The Conformations and Structures of Cyclodecane as Determined by Electron Diffraction and Molecular Mechanics Calculations

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Abstract: An attempt has been made to refine electron diffraction data collected at 130° for cyclodecane in terms of a simplified boat-chair-boat (BCB) model of C_{2h} symmetry. The resulting structural parameters were: $r_g(\text{C–C})_{av} = 1.545 \pm 0.003$ Å, $r_g(\text{C–H})_{av} = 1.115 \pm 0.003$ Å, $\angle\text{CCH(av)} = 108.7 \pm 1.0°$, $\angle C_{10}C_1C_2 = 114.6 \pm 1.2°$, and $\angle C_1C_2C_3 = \angle C_2C_3C_4 = 116.9 \pm 0.9°$. The resolution factors for the short and long camera distances were 0.99 and 0.97, respectively. It is readily conceivable that the excellence of the fit of this model is fortuitous and misleading, however, since electron diffraction analyses rarely yield a unique structure for a molecule of this size and flexibility. An alternative analytical approach has been adopted in which detailed structures and selected thermodynamic properties have been calculated for 12 stable conformations of cyclodecane. Theoretical radial distribution curves have been generated for the four conformations of lowest energy. Least-squares analysis of the experimental radial distribution curve utilizing the four theoretical curves has indicated the following composition: BCB 49 ± 3%, twist-boat-chair (TBC) 35 ± 3%, TBCC 8 ± 4%, and BCC 8 ± 4%. The two methods of analysis have been critically discussed, particularly from the point of view of the analysis of multiconformational molecules of cyclodecane's complexity.

The conformations, detailed structures, and chemical reactions of monocyclic alkanes have occupied the interest of organic, biological, and structural chemists for almost 100 yr. A host of physical methods and structure reactivity studies have provided significant information regarding these topics.[2]

Electron diffraction has played an important role in determining the structures of small and common sized ring systems such as cyclopropane,[3] cyclobutane,[4] cyclopentane,[4a,5] and cyclohexane;[6] the amount of useful information that has been obtained for monocyclic systems containing more than six carbon atoms has been very limited,[7] however.

The problems encountered in the study of medium sized rings are exemplified by the attempts of Almenningen, Bastiansen, and Jensen[7] to determine the structure of cyclooctane. None of the models that they tried for the C_8 ring system were found to be consistent with the experimental data; they were forced to conclude that the vapor phase of cyclooctane at 40° was composed of a mixture of several conformations. Nuclear magnetic resonance studies in solution strongly support this view.[8]

The multiplicity of stable conformations which medium sized cycloalkanes can assume and the equilibrium distribution among these conformations pose two formidable problems for potential electron diffraction analyses. On the other hand, the major impetus for undertaking a structural study on a system of this type is to identify the significant conformations and their relative stabilities. At the present most of our knowledge concerning the structures and conformations of the larger cycloalkanes is derived from X-ray diffraction,[2,9] nuclear magnetic resonance spectroscopy,[8,10] and a variety of less general methods.[2]

During the past decade, molecular mechanics calculations[11] have become increasingly effective in predicting complete conformational analyses and precise structural parameters for both cyclic and acyclic hydrocarbons.[12] The molecular mechanics method consists essentially of a classical calculation of the relative strain energies of various molecular conformations in terms of bond elongation and contraction, bond angle bending (Bayer), torsional strain (Pitzer), and nonbonded atomic interactions.[12] Although the number of studies employing this technique is too numerous to mention here, some of the more relevant contributions regarding cycloalkanes have been made by Hendrickson,[13–16]

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[1] (a) North Dakota State University; (b) Indiana University.

[2] See, for example, E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1966, Chapter 3.

[3] (a) O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, **17**, 538 (1964); (b) A. Almenningen, O. Bastiansen, S. J. Cyvin, and P. N. Skancke, *Acta Chem. Scand.*, **14**, 959 (1960); O. Bastiansen and S. J. Cyvin, *ibid.*, **11**, 1789 (1957).

[4] (a) A. Almenningen, O. Bastiansen, and P. N. Skancke, *Acta Chem. Scand.*, **15**, 711 (1961); (b) J. D. Dunitz and V. Schomaker, *J. Chem. Phys.*, 20, 1703 (1952).

[5] W. J. Adams, H. J. Geise, and L. S. Bartell, *J. Amer. Chem. Soc.*, **92**, 5013 (1970).

[6] (a) O. Bastiansen, L. Fernholt, H. M. Seip, Hideki Kambara, and Kozo Kuchitsu, private communication; (b) H. J. Geise, H. R. Buys, and F. C. Mijhoff, *J. Mol. Struct.*, **9**, 447 (1971); (c) M. Davis and O. Hassel, *Acta Chem. Scand.*, **17**, 1181 (1963).

[7] A. Almenningen, O. Bastiansen, and H. Jensen, *Acta Chem. Scand.*, 20, 2689 (1966).

[8] (a) J. E. Anderson, E. S. Glazer, D. L. Griffith, R. Knorr, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 1386 (1969); (b) F. A. L. Anet and M. St. Jacques, *ibid.*, **88**, 2585, 2586 (1966).

[9] J. D. Dunitz, "Perspectives in Structural Chemistry," Vol. II, J. D. Dunitz and J. A. Ibers, Ed., Wiley, New York, N. Y., 1968.

[10] T. M. Ivanova and G. P. Kugatova-Shemyaka, *Russ. Chem. Rev.*, **39** (6), 510 (1970).

[11] F. H. Westheimer, "Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 12.

[12] J. E. Williams, P. J. Stang, and P. v. R. Schleyer, *Annu. Rev. Phys. Chem.*, **19**, 531 (1968).

[13] J. B. Hendrickson, *J. Amer. Chem. Soc.*, **86**, 4854 (1964).

[14] J. B. Hendrickson, *J. Amer. Chem. Soc.*, **89**, 7036 (1967).

[15] J. B. Hendrickson, *J. Amer. Chem. Soc.*, **89**, 7043 (1967).

[16] J. B. Hendrickson, *J. Amer. Chem. Soc.*, **89**, 7047 (1967).

Wiberg,[17] Allinger,[18] Bixon and Lifson,[19] Dunitz, *et al.*,[20] and Lifson and Warshel.[21] Hendrickson,[16] in particular, has been instrumental in devising a convenient symbolic notation which is helpful in determining the number of possible conformations with at least one symmetry element.

Hendrickson[16] reports 12 conformations possessing varying degrees of strain for cyclodecane. Of these proposed conformations, the so called boat-chair-boat (BCB)[22] model is consistently predicted to be the most stable form of the C_{10} ring. These theoretical predictions are in accord with the extensive body of experimental data regarding the solid state structures of substituted cyclodecanes compiled by Dunitz and coworkers.[9] In all but one of the substituted cyclodecanes studied, they found only the BCB conformation to be present. The one exception, 1,1,5,5-tetramethylcyclodecane-8-carboxylic acid, has been interpreted in terms of a mixture of about 80% twist-boat-chair (TBC) and 20% twist-boat-chair-chair (TBCC) conformations. These experimental data seem to indicate that the two latter conformations may be only slightly less stable than the preferred BCB conformation.

An electron diffraction structure determination of cyclodecane was undertaken for several reasons. First, it appeared from structural studies (X-ray crystallographic data in this case) that cyclodecane might exist principally in a single conformation. Since crystal packing forces are known to markedly affect conformational changes in going from the gas phase or the liquid phase to the solid state,[23] an interesting structural comparison would also be provided. Moreover, the X-ray and electron diffraction data could be compared and contrasted with molecular mechanics calculations. Most interestingly, however, there are numerable ways in which molecular mechanics calculations might facilitate, complement, extend, and corroborate electron diffraction investigations, particularly when more than one stable conformation is present. It was a primary purpose of this work to more thoroughly examine the potential or molecular mechanics calculations in these respects.

Experimental Section

The cyclodecane (greater than 99% purity) was obtained from the Chemical Samples Co. of Columbus, Ohio, and was used without further purification. The purity of the sample was verified by infrared, ultraviolet, and nuclear magnetic resonance spectroscopy. Several judiciously selected high resolution gas chromatography columns were also used to check the purity. The diffraction patterns were obtained on the Indiana University electron diffraction unit using a 40 keV accelerating potential and an r^3 sector. The sample was introduced into the instrument through a heated inlet system at approximately 130° measured at the nozzle tip. Exposures ranging from 1-3 min for the 12-cm distance and 1-2 min for the 29-cm distance gave patterns in the desired density range for the 0.5-μA beam current used. During the exposures the measured background pressure was maintained at 5×10^{-5} Torr with a liquid nitrogen trap situated opposite the nozzle jet. Nozzle to plate distances were measured with a cathetometer, and the high voltage was measured using a calibrated voltage divider and precision differential voltmeter. This calibration procedure is frequently checked using as a primary standard the C–O distance in CO_2 (r_α = 1.1646 Å).

The Kodak 4 × 5 in. electron image plates were developed according to the procedure described by Foster[24] and microphotometered on the Indiana University automated single beam microdensitometer. The data were interpolated at integral q ($\pi s/10$) intervals after making appropriate corrections for sector imperfections, emulsion saturation, and plate flatness. The data from three short distance plates and two long distance plates were averaged and spliced together in the least-squares analysis.

In the preliminary refinements on the assumed BCB model, the conventional least-squares techniques were used as described previously.[25] Tables of raw density data and Cartesian coordinates of the molecular mechanics energy minimization models considered (*vide infra*) are available.[26]

Results and Discussion

The BCB Analysis. In light of the complications one might expect to encounter in an investigation of this complexity, it is worthwhile to note at the outset the nature of the information we might hope to gain by applying the gas phase electron diffraction technique. In the very minimum it should be possible to obtain information regarding certain parameters associated with the ring such as average C–C and C–H bond lengths and average values for the $\angle$HCH and $\angle$CCC valence angles. However, equality among these parameters is only dictated by symmetry in the rather unstable "crown" conformation[16] for the molecule. Thus, although we can expect reliable estimates of average ring parameters, it is unlikely that the analysis will reveal the subtle splittings in these parameters in the lower symmetry conformations expected to be present.

In view of the X-ray crystallographic studies on cyclodecane, it was decided to attempt a refinement of the data in terms of a simplified BCB model alone. The results of such an analysis might serve several useful purposes. If the BCB conformation were present with a mole fraction of 0.90 or greater, then the structure obtained would be a reasonable estimate of this predominant species. Even if this were not the case, any model which can be made to fit the experimental data would be useful in obtaining the best least-squares estimates of the average ring parameters.

The following simplified BCB model was used for this preliminary analysis: (1) all C–C bond lengths were constrained to a common value; (2) all C–H bond lengths were constrained to be equal; (3) all $\angle$CCH valence angles were constrained to be equal, thus making the plane of the $\angle$HCH angle the perpendicular bisector of the $\angle$CCC valence angle to which it is attached. The $\angle$CCC valence angles were permitted to vary during the refinement; however, after several least-squares iterations two of the angles, $\angle C_1C_2C_3$ and $\angle C_2C_3C_4$, became nearly degenerate. Accordingly, they were constrained to be equal for the remainder of the analysis.

The coordinates for this model were programmed using a variation of a standard coordinate calculating routine[27] which permitted the use of nonbonded dis-

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[17] K. B. Wiberg, *J. Amer. Chem. Soc.*, **87**, 1070 (1965).

[18] N. L. Allinger, J. A. Hirsch, M. A. Miller, I. Tyminski, and F. A. Van-Catledge, *J. Amer. Chem. Soc.*, 90, 1199 (1968).

[19] M. Bixon and S. Lifson, *Tetrahedron*, 23, 769 (1966).

[20] J. D. Dunitz, H. Eser, M. Bixon, and S. Lifson, *Helv. Chim. Acta*, 50, 1572 (1967).

[21] S. Lifson and A. Warshel, *J. Chem. Phys.*, **49**, 5116 (1968).

[22] Throughout this manuscript the convenient conformational notations of Hendrickson have been used. The notations and the conformations they refer to are shown in Figure 4.

[23] See, for example, ref 2, p 31.

[24] H. R. Foster, *J. Appl. Phys.*, **41**, 5344 (1970).

[25] R. L. Hilderbrandt and J. D. Wieser, *J. Chem. Phys.*, **55**, 4648 (1971).

[26] See the paragraph at the end of the paper regarding supplementary material.

[27] R. L. Hilderbrandt, *J. Chem. Phys.*, **51**, 1654 (1969).

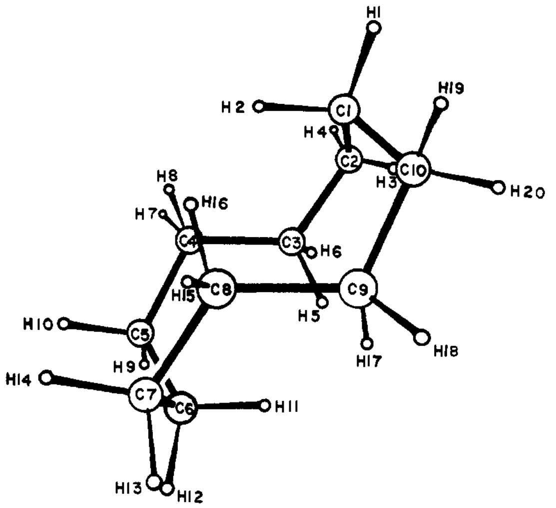

Figure 1. The numbering used in defining the parameters for the BCB model of cyclodecane.

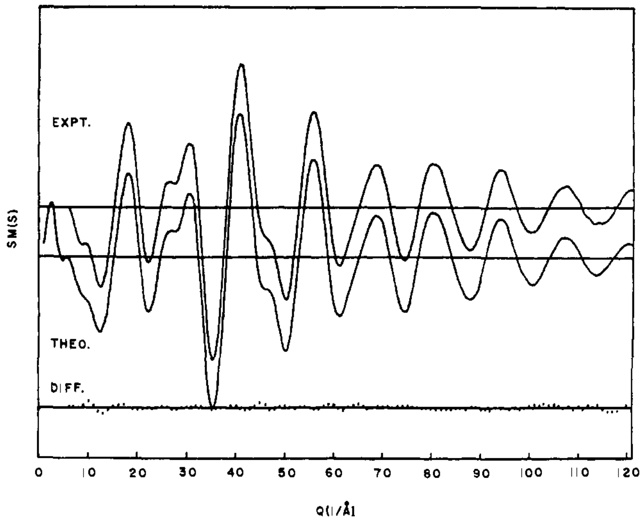

Figure 2. A comparison of the experimental leveled intensity curve for cyclodecane with the intensity curve for the least-squares adjusted BCB model.

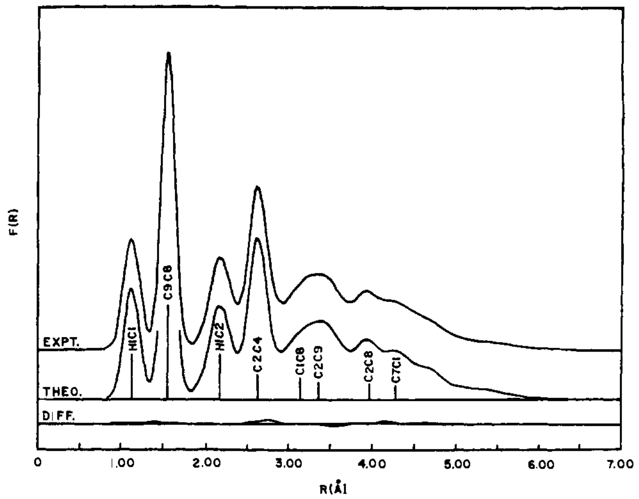

Figure 3. A comparison of the experimental radial distribution curve for cyclodecane with the theoretical radial distribution curve for the least-squares BCB model.

Table I. Structural Parameters for the BCB Conformation Obtained from the Preliminary Least-Squares Analysis[a]

Parameter	Value[b]	X-Ray av values[c]
C–C (av)	1.545 ± 0.003 Å	1.531 Å
C–H (av)	1.115 ± 0.003 Å	
$\angle C_{10}C_1C_2$	114.6 ± 1.2°	118.0°
$\angle C_1C_2C_3$	116.9 ± 0.9°	118.1°
$\angle C_2C_3C_4$	116.9 ± 0.9°	114.7°
∠CCC (av)	116.1 ± 1.1°	116.7°
∠CCH (av)	108.7 ± 1.0°	
τ $C_{10}C_1C_2C_3$	77.2 ± 1.8°	66°
τ $C_1C_2C_3C_4$	48.5 ± 1.5°	55°
τ $C_2C_3C_4C_5$	144.2 ± 2.1°	152°
l (C–H)	0.078 ± 0.002 Å	
l (C–C)	0.054 ± 0.002 Å	
l (C···H) gem	0.112 ± 0.006 Å	
l (C···C) gem	0.089 ± 0.005 Å	

[a] The numbering of the atoms used in defining the parameters is given in Figure 1. [b] Uncertainties in quoted r_g parameters are at the 99% confidence level. [c] Average results of four X-ray diffraction studies on substituted cyclodecanes; see ref 9.

tances as well as angles and bond lengths in the calculations. Through the use of this variation and the symmetry of the model (the reflection plane), it was possible to ensure ring closure and maintain C_{2h} symmetry during the refinements. This method also afforded some choice in nonbonded distances to be used as independent parameters; these quite naturally were chosen to correspond to prominent peaks in the radial distribution curve.

Mean-square amplitudes of vibration for the model were calculated from the Urey–Bradley force field for alkanes obtained by Schachtschneider and Snyder.[28] These calculations were performed using a specially adapted version of the program described previously[25] to handle the 100 internal coordinates necessary for the computation. All but a few of the mean-square amplitudes were constrained (see Table I) to their calculated values during the least-squares refinement.

Somewhat unexpectedly, the least-squares analysis of the intensity curve of this simplified BCB model converged to give excellent agreement with the experimental data. Resolution factors obtained in this analysis were 0.99 and 0.97 for the long and short camera distances, respectively. Structural parameters obtained from this preliminary investigation are listed in Table I, and the intensity curves and radial distribution curves are shown in Figures 2 and 3, respectively. Figure 1 indicates the numbering of the atoms used in defining the parameters. For comparison, the average results of the several X-ray diffraction analyses are also indicated in Table I.

It is tempting to conclude from the excellent fit obtained that other less stable conformations of the molecule do not make significant contributions to the observed diffraction patterns, and that these results are in fact a good estimate of the structure of cyclodecane in the vapor phase at 130°. A cursory comparison of these results with the X-ray structure data, however, reveals significant differences in the structural parameters. While differences are to be expected, the magnitude of these differences casts some doubt on the validity of the above conclusion. The observed bond

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(28) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 171 (1963).

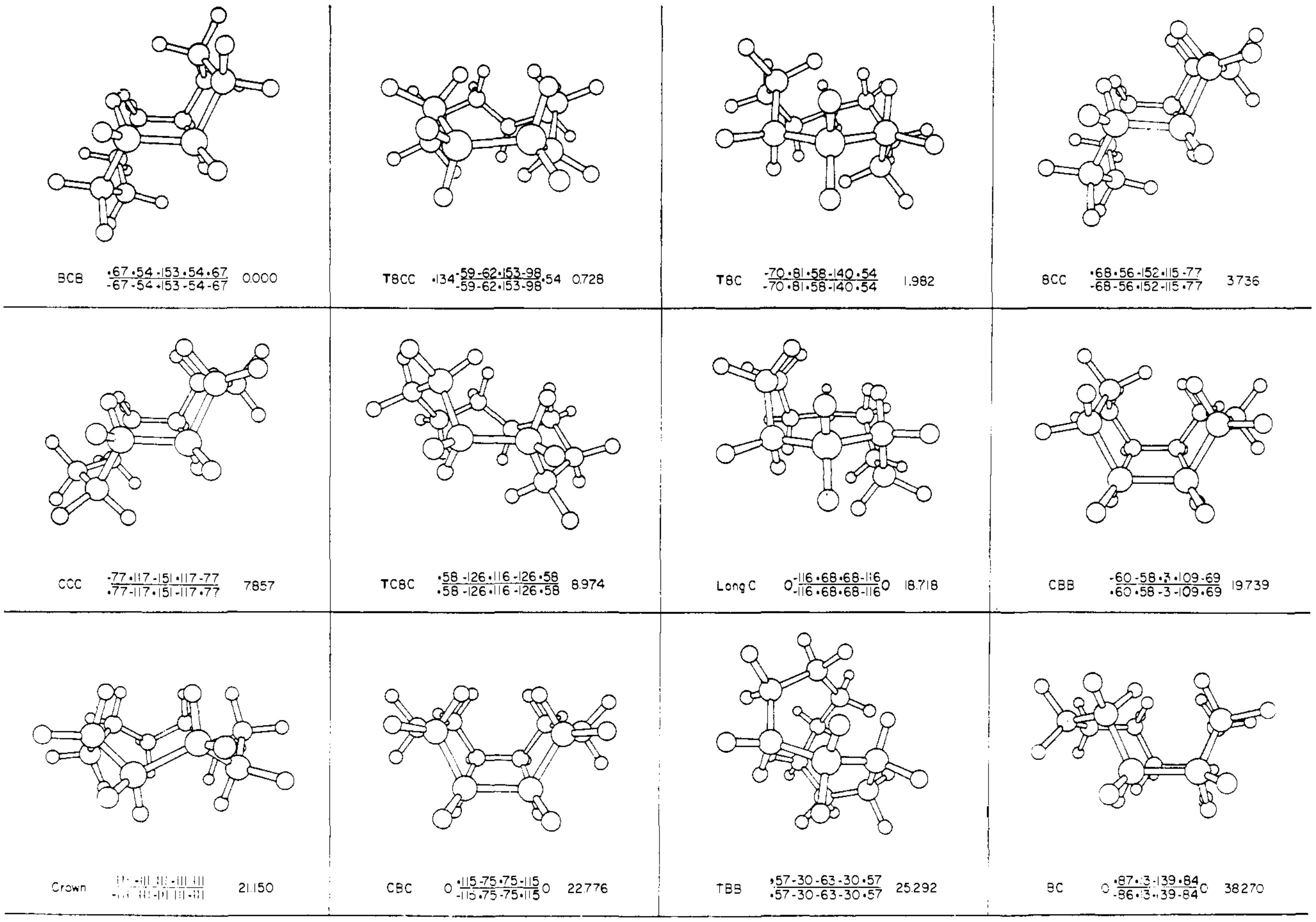

Figure 4. Energy minimization conformations of cyclodecane. For the conventions used in naming the conformations see ref 16. In the Hendrickson notation the line stands for the symmetry element, either a plane of reflection or an axis of rotation. The numbers above and below the line indicate the dihedral angles. Relative strain energies (kilocalories/mole) are listed to the right of the dihedral angles.

angles differ by 2–3°, probably the most significant variation being the $\angle C_{10}C_1C_2$ which is invariably about 118–119° in X-ray crystallographic structures.[9] The variations in dihedral angles are all much larger, in the neighborhood of 10°. These differences are most interesting, however, in light of the fact that the molecular mechanics calculations outlined below (Figure 4 and Table III) predict a BCB geometry more closely agreeing with the X-ray crystallographic data (Table I). This renders it unlikely that the electron diffraction–X-ray diffraction differences are simply attributable to phase differences.

The only objective conclusion which can be drawn from this portion of the investigation is that the C_{2h} BCB model can be made consistent with the experimental data. This conclusion, however, in no way excludes the possibility that the data may equally well be represented by an appropriate mixture of several conformations of the molecule. Clearly a more objective criterion needs to be employed. An alternative approach is offered in the sections below.

The Molecular Mechanics Assisted Approach. In an alternative approach to analyzing the cyclodecane data, it was decided to incorporate molecular mechanics models directly into the analysis procedure in a novel way. Two basic computer programs were written for performing the extensive calculations needed for this analysis.

The first of the two programs was designed to obtain the geometries and estimated strain energies of the conformations of interest by performing an energy minimization on a trial model. Jacob, Thompson, and Bartell[29] have employed a Newton–Raphson minimization procedure in internal coordinates, and while this method is preferred in many ways for the general approach employed here, it is nevertheless difficult to generalize to cyclic molecules. As an alternative we have chosen a minimization procedure employing the method of steepest descents applied to Cartesian coordinates, rather than internal coordinates. The Wilson **B** matrix[30] (the transformation from Cartesian displacement coordinates to internal coordinates) was used in each cycle of the minimization to calculate the force vectors on each atom in the molecule. The atoms were then simultaneously displaced along these vectors a distance proportional to the magnitude of the vector and appropriately scaled to obtain the maximum decrease in the total energy. By properly choosing the scaling parameter for each cycle, a rapid convergence was obtained by this technique. Since only first derivative information is required, the computation time needed for each cycle is substantially less than required

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(29) E. J. Jacob, H. B. Thompson, and L. S. Bartell, *J. Chem. Phys.*, **47**, 3736 (1967).

(30) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955.

by the Newton–Raphson method. The search for the minimum energy geometry was concluded when the energy no longer changed in the sixth significant figure (computational purposes only) on two successive minimization cycles. Tests conducted on the program, using the Jacob, Thompson, and Bartell force field, resulted in structures which were identical with the ones quoted by these authors.[29]

A second program was then written for performing normal coordinate calculations with the same force field used for the energy minimization. The calculations again were performed in Cartesian coordinates making use of the Wilson **B** matrix and its derivatives to obtain the mass weighted Cartesian force constant matrix. The matrix was diagonalized to obtain the frequencies of vibration and the eigenvectors for each normal mode of vibration. The calculated eigenvectors and frequencies were then used to compute mean-square amplitude matrices, and the entire body of calculated information was used to synthesize a theoretical radial distribution curve for the model. In this way the resulting theoretical radial distribution curves were objectively computed from the model force field without introducing any additional information. The calculated frequencies and moments of inertia were also used to compute the pertinent thermodynamic quantities of interest: absolute entropies, heat capacities, and free energy and enthalpy functions. The details of the application of this model and comparisons with experimental data will be the subject of a future publication.

The most difficult decision in performing these calculations was judiciously selecting the force field to employ. Several existing force fields were tried without success. The force field of Lifson and Warshel[21] (CFF2) was rejected, because it predicted several conformations of greater stability than the BCB model including the BCC and CCC conformations. The force field described by Jacob, Thompson, and Bartell[29] gave the best results for structural trends and expected relative stabilities of the conformations, but normal mode calculations on simple alkanes using this force field gave frequencies substantially higher than the experimental ones. The latter force field was, however, adopted as the best starting point for further refinements. In order to improve the agreement in calculated and observed frequencies, the nonbonded potential functions were modified in the following manner. The attractive portions of the potential functions were retained, and the repulsive portions were modified to agree with the spectroscopic F and F' Urey–Bradley nonbonded force constant obtained by Schachtschneider and Snyder.[28] This approach was successful for the C···C and C···H potential functions, but the results obtained for the H···H function were unsuccessful in predicting any facsimile of structural trends. A potential function similar to Bartell's was therefore adopted for H···H, and a CH–CH stretch–stretch interaction constant was introduced, in order to obtain better agreement between calculated and observed CH stretching frequencies. The significance of this alternative description of the Urey–Bradley force field involving hydrogens has been discussed by Bartell and Kuchitsu.[31] Finally, the r^0's and α^0's were adjusted to give the best agreement with the r_g structures of methane, ethane, and propane; small final adjustments were made in the potential functions to give the best possible agreement with the vibrational frequencies and isomerization energies in *n*-butane, isobutane, *n*-pentane, isopentane, and neopentane. While there are no criteria yet established for testing the validity or uniqueness of these functions, they have nevertheless been selected in an objective manner. The force field finally adopted in the calculations is indicated in Table II.

Table II. Force Field Parameters Used in Energy Minimization and Normal Coordinate Calculations

	Valence terms		
	Force constant	r^0, α^0, τ^0	
K_{CC}	300 kcal/Å^2	1.250 Å	
K_{CH}	600 kcal/Å^2	1.056 Å	
$G_{CH,CH}$[a]	−20 kcal/Å^2	1.056 Å	
H_{CCC}	90 kcal/rad^2	112°	
H_{CCH}	46 kcal/rad^2	109.47°	
H_{HCH}	52 kcal/rad^2	109.47°	
V_3[b]	2.60 kcal	60°	
	Nonbonded buckingham potential functions[c]		
	a	b	c
H···H	5,524	4.0	49.2
C···H	67,925	4.4	126
C···C	99,787	4.0	322

[a] The interaction term has the functional form: $G_{CH,CH}(R_{CH}^1 - R^0)$. [b] For torsional internal coordinates, a Pitzer type cosine potential function of height V was used. [c] The nonbonded potential functions have the form: $a \exp(-br) - (c/r^6)$. The units of a, b, and c are kcal/mol, Å^{-1}, and kcal Å^6/mol, respectively.

Using the model force field proposed above, the geometries and relative strain energies of the 12 conformations of cyclodecane suggested by Hendrickson were calculated. The results of these calculations are indicated in Figure 4 using the symbolic ring notation implemented by Hendrickson.[16]

Figure 4 indicates that there are three or four conformations possessing significantly lower strain energies than the remaining ones. Caution must be exercised, however, in relying too heavily on the calculated strain energies to make *quantitative* predictions about the composition. First of all, it is the free energy difference and not the strain energy difference which is the critical thermodynamic variable in determining the composition. Second, even though the free energy functions were calculated from the model force field, the free energy of isomerization still involves the enthalpy difference at absolute zero, which in turn depends on the differences in strain energy and zero-point vibrational energy. It was found during the refinement of the model potential functions that the relative strain energies are much more sensitive to slight changes in the potential functions than are the resulting geometries. Calculations performed with Lifson and Warshel CFF2 for instance predicted several conformations more stable than the BCB, with the TBCC being 5.8 kcal/mol more stable. While these authors quote excellent agreement with the excess enthalpy for cyclodecane, they have overlooked the fact that their force field predicts other more stable conformations than the BCB model. We therefore reject the *precise* quantitative use of our strain energies at present and use them

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(31) L. S. Bartell and K. Kuchitsu, *J. Chem. Phys.*, 37, 691 (1962).

Table III. Minimum Energy Conformations of Cyclodecane and Mole Fractions Determined by Least-Squares Fit to the Experimental Radial Distribution Curve[a]

Conformation and mole fraction	Molecular parameter[b]	Carbon atom																				
		C_1		C_2		C_3		C_4		C_5		C_6		C_7		C_8		C_9		C_{10}		C_1
BCB	r_{cc}		1.544		1.542		1.539		1.542		1.544		1.544		1.542		1.539		1.542		1.544	
$X = 0.49 \pm$	α	117.2		114.4		114.4		117.3		117.0		117.2		114.4		114.4		117.3		117.0		
0.03	τ		−67.3		−54.8		153.2		−54.9		−67.3		67.3		54.8		−153.2		54.9		67.3	
TBC	r_{cc}		1.543		1.539		1.539		1.543		1.539		1.537		1.541		1.540		1.537		1.539	
$X = 0.35 \pm$	α	115.8		118.2		115.9		116.7		113.9		114.1		115.1		114.0		113.9		116.7		
0.02	τ		80.2		−70.2		−69.7		80.3		58.7		−139.3		54.0		54.1		−139.4		58.9	
TBCC	r_{cc}		1.545		1.539		1.539		1.539		1.540		1.540		1.540		1.538		1.539		1.539	
$X = 0.08 \pm$	α	115.1		112.8		114.4		114.7		113.9		113.8		114.6		114.3		112.8		115.1		
0.04	τ		54.1		−98.7		152.5		−62.1		−59.2		134.1		−59.4		−62.3		152.8		−98.5	
BCC	r_{cc}		1.541		1.539		1.536		1.537		1.542		1.542		1.537		1.536		1.539		1.541	
$X = 0.08 \pm$	α	114.4		112.9		114.4		117.0		116.3		117.0		114.4		112.9		114.5		115.2		
0.04	τ		76.9		−115.1		151.7		−56.0		−67.9		67.9		56.0		−151.8		114.9		−76.8	

[a] Models shown in Figure 4. [b] r_{cc}, bond in Å; α, ∠CCC in degrees; τ, torsional angles in degrees as defined in ref 16.

only as a crude guide for selecting models for more detailed consideration (*vide infra*).

On the basis of the strain energy calculations, four models were selected for comparison with the experimental data: BCB, TBCC, TBC, and BCC. Detailed geometric parameters for these four models are given in Table III. Normal coordinate and mean-square amplitude calculations were performed for each of these models, and complete theoretical radial distribution curves were calculated. The curves calculated from the models are compared with the experimental radial distribution curve in Figure 5.

It is interesting to note that none of the curves generated by this technique agree very well with the experimental curve. Of the four conformations considered, the BCB model gives the smallest standard deviation with the experimental curve; nevertheless, the agreement is very unsatisfactory. Note, as indicated above, that the dihedral angles of the calculated BCB model in Table III agree remarkably well with the observed X-ray crystallographic data in Table I, but not with the parameters obtained by the least-squares BCB analysis. This unfavorable comparison, coupled with the molecular mechanics calculations in Table III, further reinforce our expectations that the vapor phase at 130° is a mixture of several conformations rather than the BCB conformer alone.

It is also interesting to note that the radial distribution curve can effectively be divided into two portions at 3.0 Å. The portion of the curve for r less than 3.0 Å is essentially conformation independent, except for rather subtle differences. It is this portion of the curve which is determined by the average parameters discussed previously. The portion of the curve for r greater than 3.0 Å is the "fingerprint" portion of the curve, which is sensitive to the secondary structure (dihedral angles) and molar composition.

In an effort to determine the detailed composition of the vapor phase, the radial distribution curves for the four conformations selected were averaged together with appropriate mole fractions weighting the contribution of each species. A least-squares fit to the experimental radial distribution function was then obtained varying only the mole fractions. It is interesting to note parenthetically that since this is a truly linear problem, the method of differential least squares converged in one cycle. The least-squares radial distribution curve is indicated in Figure 6, and the calculated mole fraction composition is shown in Table III.

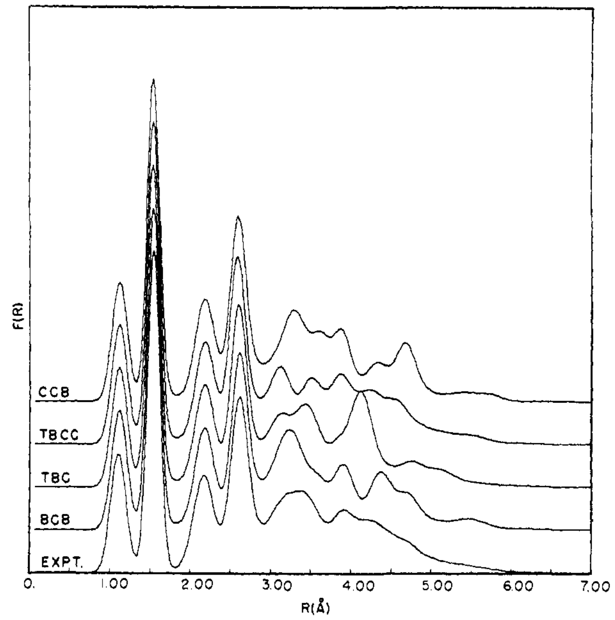

Figure 5. A comparison of the experimental radial distribution curve with the radial distribution curves calculated for the four least strained conformations of cyclodecane as determined by energy minimization techniques.

The agreement is quite satisfactory when one considers the crudeness of the model employed and the fact that it was normalized using structures and frequencies of normal and branched alkanes. It is noteworthy that the average structural parameters derived from the data in Table III generally agree with the average structural parameters from the BCB analysis (Table I) within two standard deviations. In all likelihood even better agreement could have been obtained by a least-squares analysis of the four conformations simultaneously. This approach was not explored, however, because it was felt that it would seriously mar the objectivity of the molecular mechanics procedure and provide little meaningful structural information.

A Brief Discussion of the Two Methods. The two analyses presented here represent alternative interpre-

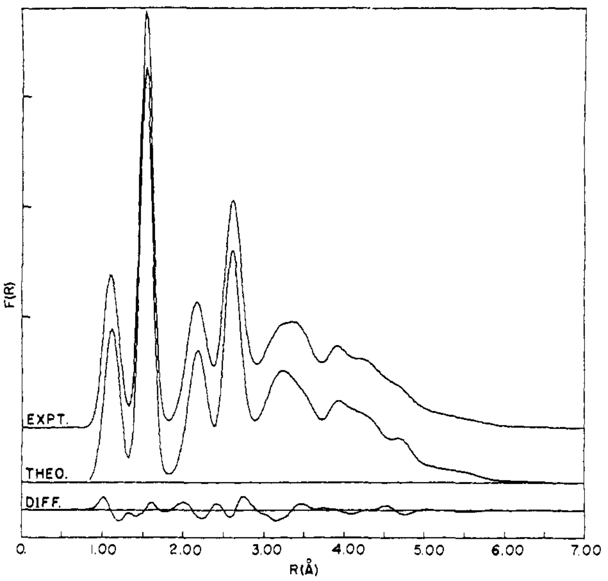

Figure 6. A comparison of the experimental radial distribution curve for cyclodecane with the theoretical radial distribution curve for the mixture of conformations indicated in Table III.

tations of the experimental data. The simple BCB model fits the data extremely well. We are, nevertheless, acutely aware of the pitfalls encountered in accepting agreement between an electron diffraction model and experimental data as the sole criterion for basing a structural conclusion. It is interesting in this regard that the molecular mechanics derived BCB model corresponds more closely to X-ray crystallographic BCB structures than the electron diffraction BCB model obtained here. On the other hand, the mixture model does not fit the experimental quite as well. It is, however, derived in an objective manner and by its very nature supported by molecular mechanics calculations. At the very least the mixture model analysis suggests that the TBC conformation should be given serious consideration as an important contributor to the gas phase molecular structure of cyclodecane at 130°. While the second method of analysis is a drastic departure from the more conventional least-squares procedure, it is, nevertheless, a practical and useful expedient in dealing with an electron diffraction structural problem of this complexity. Obviously, much can be done to test, verify, modify, and improve such calculations.

The results of the two methods of calculation should also be amenable to experimental tests. One method predicts that the BCB conformation is the sole component in the vapor phase, while the other maintains that this conformation constitutes 50% or less of the total conformations. In addition the TBC conformation makes up 35% of the remaining conformers in the second case. It is worth noting that this conformation is the principal form in crystalline 1,1,5,5-tetramethylcyclodecane-8-carboxylic acid.[9] To what extent the TBCC and BCC conformations (8 ± 4%) should be given serious consideration remains to be determined. At any rate, it should be possible to probe the two contrasting interpretations experimentally. For example, the BCB model does not have a dipole moment, while the other forms do. If the molecule exhibits a microwave spectrum, then some conformation other than the BCB model must be present. A temperature study of the line intensities should reveal whether the species with dipole moments are more or less stable than any species without a dipole moment. Finally, if an interpretation of the microwave spectrum were possible, the moments of inertia could be compared with the geometries suggested here for the other forms such as the TBC, TBCC, and BCC conformations. A critical Raman and infrared study also ought to be of interest. It is possible that nuclear magnetic resonance spectroscopy investigations in solution might also be instructive.[32]

Our calculated strain energies are not in quantitative agreement with the experimental results of the molecular mechanics assisted analysis. Two points are worth noting in this context. First, it should be reiterated that it is the free energy differences and not the strain energy differences which determine the composition of the vapor phase. Secondly, it is appropriate to give some estimate of the expected accuracy of the thermodynamic calculations employed in this study. The ever-increasing number of comparisons of detailed structural data with molecular mechanics calculations render it unlikely that the present strain energy difference calculations are *generally* good to a kilocalorie or better. In contrast, it is quite unlikely that they are off by large numbers of kilocalories. This is, in fact, a cornerstone of the second method of data analysis presented herein.

In order to gain some indication as to how refining the strain energy data in Figure 4 might improve the agreement between the experimentally determined distribution of the four cyclodecane conformations (Table III) and their calculated thermodynamic properties (Figure 4), additional thermodynamic calculations were performed.

In estimating the free energies of isomerization from the mole fractions, it is necessary to assign a statistical weight of 2 to the TBC conformation, since this form has an enantiomer. Taking this into account, we then estimate the free energies of isomerization relative to the BCB conformation to be: 0.82 kcal/mol for the TBC form, 1.41 kcal/mol for the BCC form, and 1.42 kcal/mol for the TBCC form. If we then combine this result with our calculated values for the absolute entropies of the conformations at 400°K, we obtain the following estimates for the enthalpies of isomerization: 1.01 kcal/mol for TBC, 1.60 kcal/mol for TBCC, and 3.33 kcal/mol for BCC. The reason that the enthalpy of isomerization for the BCC form is so large is that the symmetry number for this conformation is 1, while the other conformations all have symmetry numbers of 2; thus there is a large entropy of isomerization in going from the BCB form to the BCC conformation. Finally, if we employ our calculated enthalpy functions to extrapolate these isomerization enthalpies to absolute zero, and make corrections for the differences in zero-point vibrational energies, we obtain experimental estimates of the strain energies relative to the BCB conformation

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[32] In unpublished results of M. Manion and L. K. Montgomery, it has been shown that the deuteron nuclear magnetic resonance spectrum of cyclodecane-d_{12} consists of a single line down to at least −100°. This suggests that cyclodecane's conformation(s) pseudo-rotates or interconverts rapidly on the nmr time scale at this temperature. Hendrickson (ref 16) has outlined a pathway for the pseudo-rotation of BCB forms utilizing the TBC and TBCC conformations. The data in Figure 4 indicate that the pseudo-rotation process should be a very rapid one.

as follows: 1.10 kcal/mol for TBC, 1.93 kcal/mol for TBCC, and 3.46 kcal/mol for BCC. While the results for the TBC and TBCC forms are still reversed when compared with the energy minimization calculations, we nevertheless feel the agreement is sufficiently good to at least justify our use of these calculated strain energies as a guide in selecting which conformations to consider in the analysis.

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Supplementary Material Available. A tabulation of the raw intensity data and cartesian coordinates of the models will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-8598.

Heats of Hydrogenation. X. Conjugative Interaction in Cyclic Dienes and Trienes

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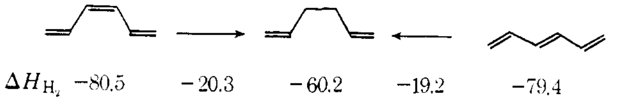
Abstract: The heats of hydrogenation of the two cyclohexadienes, two cycloheptadienes, and three cyclooctadienes are reported and discussed in terms of empirical strain and conjugative interaction. The heats of hydrogenation of *cis*- and *trans*-hexa-1,3,5-triene are reported and related to those of cycloheptatriene, the two cyclooctatrienes, and cyclooctatetraene. Data on unsaturated cyclononanes and cyclodecanes can be interpreted to reveal the possible importance of adverse transannular interaction of suitably disposed pairs of double bonds. This hypothetical interaction is coupled with the Dewar–Schmeising theory of conjugative interaction to reinterpret the thermochemistry of several of the unsaturated cyclooctanes.

Heats of hydrogenation in acetic acid solution at 25° of various cyclic dienes and trienes as well as of the triene model compounds, *cis*-hexatriene, *trans*-hexatriene, and 1,5-hexadiene, are listed in Table I along with some related, but previously published data.[2,3] In view of the special properties associated with compounds possessing medium-sized rings, interpretation of much of the data is neither simple nor lacking in elements of uncertainty. We wish, however, to call attention to several items of interest that emerge from this work.

A reference point for a portion of the ensuing discussion is provided by *cis*- and *trans*-hexatriene, which are presumed to be strain-free and have the essentially



planar conformations shown in the diagram, although the *cis*-triene possesses a slight twist (about 10°) at the central double bond.[4] If the validity of the theoretical treatment of Dewar and Haselbach[5] is accepted, such

Table I. Heats of Hydrogenation in Acetic Acid Solution at 25°

Compound	$-\Delta H$, kcal/mol
Hexa-1,5-diene	60.17 ± 0.37
cis-Hexa-1,3,5-triene	80.50 ± 0.33
trans-Hexa-1,3,5-triene	79.43 ± 0.22
Cycloheptene	25.85 ± 0.09[a]
Cyclohepta-1,3-diene	49.92 ± 0.08
Cyclohepta-1,4-diene	55.88 ± 0.08
Cyclohepta-1,3,5-triene	70.49 ± 0.39[a]
cis-Cyclooctene	22.98 ± 0.10[b]
trans-Cyclooctene	32.24 ± 0.21[b]
Cycloocta-1,3-diene	48.96 ± 0.08
Cycloocta-1,4-diene	52.09 ± 0.28
Cycloocta-1,5-diene	53.68 ± 0.02
Cycloocta-1,3,5-triene	76.39 ± 0.44[c]
Cycloocta-1,3,6-triene	79.91 ± 0.17
Cycloctatetraene	97.96 ± 0.05[d]
cis-Cyclononene	23.62 ± 0.07[b]
trans-Cyclononene	26.49 ± 0.14[b]
cis,cis-Cyclonona-1,5-diene	46.32 ± 0.26
cis,trans-Cyclonona-1,5-diene	50.63 ± 0.32
cis,cis,cis-Cyclonona-1,4,7-triene	76.88 ± 0.05[e]
cis-Cyclodecene	20.67 ± 0.08[b]
trans-Cyclodecene	24.01 ± 0.09[b]
cis,cis-Cyclodeca-1,6-diene	43.73[f]
trans,trans-Cyclodeca-1,6-diene	47.63[f]
Cyclohexa-1,3-diene	53.64 ± 0.29
Cyclohexa-1,4-diene	53.90 ± 0.33

[a] Reference 2a. [b] Reference 2b. [c] A value of −72.36 ± 0.26 kcal/mol was previously published (ref 3) for this substance. The figure reported here is the average of six new determinations carried out at three different times over a period of 5 years. Explanation for the earlier low value has not been ascertained. [d] Reference 3. [e] W. R. Roth, W. B. Bang, P. Goebel, R. L. Sass, R. B. Turner, and A. P. Yu, *J. Amer. Chem. Soc.*, **86**, 3178 (1964). [f] Sample sufficient for one run only.

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