcal/mol) and a complete inversion of the four protons at C_4 and C_5 ($\Delta G^{\ddagger}$ = 8.2 kcal/mol).[48] A model of XIII, however, suggests that the first barrier observed *via* nmr is actually a time-average mirror plane passing through and perpendicular to the C_1–C_2 and C_5–C_6 bonds. The chair form would probably be the transition state for the interconversion and our calculated $\Delta H^{\ddagger}$ is 7.44 kcal/mol. The second barrier probably involves chair–chair interconversion, but we found it impossible to select appropriate transition states and thus could not calculate a $\Delta H^{\ddagger}$. In a study of coupling constants in small and medium ring cyclenes, the torsional angles between the vinyl proton and adjacent protons of the methylene group were calculated to be 15 and 135° in *cis*-cyclooctene.[49] These angles for our lowest energy form are 32, 43, 142, and 156° and for the chair form are 29 and 138°. We made no attempt to find a process which would give lower time-average values for these angles. Our calculated heat of hydrogenation for *cis*-cyclooctene is within 0.25 kcal/mol of the experimental gas-phase value.


chair

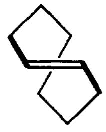

boat


twist



XIII

Models of *trans*-cyclooctene show it to be quite strained and capable of existing in two unambiguous conformations, chair and twist. An X-ray study of its copper complex found the ring to exist in the twist form with a dihedral angle across the double bond of 134°.[50] A preliminary report of its platinum complex X-ray structure[51] also indicates a twist form, but large experimental errors and certain anomalous bond lengths and angles disallow any other worthwhile structural comments. Our calculations favor the twist form over the chair by 2.43 kcal/mol. Our 149° dihedral angle in the twist is somewhat larger than the experimental value, but this was expected since in the experimental structure the perturbation by the metal atom should somewhat delocalize the π electrons and thus weaken the π bonds.


twist


chair

A simple twisting of the *trans*-cyclooctene double bond, as in III, to yield a 149° dihedral angle, would result in a 31° angle between the p π-atomic orbitals and a negligible dipole moment for the molecule. By our calculated rehybridization, XIV, which corresponds to an sp^{54} π-atomic orbital, the angle between the lobes is 16.3° (including the slight amount of tilt away from one another along the bond axis as in IV), and using Slater orbitals with an effective charge of 3.25, the dipole moment caused by a single electron in the orbital is calculated to be 0.6 D.[52] Neglecting any other factors, the dipole moment due to the π bond is thus about 1.2 D which compares adequately with the 0.8 D experimental value for the molecule.[32] The calculated heat

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(47) E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Amer. Chem. Soc.*, 87, 934 (1965).

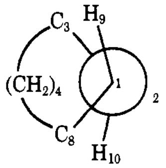
(48) M. R. St-Jacques, *Diss. Abstr.*, *B*, 28, 4076 (1968).

(49) G. V. Smith and H. Kriloff, *J. Amer. Chem. Soc.*, **85**, 2016 (1963).

(50) P. Ganis, U. Lepore, and G. Paiaro, *Chem. Commun.*, 1054 (1969).

(51) P. C. Manor, D. P. Shoemaker, and A. S. Parkes, *J. Amer. Chem. Soc.*, **92**, 5260 (1970).

(52) C. A. Coulson, "Valence," Oxford University Press, London, 1963, p 218.



XIV

ω 3–2–1–8 = 149°

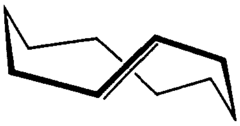
ω 10–2–1–9 = 171°

of hydrogenation is 0.6 kcal/mol greater than the experimental value in acetic acid. Since acetic acid results tend to be about 1 kcal/mol lower than gas-phase values for cis olefins, however, our agreement with experiment is satisfactory for such a polar *trans*-cyclene.

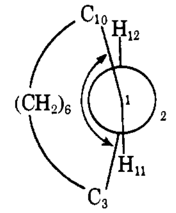
Models indicate no unique conformations for *cis*-cyclodecene; consequently, a number of rather similar but nondescript forms had to be studied. Our choice of XV as the preferred conformation is supported by its calculated heat of hydrogenation. *trans*-Cyclodecene is also quite flexible, *via* models, and displays little of the strain present in smaller *trans*-cyclenes. We considered only two conformations, with the twist form calculated to be more stable than the chair by 1.58 kcal/mol. An X-ray study of the silver nitrate adduct[53] also finds a twist form, but the 138.3° ring dihedral angle across the olefinic linkage in the crystal is considerably smaller than the 164° angle found in our calculated structure (XVI). The distortion of the π bond in the crystal is much greater than one might have expected, its value being comparable to that reported for the *trans*-cyclooctene copper complex. Adding to the anomaly is the fact that Ag(I) π complexes are generally weaker than those of Cu(I).[54] The X-ray structure of a silver complex of germacratriene (XVII) shows dihedral angles of only 167° for the 4–5 bond and 160° for the 8–9 bond,[55] both of which are complexed with the silver ion, with the authors commenting on the rather slight effect that a silver ion generally has on its complexed π bond. One may therefore conclude that the 138° torsional angle in *trans*-cyclodecene is either an error or a result of appreciable crystal packing forces.

XV

chair



twist

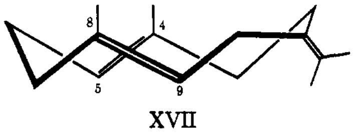


XVI

ω 10–1–2–3 = 164°

ω 11–1–2–12 = 179°

ω 10–1–2–12 = 7°

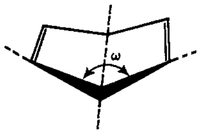


XVII

As in the smaller *trans*-cyclenes, although to a lesser extent, our calculated bond is rehybridized rather than simply being twisted. The resulting 0.06 D dipole moment calculated for *trans*-cyclodecene is in agreement with the 0.15 ± (0.06–0.17) D experimental value.[56] Our calculated heat of hydrogenation is 1.29 kcal/mol lower than the acetic acid value.

Nonconjugated dienes were studied with the same force field and heat of formation calculations. A calculation on 1,4-pentadiene gave a heat of formation of 25.51 kcal/mol, in agreement with the experimental value of 25.41 kcal/mol.[11]

We next studied 1,4-cyclohexadiene, since contradictory electron diffraction structures have recently been published. Oberhammer and Bauer[57] report a folded structure (XVIII) with double bond lengths of 1.347 Å. Dallinga and Toneman,[58] considering planar, boat, chair, and skew forms, concluded that the molecule was planar with probably some chair deformations. The deviations from planarity were extremely small, amounting to 0.02–0.03 Å. Their double bond length (1.334 ± 0.002 Å) is somewhat shorter than that of the other diffraction structure and is consistent with the normal olefinic value. From allylic–allylic proton coupling constants, Garbisch[59] has deduced a near planar conformation for this molecule, a conclusion which is also supported by the vibrational[60] and rotational[61] spectra. Our calculations find the planar form at the energy minimum of a shallow boat-boat inversion potential. This potential, illustrated in Figure 9, indicates that the molecule is planar on the average, but is oscillating between boat forms. Our calculated planar geometry agrees with the latter diffraction structure except for our longer C_{sp^3}–C_{sp^2} bond length of 1.507 Å (1.496 ± 0.001 Å expt). The calculated heat of formation (24.22 kcal/mol) is somewhat lower than the 26.3 kcal/mol experimental value,[11] but inaccuracy in the latter may be responsible for much of this difference.



XVIII

ω (angle between planes) = 159.3°

Lord has concluded from vibrational spectra[62] that the molecule has an energy minimum at the planar form, but the molecule shows a wide amplitude vibra-

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[53] J. D. Dunitz, *Helv. Chim. Acta*, 50, 2379 (1967).

[54] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967, p 531.

[55] F. H. Allen and D. Rogers, *J. Chem. Soc. B*, 247 (1971).

[56] N. L. Allinger, *J. Amer. Chem. Soc.*, 79, 3443 (1957).

[57] H. Oberhammer and S. Bauer, *ibid.*, 91, 10 (1969).

[58] G. Dallinga and L. H. Toneman, *J. Mol. Struct.*, 1, 117 (1967).

[59] E. W. Garbisch and M. G. Griffith, *J. Amer. Chem. Soc.*, 90, 3590 (1968).

[60] H. D. Stidham, *Spectrochim. Acta*, 21, 23 (1965).

[61] B. J. Monostori and A. Weber, *J. Mol. Spectrosc.*, 12, 129 (1964).

[62] R. C. Lord, personal communication, 1971.

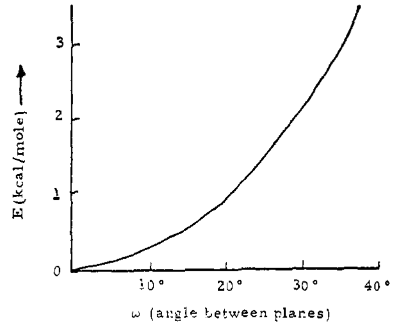
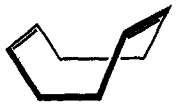


Figure 9. 1,4-Cyclohexadiene inversion potential.

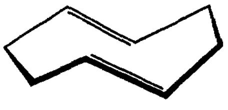
tion to boat forms, just as we calculate. The puckered form of Bauer was apparently deduced without realizing that many of the rms distances are necessarily shorter in the vibrating molecule, as they would also be in the puckered form.[62]

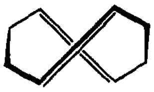
Although little experimental data are available for comparison, several medium ring dienes were studied. We found the chair form of *cis,cis*-1,5-cyclooctadiene to be favored over the boat by 1.79 kcal/mol with a calculated heat of hydrogenation of 31.80 kcal/mol for the first double bond. This conformational preference is



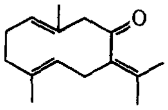
contradictory to a previous calculation of Pauncz and Ginsburg[36] which favored the boat by 0.51 kcal/mol.

For the trans,trans isomer of 1,5-cyclooctadiene, a chair and twist form were calculated with the latter favored by 5.35 kcal/mol. The double bonds are de-





formed to an extent somewhere between *trans*-cycloheptene and *trans*-cyclooctene with a C–C=C–C dihedral angle of 140°. The calculated heat of hydrogenation for the first double bond is 39.47 kcal/mol, a value indicating considerable strain in the diene ring. The only structural information available for this molecule is a uv spectrum[63] which shows λ_{max} 246 mμ (ϵ ~1500). This unusual absorption probably owes its low energy to the proximity of the π orbitals of the double bonds. The anomalous absorption of germacrone (XIX) at 213 mμ (ϵ ~12,600)[64] provides a precedent since the X-ray structure[55] of the parent hydrocarbon, germacratriene (XVII), shows the endo double bonds to be crossed, just as in our calculated *trans,trans*-1,5-cyclooctadiene structure.



XIX

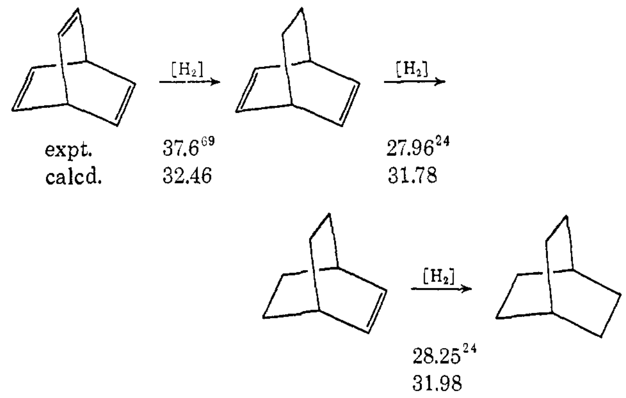
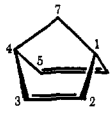


Figure 10. Heats of hydrogenation of bicyclo[2.2.2]octatriene.

A few bicyclic systems were studied, but the lack of good experimental data allows few conclusions to be drawn concerning the validity of our model for such systems. The heat of hydrogenation of norbornene was calculated to be 34.10 kcal/mol which agrees with the value in acetic acid of 33.13 kcal/mol.[24] The double bond length is calculated to be 1.335 Å and the C_{sp^3}–C_{sp^2} length is 1.514 Å.

The first double bond in norbornadiene (XX) has a



XX

calculated heat of hydrogenation of 35.30 kcal/mol compared to a 34.98 kcal/mol solution value.[24] A lot of experimental work has been done on the structure of norbornadiene, but the results are so contradictory that in a recent electron diffraction study, Dallinga and Toneman[65] were forced to conclude that the best structure is probably the average of all experimental structures. The electron diffraction double bond length (C_2–C_3) ranges from 1.333 ± 0.008[66] to 1.357 ± 0.005[67] while the C_{sp^3}–C_{sp^2} length (C_1–C_2) varies from 1.522 ± 0.022[66] to 1.554 ± 0.002.[65] The largest variation is the C_{sp^3}–C_{sp^3} (C_1–C_7) length which has the extreme values of 1.514 ± 0.004[65] and 1.573 ± 0.010.[68] Our calculated values for these three bond lengths are 1.339, 1.517, and 1.541 Å. The 1–7–4 angle is calculated to be 93.7° which is within experimental error of most of the structures.

Heats for the stepwise hydrogenation of bicyclo[2.2.2]octatriene were calculated and the results are quite different from the experimental solution values (see Figure 10).

The total heat of hydrogenation of the triene measured experimentally (93.8 kcal/mol[69]), when corrected to the gas phase (96.8 kcal/mol), gives a value with which the calculated heat of hydrogenation (96.22 kcal/mol) agrees quite well. However, the calculated heats of hydro-

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(63) G. M. Whitesides, G. L. Goe, and A. C. Cope, *J. Amer. Chem. Soc.*, **89**, 7136 (1967).

(64) F. Sorm, *Pure Appl. Chem.*, **2**, 533 (1961).

(65) G. Dallinga and L. H. Toneman, *Recl. Trav. Chim. Pays-Bas*, **87**, 805 (1968).

(66) V. Schoemaker and W. Hamilton, mentioned by W. G. Woods, R. A. Carboni, and J. D. Roberts, *J. Amer. Chem. Soc.*, **78**, 5653 (1956).

(67) T. W. Muecke and M. I. Davis, *Trans. Amer. Crystallogr., Ass*, **2**, 173 (1966).

(68) Y. Morino, K. Kuchitsu, and A. Yokozeki, *Bull. Chem. Soc. Jap.*, **40**, 1552 (1967).

(69) R. B. Turner, *J. Amer. Chem. Soc.*, **86**, 3586 (1964).

genation for the individual double bonds do not agree at all with those found experimentally. Such deviations are of great interest, of course, because they suggest substantial inadequacies of our force field, or errors in the experimental data.

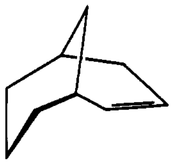
We note that the calculated heats of hydrogenation for the mono- and diolefins are each too high by about 2 kcal (corrected to the gas phase). This means these molecules actually contain less strain energy than we calculate. The angle bending strain and torsional strain seem clearly to be present, so that we find the disagreement between calculation and experiment very puzzling. Initially we felt the problem was experimental error, but recently an independent determination of the heat of formation of the monoolefin[70] has given the value in good agreement with that derived from the heat of hydrogenation, so that it seems that it is in fact the calculation that is in error.

The unusually large heat of hydrogenation determined experimentally for the triene has been viewed as due to "antiaromaticity."[71] The latter term is one which is accompanied with some misunderstanding on the part of many chemists. A compound is said to be "antiaromatic" if the heat of formation of the compound is more positive than that of the corresponding open chain polyene. In other words, the closing of an open chain polyene to a cyclic polyene may be accompanied by a lowering of energy (aromatic), or an increase in energy (antiaromatic). This does not mean that putting together the individual unsaturated fragments is unfavorable in the case of an antiaromatic compound, only that putting them together in that particular way is less favorable than putting them together in the form of a polyene. From this view, the triene would be antiaromatic, but would not necessarily show a heat of hydrogenation which was any larger than would be expected for a simple unconjugated triene.

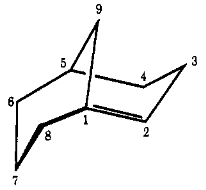
Recently, Goldstein and Hoffman[71b] have pointed out that if one includes overlap in an SCF calculation, bringing together three olefinic fragments as they are in the triene will lead to an increase in ground state energy, not just a lack of decrease in ground state energy, relative to the three isolated double bonds. This means that calculations which neglect overlap lead to results which are in doubt in such cases. However, it may be that there are compensating changes in the other orbitals in the system which were not considered in the simple treatment, and to really understand a molecule such as this, it would appear that an *ab initio* calculation will be necessary. In any event, it is tempting to ascribe the excess heat of hydrogenation of the triene to antiaromaticity, and unless there are some compensating changes in the rest of the system, we would not expect this "antiaromaticity" to show up in the molecular mechanics calculations.

Until more experimental data are available for comparison, we are not certain where the difficulty lies with these molecules, nor what should be done about it. We note that norbornadiene, an even more strained diene than the one under present consideration, has a calculated heat of formation in good agreement with experiment. We suspect a difficulty may arise from the unusual van der Waals interactions between carbon, which are a function of hybridization in our calculation. The interactions between carbon atoms are very different in these cage compounds from what they are in most other organic structures, since the carbons are actually very close together, not separated by hydrogens. Replacing the van der Waals potential function for the olefinic carbons with a more highly parameterized nonspherical potential would probably bring the calculations into better agreement with experiment, but we have not chosen to do so because of the lack of sufficient experimental data to really justify such an approach.

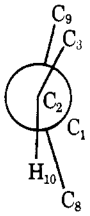
Bicyclo[3.3.1]nonene is an interesting system in that there are two reasonable possibilities for the location of the double bond, XXI and XXII, the latter being a bridgehead position. This bridgehead isomer, which has only recently been synthesized,[72,73] is of interest because it violates Bredt's rule. Our calculated heats of hydrogenation for these two molecules are 25.37 and 38.23 kcal/mol, respectively, with 12.85 kcal/mol difference representing the additional strain of the bridgehead position. This value is in agreement with a 12 kcal/mol estimated strain for the bridgehead bond based on the reaction of bicyclo[3.3.1]non-1-ene with acetic acid.[74] The bridgehead double bond (XXIII) is rehybridized to only a slightly greater extent than the *trans*-cyclooctene double bond and it would require a considerable amount of energy to completely disrupt it. The validity of Bredt's rule thus rests on a sizable energy difference (of the order of 10 kcal/mol), but one which can be overcome if the technical details can be arranged.



XXI



XXII



XXIII

ω 8–1–2–3 = 138°

ω 9–1–2–3 = 3°

ω 8–1–2–10 = 17°

ω 9–1–2–10 = 158°

Strain Energy

Throughout this work we have used calculated heats of formation in comparing the energies of isomeric alkenes. In order to allow comparisons for molecules which are not isomers, "strain energies" are required; consequently, we have extended the set of hydrocarbon

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[70] S. Wong and E. F. Westrum, Jr., *J. Amer. Chem. Soc.*, **93**, 5317 (1971).

[71] (a) E. Haselbach, E. Heilbronner, and G. Schroeder, *Helv. Chim. Acta*, **54**, 153 (1971); (b) M. J. Goldstein and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 6193 (1971).

[72] J. A. Marshall and H. Faubl, *ibid.*, **92**, 948 (1970).

[73] J. R. Wiseman and W. A. Pletcher, *ibid.*, **92**, 956 (1970).

[74] P. M. Lesco and R. B. Turner *ibid.*, **90**, 6888 (1968).

strain energies developed earlier[5,6] so as to include alkenes. The additional "strainless" enthalpy increments required for these calculations are listed in Table VII. Ethylene, propene, and isobutene were taken as the strainless reference compounds.

Table VII. Strainless Bond Enthalpy Increments

C_{sp^3}–C_{sp^3}	3.75[a]	Iso (C_{sp^3})	−3.31[a]
C_{sp^3}–C_{sp^2}	−0.43	Iso (C_{sp^2})	−1.28
C_{sp^2}=C_{sp^2}	30.50	Neo	−7.78[a]
C–H (all)	−4.47[a]	Methyl group	1.55[a]

[a] Obtained from ref 5.

The results of these calculations are listed in Table VII, and as expected, the cyclohexenes and most of the noncyclic molecules have low strain energies while the medium ring *trans*-cyclenes and the bicyclics are usually quite strained.

Table VIII. Strain Energies

	ΔH_f^s (strainless)	ΔH_f° (calcd)	Strain energy
Ethylene	12.62	12.62	0.0
Propene	4.80	4.80	0.0
1-Butene	−0.39	0.48	0.87
cis-2-Butene	−3.02	−1.81	1.21
trans-2-Butene	−3.02	−2.97	0.05
Isobutene	−4.30	−4.30	0.0
cis-2-Pentene	−8.21	−6.46	1.75
trans-2-Pentene	−8.21	−7.31	0.90
2-Methyl-2-butene	−12.12	−10.52	1.60
2-Methyl-2-pentene	−17.31	−15.38	1.93
2,3-Dimethyl-2-butene	−21.22	−16.62	4.60
cis-Di-*tert*-butylethylene	−43.52	−27.15	16.37
trans-Di-*tert*-butylethylene	−43.52	−37.51	6.01
Cyclopentene	1.38	8.31	6.93
Methylenecyclopentane	−5.09	3.58	8.67
Methylcyclopentene	−7.72	−1.14	6.58
Cyclohexene	−3.81	−1.20	2.61
Methylenecyclohexane	−10.28	−7.52	2.76
Methylcyclohexene	−12.91	−10.23	2.68
3-Methylcyclohexene	−10.76	−7.32	3.44
4-Methylcyclohexene	−10.76	−8.33	2.43
cis-Cycloheptene	−9.00	−1.65	7.35
trans-Cycloheptene	−9.00	18.67	27.67
cis-Cyclooctene	−14.19	−5.38	8.81
trans-Cyclooctene	−14.19	3.66	17.85
cis-Cyclodecene	−24.57	−12.94	11.63
trans-Cyclodecene	−24.57	−12.62	11.95
Norbornene	−2.93	20.69	23.62
Norbornadiene	24.40	55.99	31.59
Bicyclo[2.2.2]octene	−8.12	7.87	15.99
Bicyclo[2.2.2]octadiene	19.21	39.65	20.44
Bicyclo[2.2.2]octatriene	46.54	72.11	25.57
Bicyclo[3.3.1]non-1-ene	−15.46	7.94	23.40
Bicyclo[3.3.1]non-2-ene	−13.31	−6.72	6.59
1,4-Pentadiene	24.38	25.51	1.13
1,4-Cyclohexadiene	23.52	24.22	0.70
1,4-Dimethylenecyclohexane	10.58	14.99	4.41
cis,cis-1,5-Cyclooctadiene	13.14	26.42	13.28
trans,trans-1,5-Cyclooctadiene	13.14	40.96	27.82
cis,cis-1,6-Cyclodecadiene	2.76	8.78	6.02

In Table IX are listed the strain energy differences between the alkenes and corresponding alkanes. These numbers are interesting in that they represent the change in strain energy of a molecule as the C_{sp^2}=C_{sp^2} linkage is replaced by C_{sp^3}–C_{sp^3} and can be useful in understanding and predicting the effect of steric energy on chemical reactions in which these linkages are interconverted.

Table IX. Strain Energy Differences (Alkene Minus Alkane)

Alkene	Alkene strain energy	Alkane[a] strain energy	Difference (alkene − alkane)
cis-Di-*tert*-butylethylene	16.37	6.55	9.82
trans-Di-*tert*-butylethylene	6.01	6.55	−0.54
Cyclopentene	6.93	7.53	−0.60
Cyclohexene	2.61	1.75	0.86
cis-Cycloheptene	7.35	8.04	−0.69
trans-Cycloheptene	27.67	8.04	19.63
cis-Cyclooctene	8.81	11.52	−2.71
trans-Cyclooctene	17.85	11.52	6.33
cis-Cyclodecene	10.27	15.68	−5.41
trans-Cyclodecene	11.63	15.68	−4.05
Norbornene	23.62	17.90	5.72
Bicyclo[2.2.2]octene	15.99	11.69	4.30
Bicyclo[3.3.1]non-1-ene	25.25	10.35	14.90
Bicyclo[3.3.1]non-2-ene	6.61	10.35	−3.74

[a] Obtained from ref 5.

A few of these numbers are perhaps worthy of comment. Note that in Table VIII, methylcyclohexene has about the same strain energy as methylenecyclohexane. The difference in stability between these two compounds is a result of one being disubstituted and one trisubstituted, not a result of strain. On the other hand, methylenecyclopentane is more strained by roughly 2 kcal/mol than is methylcyclopentene. The extra strain in the former case comes mostly from the fact that the methylene groups attached to the olefinic carbon have the hydrogens staggered with respect to the double bond, and this corresponds to a torsionally excited arrangement, as the hydrogens would ordinarily want to eclipse the double bond, but cannot because of the constraints brought about by the ring.

The strain in *trans*-cycloheptene is 27.7 kcal/mol, a very large number, sufficient to prevent the easy isolation of the compound. *trans*-Cyclooctene, a highly reactive olefin, by way of comparison has 17.9 kcal/mol of strain energy. Norbornene and norbornadiene have very large strain energies, and are quite reactive compounds. They cannot undergo isomerization of the cis–trans type, as *trans*-cycloheptene does, so they are stable and isolable, even though the latter has more strain energy than does *trans*-cycloheptene.

Bicyclo[3.3.1]non-2-ene contains a moderate amount (6.6 kcal) of strain, whereas the 1 isomer, which violates Bredt's rule, contains some 23 kcal of strain. The latter compound has been isolated, and would seem to owe its isolability to the fact that it is not possible for it to isomerize to another geometric isomer, and migration of the double bond requires too great an activation energy unless the reaction is catalyzed. Note that this compound has less strain than does norbornadiene, a reactive but perfectly isolable material. These numbers, if available at an earlier time, would have led to the prediction that bicyclo[3.3.1]non-1-ene should be an isolable compound.

trans,trans-1,5-Cyclooctadiene is highly strained, and like *trans*-cycloheptene, can relieve its strain to a large extent if it isomerizes to the cis,cis isomer. Since we have not calculated the energy of the transition state, we cannot be certain, but it seems likely that the compound would not be stable at room temperature, but would spontaneously isomerize one or both of the linkages to the cis configuration.

Looking at Table IX, we see that *trans*-di-*tert*-butylethylene is essentially strainless relative to the saturated hydrocarbon, and we could predict the heat of hydrogenation should be normal, while that for the cis isomer should be some 9.8 kcal above the normal strainless value. With cyclohexene, the alkene is slightly more strained than the alkane, while for the five-membered ring the reverse situation is true, the alkane is slightly more strained. In the latter case the alkene has unfavorable bond angles, and angular strain which is worse than what is found in the alkane, but the torsional energy from eclipsing in the alkane is worse in the alkane than in the alkene, and by a larger amount, so the numbers are as found. The heat of hydrogenation of cyclopentene is thus rather small and similarly for *cis*-cycloheptene. For *cis*-cyclooctene and *cis*-cyclodecene, the same situation prevails qualitatively, but the numbers become increasingly large. This is because the torsional situation and the congestion in the larger ring alkanes become increasingly severe, and the double bond helps to relieve the situation. For the *trans*-cycloalkenes, the situation is quite different. For *trans*-cyclodecene, the alkene, by relieving torsional strain mostly, is less strained than the cycloalkane by 4.1 kcal, and so the heat of hydrogenation would be small. As the ring size of the cycloalkene gets smaller, the torsional strain about the double bond becomes rapidly very severe, so that we see *trans*-cyclooctene has 6.3 kcal of strain more than does the saturated hydrocarbon, while for *trans*-cycloheptene, the number is 19.6 kcal/mol. The remaining numbers in Tables VIII and IX are similarly capable of yielding predictions and/or interpretations of experimental facts.

Conclusions

The force field and minimization scheme described above is capable of supplying structures and energies for a variety of olefins in good agreement with available experimental data. As with any empirical scheme, however, the results can be no more reliable than the accuracy and diversity of the data used to generate the model. For olefins, good structural and thermodynamic information is available only for small acyclic molecules and a very limited number of cyclics; consequently, while all of our calculated data seem qualitatively correct, it is felt to be quantitative only for relatively unstrained systems. It should also be noted that the calculations reported here are not intended to be a compendium of olefin structures, but rather an example, verified where possible, of the utility of the method.

One of the strong points of the program is its ability to study in detail the conformational mobility of a given molecule with particular emphasis on π-bond deformations. This was done, to some extent, for cycloheptene with the implication that most any other system could be similarly studied. An important restriction, however, is that while the program will successfully locate minima on the potential energy surface, saddle points, corresponding to transition states between stable conformations are located only by restricting certain degrees of freedom, r, for the molecule such that the n dimensional saddle point becomes an $(n - r)$ dimensional potential well. Since these restrictions are based on an examination of models along with a certain amount of intuition, our calculated activation enthalpies are subject to a somewhat greater error than is associated with other calculations. The method is also well suited to studies of double bond hybridization and stability as a function of geometrical or steric constraints, such as the trends found in the medium ring *trans*-cyclenes. Such information may be useful in quantitatively explaining and predicting olefin reactivity.

A Test For "Intimacy" in Organic Ion-Pair Transition States by Evaluation of Solvent Electrostriction

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Abstract: Volumes of activation have been determined separately for solvolysis and ion-pair return with rearrangement in benzhydryl thiocyanate and *trans*-α-phenyl-γ-methyallyl *p*-nitrobenzoate. The difference indicates that electrostriction of solvent is only 1–4 ml greater for the solvolytic transition states than for the rearrangement transition states. Both sets of ion-pair transition states cause nearly as much contraction as ordinary ionization reactions for which values of 20–40 ml are commonly observed. The sensitivity of solvent electrostriction to charge separation has been demonstrated by comparison of the partial molar volumes of isomeric hydroxytrimethylanilinium hydroxide inner salts to those of some uncharged structural isomers.

Twenty years ago Winstein and his coworkers[1] reported the first of a long series of studies of solvolytic reactions in which by-products which are isomers of the starting material arise presumably by return from a partially ionized state which has been called the "intimate" ion pair. The kinds of isomerization now

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[1] W. G. Young, S. Winstein, and H. L. Goering, *J. Amer. Chem. Soc.*, 73, 1958 (1951).