

is found in quartz crystals at low temperatures. For $\omega\tau \leq 1$ ($\lambda >$ mean phonon path), no direct interaction occurs between the sound phonons and lattice phonons, but rather a modulation of the phonon energies by the sound wave, and the relaxation of the phonons back to their equilibrium states gives rise to the observed absorption. This absorption is proportional to τT and is, as long as $\tau \sim 1/T$ (in good crystals), independent of temperature. Considering the variation of $\omega\tau$ with temperature, the total shape of the loss-temperature curves (Figure 5a) can thus be explained. Figures 1 and 2 demonstrate the same temperature dependence in the case of dielectric absorption: at low temperatures a T^4 law and then the gradual transition to a rather temperature-independent value. From this it seems reasonable to assume that it is the same mechanism which gives rise to absorption in both cases.

The Exponent n ($1 < n \leq 4$). Maris⁸ and also Fraser and Spencer⁹ reported a flattening of the loss-temperature curves in the ultrasonic absorption with increasing defects in the crystal structure. The same is found in the dielectric case comparing, *e.g.*, the quartz and quartz glass curves of Figure 2. It seems to us that this feature can be generalized, that the exponent n , characterizing the intrinsic phonon absorption, is a new and sensitive means to characterize a "lattice quality." In this line, the "lattice" of the quartz glass does not show as much deviation from the ideal crystal lattice of SiO₂ as, for instance, the over-all lattice quality of a still 40% crystalline polyethylene sample. This

(9) D. B. Fraser and W. J. Spencer, to be published.

close similarity in the structures of crystalline and amorphous SiO₂ has often been suggested¹⁰ by different approaches. The sensitivity of the exponent n on the lattice quality is clearly marked in the example of the different polyethylenes. n can be chosen as a measure of the degree of crystallinity (which again determines the order in the amorphous as well as in the crystalline phase¹¹). The polyoxymethylene fits well into this line, with a crystal content of about 70% and a slope slightly less than the 75% crystalline polyethylene. This again demonstrates that absorption of electromagnetic radiation in the considered range of frequency and temperature is not dependent on polar units in the structure but is, in fact, an intrinsic lattice property.

Summarizing we may say that there seemed to be enough evidence for us to consider it worthwhile to present our interpretation of microwave low-temperature absorption for further discussion and measurements.

Acknowledgments. We wish to thank Ing. Hilge Röder for her excellent assistance in the liquid helium resonator design and measurements and Dr. Kilian for helpful discussions. We also thank Mr. Strohrigel for the technical construction of the resonator and Mr. Ritter for his help during the experiments. Finally we thank the Deutsche Forschungsgemeinschaft for the financial support of this work.

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The Structures of Norbornane and 1,4-Dichloronorbornane as Determined by Electron Diffraction

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Abstract: The structures of norbornane and 1,4-dichloronorbornane in the vapor state, as determined by electron diffraction, provide geometric parameters (i) for calculating strain and nonbonded interaction energies in a representative rigid bicyclic hydrocarbon, and (ii) for assessing the influence on the skeletal structure due to substitution of highly electronegative groups at the 1,4 positions. Sectorial diffraction photographs obtained at Cornell University and at the University of Oslo of the same samples gave scattered intensity which were in complete agreement both in magnitude and angular scale over the regions they overlapped. The strain energy for norbornane as calculated according to the scheme of Allinger was compared with the experimentally determined value.

Bicyclic molecules, particularly derivatives of bicyclo[2.2.1]heptane, have held a prominent position in the investigation of phenomena associated with nonclassical ions.¹ While the interpretation of these phenomena is still controversial,² there is general agreement that the properties depend critically on the detailed geometry of the molecules. In general, those properties

(1) T. P. Nevell, E. DeSalas, and C. L. Wilson, *J. Chem. Soc.*, 1188 (1939).

(2) (a) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965; (b) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).

of bicyclic compounds wherein they differ from the corresponding acyclic alkanes find rationalization in terms of several types of "strain" imposed by their geometries. Bicyclic molecules are of interest also because, compared to acyclic molecules, the relatively rigid structures of the carbon skeletons lead to unambiguous orientations and magnitudes of separation of substituents. The absence of complications from having to consider averages over several widely different conformations has made this group of molecules useful for testing numerous theories.³

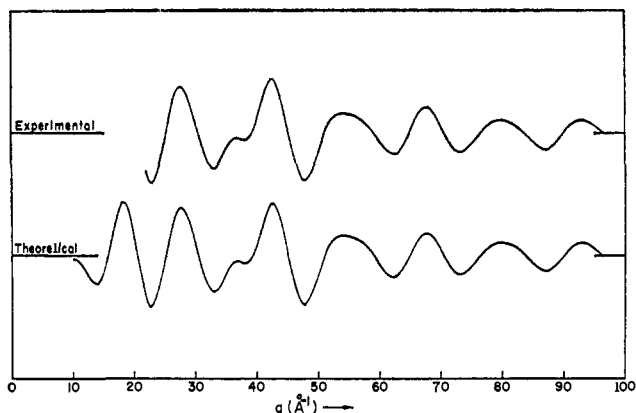


Figure 1. Molecular experimental and theoretical intensity curves for norbornane (CU data).

The present paper, the first of a series concerned with the structures of strained hydrocarbons and their derivatives as determined by gas-phase electron diffraction, is primarily focused on the structure of bicyclo-[2.2.1]heptane. It has been the subject of an early electron diffraction study by Berndt⁴ and currently was reinvestigated by refined electron diffraction techniques in two laboratories, the University of Tokyo⁵ and Cornell University. With a precise structure available, a preliminary test of several schemes for calculating strain and nonbonded interactions is made. These are to be compared with empirical calculations made for the structure of norbornane,⁶ a host of compounds which incorporated the norbornane skeleton has been extensively studied by X-ray crystal diffraction techniques.⁷

In this paper the structure of 1,4-dichlorobicyclo-[2.2.1]heptane is also investigated. It not only serves as a comparison for the structures of the bicyclic ring system but also as an indicator of the influence of substitution of two highly electronegative groups at the 1,4 positions and the consequent distortion of the skeletal geometry.

Experimental Section

Samples of norbornane and 1,4-dichloronorbornane were prepared in this laboratory.⁸ Sected diffraction photographs were taken with the first Cornell apparatus,⁹ using a 40-kV electron beam. During the taking of the photographs, the norbornane was kept at -20° , while the 1,4-dichloronorbornane was maintained at room temperature. Kodak projection slide plates were used. The diffraction patterns were read with a Leeds and Northrup microdensitometer; during scanning the plates were oscillated about their centers of diffraction to minimize fluctuations due to emulsion

(3) For examples, see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 10.

(4) A. F. Berndt, Ph.D. Thesis, California Institute of Technology, 1957.

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

(6) (a) A. J. Kltagorodsky, *Tetrahedron*, **9**, 183 (1960); **14**, 930 (1961); (b) C. F. Wilcox, Jr., *J. Am. Chem. Soc.*, **82**, 414 (1960).

(7) (a) G. Ferguson, C. J. Fritchie, J. M. Robertson, and G. A. Sim, *J. Chem. Soc.*, 1796 (1962); (b) D. A. Brueckner, R. A. Hamor, J. M. Robertson, and G. A. Sim, *ibid.*, 799 (1962); (c) A. C. MacDonald and J. Trotter, *Acta Cryst.*, **18**, 243 (1965); **19**, 456 (1965); (d) A. V. Fratini, K. Britts, and I. L. Karle, *J. Phys. Chem.*, **71**, 2482 (1967).

(8) C. F. Wilcox, Jr., and J. G. Zajaček, *J. Org. Chem.*, **29**, 2209 (1964).

(9) J. M. Hastings and S. H. Bauer, *J. Chem. Phys.*, **18**, 13 (1950).

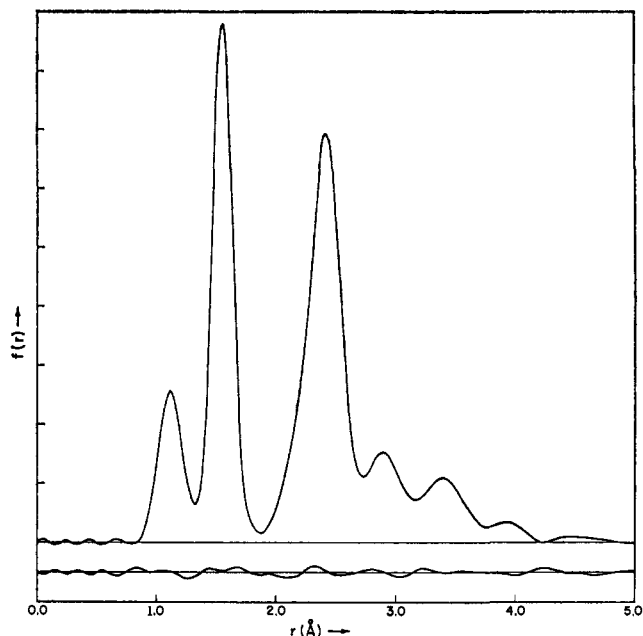


Figure 2. Complete radial distribution curve for norbornane. The lower oscillating curve is the difference between the experimental $f(r)$ and that calculated for the final model.

granularity. Gold foil patterns were taken concurrently for wavelength calibration. The method for reduction of data has been described previously.¹⁰

The experimental total intensities for these two compounds as obtained in this laboratory were compared with photographs taken by Bohn¹¹ in Oslo University (courtesy of Professor Otto Bastiansen); portions of the same samples were used. For norbornane, the range of q values recorded at CU was $q = 22$ to 96, while the Oslo data extended from $q = 5$ to 140. The reduced experimental intensities for these two sets of data agree to within the random fluctuations of adjacent intensity readings over the range they overlap. For 1,4-dichloronorbornane the CU patterns extended from $q = 13$ to 96, while the Oslo data cover $q = 5$ to 155. Here also there is excellent agreement between the two sets of diffraction curves.

Analysis and Results

Norbornane. The reduced experimental intensity curve (CU) and the theoretical intensity for the best models are shown in Figure 1. The final refined experimental radial distribution curve, and the difference between the theoretical and experimental radial distribution curves, are shown in Figure 2, computed with a damping factor $\gamma = 0.00022$.

The first peak at 1.115 Å is a superposition of the bonded C-H distances. The second peak, at 1.555 Å, is replotted on an enlarged scale in Figure 3. It is resolved into the bonded C-C distances, *i.e.*, $C_1-C_2 = 1.556$ Å, $C_2-C_3 = 1.551$ Å, $C_1-C_7 = 1.559$ Å. The atoms are numbered in conventional sequence as shown in Figure 10. The third peak at $r = 2.420$ Å was resolved into 15 nonbonded $C \cdots C$ and $C \cdots H$ distances (Figure 4). Of these only $C_1 \cdots C_3 = 2.452$ Å, $C_1 \cdots C_4 = 2.317$ Å, $C_2 \cdots C_6 = 2.440$ Å, and $C_2 \cdots C_7 = 2.411$ Å contribute significantly. The remaining peaks are due to more distant nonbonded $C \cdots C$, $C \cdots H$, and $H \cdots H$ distances. Since there are 28 such contributions, which if shown in detail would lead to a confusing graph, only the positions of the maxima of

(10) J. L. Hencher and S. H. Bauer, *J. Am. Chem. Soc.*, **89**, 5527 (1967).

(11) R. K. Bohn, private communication.

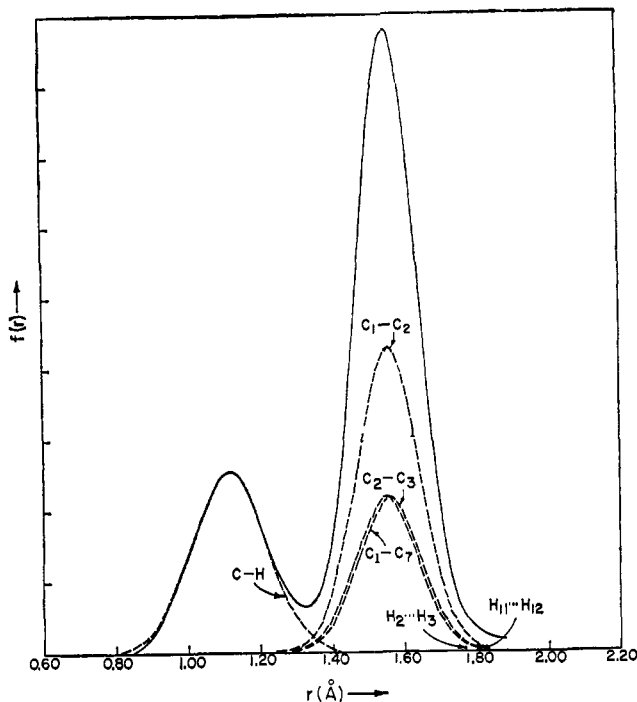


Figure 3. Resolution of the 0.8–1.8-Å region of Figure 2.

these peaks were drawn in as vertical lines, with the height of each set equal to $C_{ij} = n_{ij}Z_iZ_j/r_{ij}$, where n_{ij} is the number of atom pairs separated by the distance, r_{ij} , between atoms of atomic number Z_i and Z_j .

The geometrical parameters introduced to characterize the model are the bridge angle, defined as the angle at $\angle C_1C_7C_4$; the flap angle, defined as the angle between the two planes $C_1C_2C_3C_4$ and $C_1C_6C_5C_4$; all bonded distances C_1-C_2 , C_1-C_7 , C_2-C_3 , and $C-H$; and the angles of $\angle H_2C_2H_3$ and $\angle H_{11}C_7H_{12}$, which bisect the angles $\angle C_1C_2C_3$ and $\angle C_1C_7C_4$, respectively. A least-squares refinement program on the experimental intensity was then applied.

During the first runs of the least-squares program the flap angle, the length of the $C-H$ bond, $\angle H_2C_2H_3$, and $\angle H_{11}C_7H_{12}$ were constrained to values experimentally observed in unstrained hydrocarbons. After 14 cycles the iteration converged to a minimum in the squares of the sum of residuals and of errors. During the second execution of the program the eight geometrical parameters listed in Table I and the root-mean-square amplitudes l_{12} , l_{13} , l_{23} , l_{17} , and l_{C-H} were allowed to vary. H_1 and H_6 were constrained to the plane of $C_1C_7C_4$; the plane of $H_2C_2H_3$ was set to bisect $\angle C_1C_2C_3$ (refer to Figure 10) [that is, $(\theta_1 + \theta_2) = \angle C_1C_2C_3$; $\delta_1 + \delta_2 = \angle H_2C_2H_3$], and the constraint was set such that the ratios of $\theta_1/\theta_2 = 1$ and δ_1/δ_2 were equal to 1. Also, the plane of $H_{11}C_7H_{12}$ was set to bisect $\angle C_1C_7C_4$. All the remaining l_{ij} 's were set at reasonable values. These constraints had to be imposed, as otherwise no convergence was obtained in the least-squares analysis. In particular, the ratio (θ_1/θ_2) showed a high correlation with the magnitude of $(\delta_1 + \delta_2)$. A third set of calculations were then run with $\theta_1/\theta_2 = 0.90$, 1.00, and 1.10. The standard deviations for the variables tested were quite close for the ratios 0.90 and 1.00 but were somewhat higher for 1.10. Hence, within the specified uncertainties one may

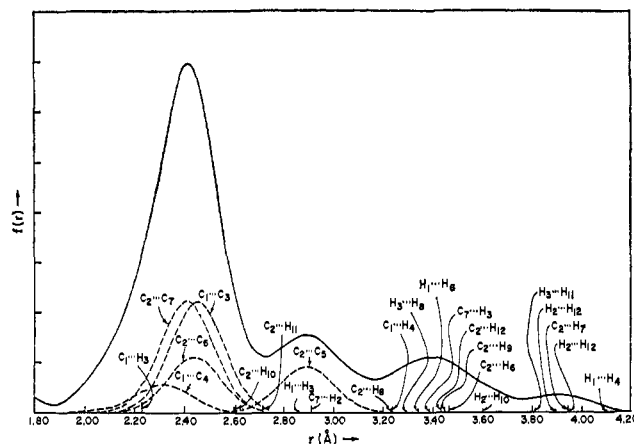


Figure 4. Resolution of the 1.8–4.2-Å region of Figure 2.

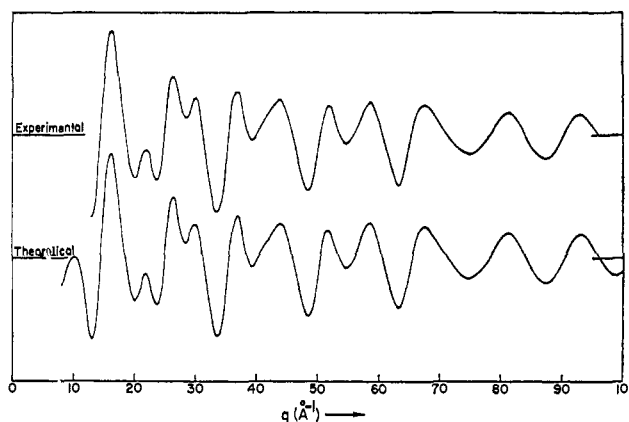


Figure 5. Molecular experimental intensity and theoretical intensity curves of 1,4-dichloronorbornane (CU data).

accept either $\theta_1/\theta_2 = 0.9$ with $\delta_1 + \delta_2 = 108 \pm 1.0^\circ$ or $\theta_1/\theta_2 = 1.00$ with $\delta_1 + \delta_2 = 105 \pm 2^\circ$. The other parameters, several deduced nonbonded distances, and the corresponding l_{ij} 's are listed in Table I. The Cartesian coordinates of the atoms for the model with $\theta_1/\theta_2 = 0.90$ are given for reference in Table II. The estimated uncertainties were taken to be three times the calculated standard deviations. An error matrix, the diagonal elements of which are the square roots of standard calculated errors and the off-diagonal elements are the square roots of the products of the standard errors for the corresponding pairs of parameters, is presented in Table III.

The experimental and final theoretical intensities are shown in Figure 1; the difference between the theoretical and experimental radial distribution curves, plotted in the lower part of Figure 2, is within the generally acceptable range. Models with C_2 symmetry (bonds C_2-C_3 and C_5-C_6 not parallel) and various bond distances and angles were tested. No combination was found which fitted the experimental intensity and radial distribution curves as well as the C_{2v} model. When the twist parameter was allowed to vary in the least-squares calculation, it reduced to zero in the converged structure.

1,4-Dichloronorbornane. The reduced experimental intensity and the theoretical intensity curves are given in Figure 5. The refined radial distribution curve is plotted in Figure 6 along with the difference between the

Table I. Distances in Norbornane

Bonded	r_{ij} , Å	l_{ij} , Å
C ₁ -C ₂ , C ₃ -C ₄ , C ₁ -C ₆ , C ₄ -C ₆	1.556 ± 0.012	0.057 ± 0.004
C ₂ -C ₃ , C ₅ -C ₆	1.551 ± 0.015	0.057 ± 0.004
C ₁ -C ₇ , C ₄ -C ₇	1.559 ± 0.015	0.057 ± 0.004
(C-H) _{av}	1.115 ± 0.015	0.080 ± 0.002
Bridge angle	96.0 ± 1.00°	
Flap angle	108.0 ± 1.50°	
∠H ₁₁ C ₇ H ₁₂	108.0 ± 1.5°	
∠H ₂ C ₂ H ₃	108.0 ± 1.0°	
(Assume $\theta_1/\theta_2 = 0.90$ and $\delta_1/\delta_2 = 1.00$)		
Nonbonded Internuclear Distances (Å)		
C ₁ ···C ₄	2.317 ± 0.020	0.093 ± 0.009
C ₁ ···C ₃ , C ₂ ···C ₄ , C ₁ ···C ₅ , C ₄ ···C ₆	2.453 ± 0.030	0.083 ± 0.008
C ₂ ···C ₆ , C ₃ ···C ₅	2.440 ± 0.033	0.083 ± 0.008
C ₂ ···C ₇ , C ₃ ···C ₇ , C ₅ ···C ₇ , C ₆ ···C ₇	2.411 ± 0.027	0.085 ± 0.007
C ₂ ···C ₅ , C ₃ ···C ₆	2.891 ± 0.036	0.086 ± 0.009

Table II. Cartesian Coordinates for Least-Squares Models

	Norbornane ($\theta_1/\theta_2 = 0.90$)			1,4-Dichloronorbornane			
	x	y	z	x	y	z	
C ₁	1.158	0	0	1.115	0	0	
C ₂	0.776	1.220	-0.886	0.777	1.229	-0.892	
C ₃	-0.776	1.220	-0.886	-0.777	1.229	-0.892	
C ₄	-1.158	0	0	-1.115	0	0	
C ₅	-0.776	-1.220	-0.886	-0.777	-1.299	-0.892	
C ₆	0.776	-1.220	-0.886	0.777	-1.229	-0.892	
C ₇	0	0	1.043	0	0	1.061	
H ₁	2.138	0	0.532	1.201	2.153	-0.411	
H ₂	1.152	2.184	-0.472	1.201	1.028	-1.914	
H ₃	1.152	1.123	-1.931	-1.201	2.153	-0.411	
H ₄	-1.152	2.184	-0.472	-1.201	1.028	-1.914	
H ₅	-1.152	1.123	-1.931	-1.201	-2.153	-0.411	
H ₆	-2.138	0	0.532	-1.201	-1.028	-1.914	
H ₇	-1.152	-2.184	-0.472	1.201	-2.153	-0.411	
H ₈	-1.152	-1.123	-1.931	1.201	-1.028	-1.914	
H ₉	1.152	-2.184	-0.472	0	-0.918	1.710	
H ₁₀	1.152	-1.123	-1.931	0	0.918	1.710	
H ₁₁	0	0.902	1.699				Cl ₁
H ₁₂	0	-0.902	1.699				Cl ₂
				2.792	0	0.572	
				-2.792	0	0.572	

Table III. Error Matrix for Norbornane ($\theta_1/\theta_2 = 0.90$)^a

	C ₁ -C ₂	C ₁ -C ₇	C ₂ -C ₃	C-H	Bridge angle	Flap angle	∠HCH at C ₇	∠HCH at C ₂	l_{12}	l_{13}	l_{C-H}
C ₁ -C ₂	0.0040										
C ₂ -C ₇	-0.0056	0.0051									
C ₂ -C ₃	-0.0030	0.0044	0.0050								
C-H	0.0008	-0.0010	0.0009	0.0049							
Bridge angle	0.0075	-0.0075	-0.0071	0.0051	0.0056						
Flap angle	0.0092	0.0059	0.0081	0.0010	0.0050	0.0085					
∠HCH at C ₇	-0.0091	0.0070	0.0069	-0.0015	0.0089	0.0064	0.0120				
∠HCH at C ₂	-0.0061	0.0060	0.0060	-0.0020	-0.0067	-0.0058	0.0090	0.0090			
l_{12}	0.0059	0.0048	0.0064	0.0007	-0.0075	0.0052	-0.0085	0.0040	0.0015		
l_{13}	0.0032	-0.0029	-0.0029	0.0005	0.0034	-0.0030	-0.0031	0.0020	-0.0020	0.0030	
l_{C-H}	0.0062	0.0060	-0.0035	0.0004	-0.0059	0.0052	0.0025	-0.0061	0.0018	0.0050	0.0010

^a Units for distances in Å; for angles in radians. The elements in the matrix are given by $\sigma_{ij} = \text{sgn}[(BJ^{-1})_{ij}][|(BJ^{-1})_{ij}| \chi_R / (n_q - n_p)]^{1/2}$; $[B] = [J]^T[w]J$. χ_R is the sum of the squares of the residuals, n_q is the number of observations (75), n_p is the number of variable parameters (11), $[J]$ is the Jacobian matrix, $[w]$ is the weight matrix. $w = \exp[-w_1(q_1 - q)]$, $q < q_1$; $w = 1$, $q_1 < q < q_2$; $w = \exp[-w_2(q - q_2)]$, $q > q_2$. The error limits cited in Table I are three times the magnitudes of the σ_{ij} 's.

theoretical and experimental curves. Figure 7 shows in detail the resolution of the asymmetric peak into Gaussians which correspond to C₁-C₂ = 1.556 Å, C₁-C₇ = 1.539 Å, C₂-C₃ = 1.553 Å, and C₁-Cl₁ = 1.773 Å; there are also two nonbonded H···H peaks which contribute a small amount to the total; these

are represented by vertical lines at H₁···H₂ = 1.877 Å and H₉···H₁₀ = 1.836 Å. The third and fourth peaks for $r = 2.0$ -3.6 Å are resolved in Figure 8. These are due to nonbonded distances; only the ones which contribute considerably to the total area were plotted, i.e., C₁···C₄ = 2.229 Å, C₁···C₃ = 2.426 Å, C₂···C₇

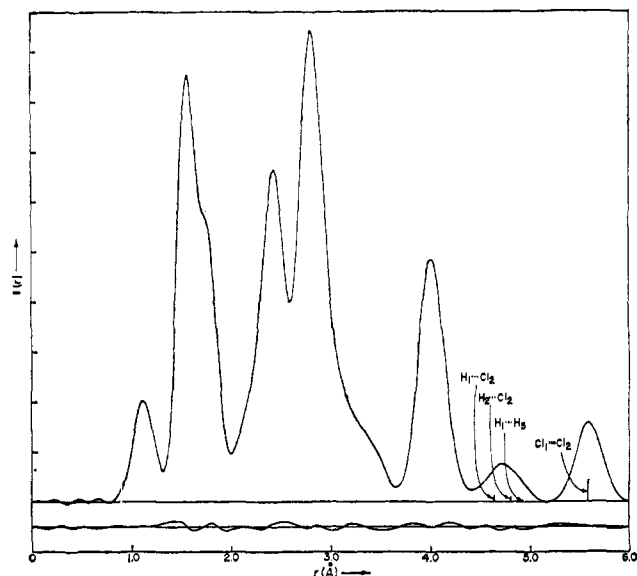


Figure 6. Complete radial distribution curve of 1,4-dichloronorbornane.

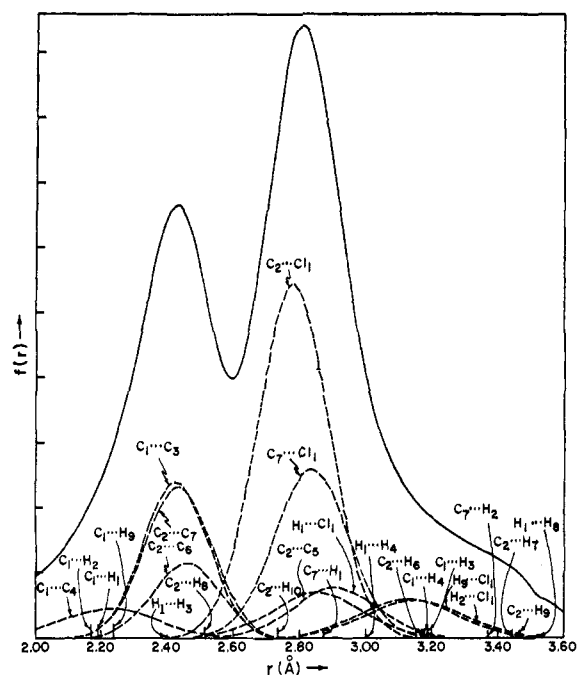


Figure 8. Detailed analysis of the 2.0–3.6-Å region of Figure 6.

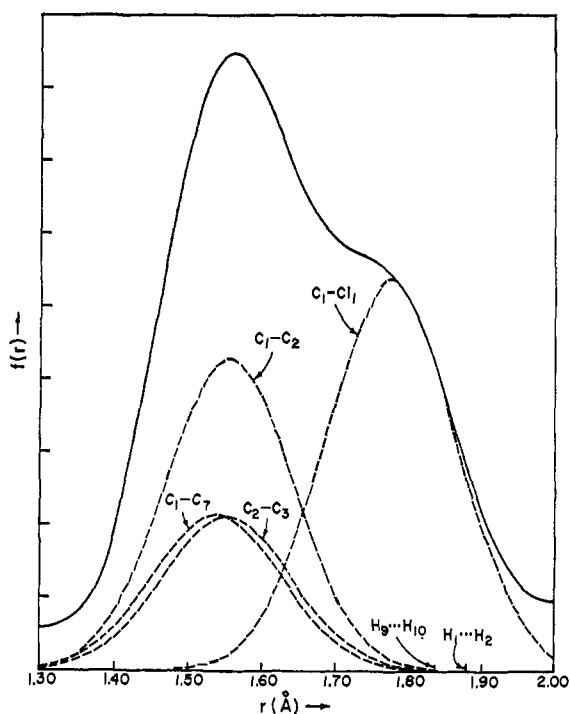


Figure 7. Detailed analysis of the 1.3–2.0-Å region of Figure 6.

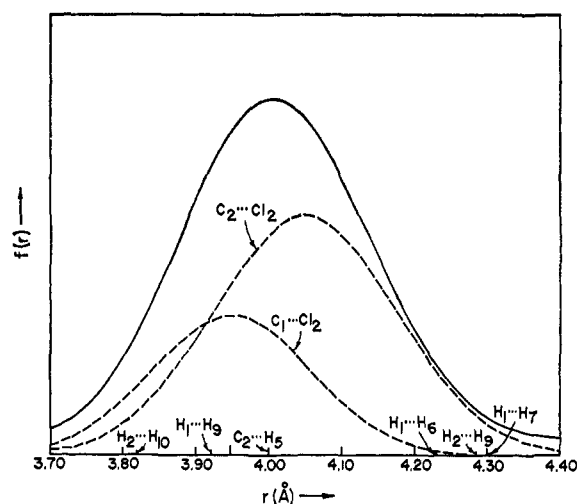


Figure 9. Detailed analysis of the 3.7–4.7-Å region of Figure 6.

$= 2.435 \text{ \AA}$, $C_2 \cdots C_6 = 2.459 \text{ \AA}$, $C_2 \cdots Cl_1 = 2.778 \text{ \AA}$, $C_7 \cdots Cl_1 = 2.835 \text{ \AA}$, $H_1 \cdots Cl_1 = 2.852 \text{ \AA}$, $C_2 \cdots C_5 = 2.909 \text{ \AA}$, $H_2 \cdots Cl_1 = 3.125 \text{ \AA}$, and $H_9 \cdots Cl_2 = 3.152 \text{ \AA}$. The remaining distances were represented by vertical lines.

The fifth peak is shown resolved in Figure 9. It is due to nonbonded distances $H_2 \cdots H_{10} = 3.920 \text{ \AA}$, $C_2 \cdots H_5 = 3.948 \text{ \AA}$, $H_1 \cdots H_6 = 4.260 \text{ \AA}$, $H_2 \cdots H_9 = 4.285 \text{ \AA}$, $H_1 \cdots H_7 = 4.306 \text{ \AA}$, $C_1 \cdots Cl_2 = 3.949 \text{ \AA}$, $C_2 \cdots Cl_2 = 4.049 \text{ \AA}$. The sixth peak is a superposition of $H_1 \cdots Cl_2 = 4.642 \text{ \AA}$, $H_2 \cdots Cl_2 = 4.815 \text{ \AA}$, and $H_1 \cdots H_5 = 4.930 \text{ \AA}$, and the last peak is clearly the single nonbonded $Cl_1 \cdots Cl_2$ distance.

The structural parameters for the carbon skeleton were defined as for norbornane. Six additional variables had to be introduced: θ_1 , ϕ_1 , θ_2 , ϕ_2 define in polar coordinates the positions of the hydrogen atoms 1, 2; r_{C-Cl} and $r_{Cl \cdots Cl}$ locate the chlorine atoms attached to C_1 and C_4 .

In the first execution of the least-squares program the following parameters and l_{ij} 's were allowed to vary: C_1-C_2 , C_1-C_7 , C_2-C_3 , bridge angles, $C-Cl$, l_{12} , (l_{17} , l_{23}), l_{13} , and l_{C-Cl} . In the second set, no constraints were imposed on any of the geometrical parameters and on the following l_{ij} 's: l_{12} , l_{13} , l_{C-Cl} , and l_{C-H} . After 14 cycles, the squares of the sum of the residuals and errors converged to a minimum. This set is listed in Table IV and the corresponding Cartesian coordinates for all the atoms are given in Table II. The error matrix for 1,4-dichloronorbornane is presented in Table V. The quoted uncertainties were taken at three times the calculated standard deviations.

Table IV. Distances in 1,4-Dichloronorbornane

Bonded	r_{ij} , Å	l_{ij} , Å
C ₁ -C ₂ , C ₃ -C ₄ , C ₄ -C ₅ , C ₁ -C ₆	1.556 ± 0.011	0.058 ± 0.003
C ₂ -C ₃ , C ₅ -C ₆	1.553 ± 0.015	0.058 ± 0.003
C ₁ -C ₇ , C ₄ -C ₇	1.539 ± 0.015	0.058 ± 0.003
<C-H> _{av}	1.124 ± 0.021	0.079 ± 0.003
C-Cl	1.773 ± 0.008	0.056 ± 0.003
Bridge angle	92.8 ± 1.0°	
Flap angle	108.1 ± 1.8°	
θ_1	64.65 ± 1.5°	
ϕ_1	65.31 ± 1.5°	
θ_2	155.30 ± 2.0°	
ϕ_2	-25.40 ± 1.8°	
Nonbonded Internuclear Distances (Å)		
C ₁ ...C ₄	2.229 ± 0.009	0.130
C ₁ ...C ₃ , C ₂ ...C ₄ , C ₁ ...C ₅ , C ₄ ...C ₆	2.426 ± 0.009	0.073
C ₂ ...C ₆ , C ₃ ...C ₅	2.459 ± 0.010	0.077
C ₂ ...C ₇ , C ₃ ...C ₇ , C ₅ ...C ₇ , C ₆ ...C ₇	2.435 ± 0.008	0.077
C ₂ ...C ₅ , C ₃ ...C ₆	2.909 ± 0.011	0.110
Cl ₁ ...Cl ₂	5.585 ± 0.003	

Discussion of Structures

The structure of norbornane as derived from this study is shown in Figure 10. The bridge angle is 96.0°; the average C-C bond distance is 1.555 Å, essentially like that reported by Berndt.⁴ The flap angle is 108°,

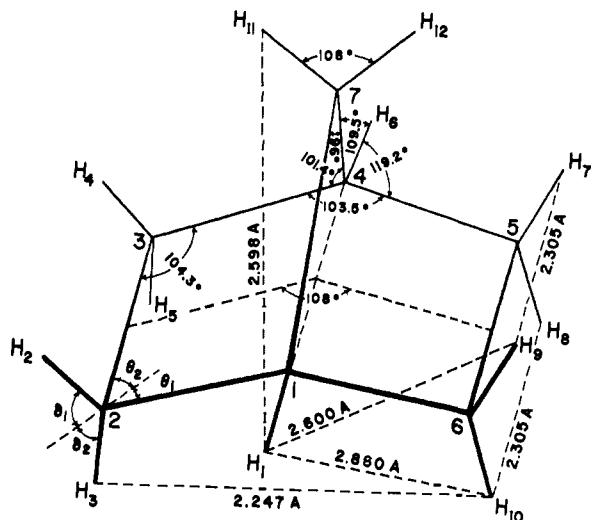


Figure 10. Norbornane.

but the angle C₂C₁C₆ is smaller than that calculated by Kitaygorodsky.^{6a} It is close to the corresponding angle in *anti*-7-norbornylbromobenzoate^{7c} and *anti*-8-tricyclo[3.2.1.0^{2,4}]octyl-*p*-bromobenzenesulfonate.^{7c} The bond angles as derived from this study check those calculated by Wilcox^{6b} using a simple bending force field; they are less than tetrahedral, indicating considerable strain in the carbon skeleton. A comparison of bond lengths and bond angles for norbornane and its related compounds is presented in Table VI. A preliminary electron diffraction study of norbornane was reported by Morino, *et al.*;⁵ they cited 1.547 Å for the average C-C bond distances; this is 0.008 Å shorter than that found in this study. However, the two structures agree within the stated experimental errors.

In considering the structure of 1,4-dichloronorbornane, note that the nonbonded distances between Cl₁

and H₁, H₂, and H₃ place the chlorine atom in a position which is almost equidistant from all nearest neighboring hydrogen atoms; *i.e.*, Cl₁...H₁ = 2.852 Å, Cl₁...H₂ = 3.125 Å, Cl₁...H₃ = 3.152 Å, etc. ∠H₁C₂H₂ is 113° and H₂...H₃ (2.056 Å) is closer than is the corresponding nonbonded H₃...H₁₀ (2.267 Å) in norbornane. In assigning geometric parameters for this compound, we allowed three degrees of freedom for the hydrogen atoms; *i.e.*, we defined all hydrogen atoms except H₉ and H₁₀ in polar coordinates. Thus θ_1 , ϕ_1 , and C-H define the position of H₁ while θ_2 , ϕ_2 , and C-H define H₂; H₃ and H₈ are located by C_{2v} symmetry. Even

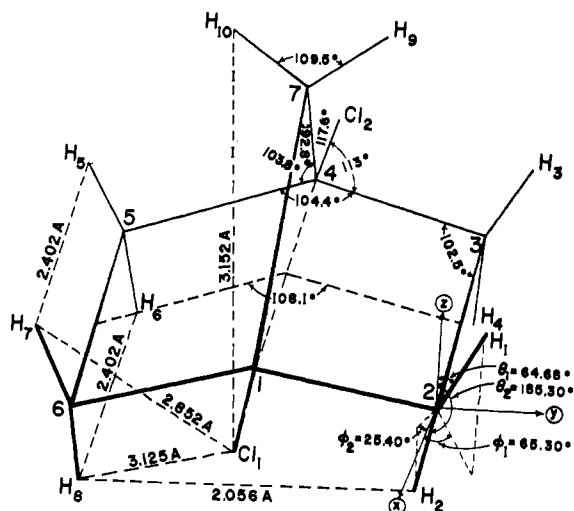


Figure 11. 1,4-Dichloronorbornane.

though each H atom has three degrees of freedom, H₁...H₃ was found to be equal to H₂...H₄ (2.402 Å). Likewise, H₁ in norbornane is also oriented as to be approximately equidistant from its nearest neighboring hydrogen atoms, *i.e.*, H₁...H₂ = 2.580 Å, H₁...H₃ = 2.860 Å, H₁...H₁₁ = 2.598 Å, etc. These nonbonded Cl₁...H and H₁...H distances for 1,4-dichloronorbornane and norbornane are shown in Figures 10 and 11, respectively. The shortening of the H₂...H₃ in 1,4-dichloronorbornane is probably due to the attractions between Cl₁ (or Cl₂) and H₂, H₃ (or H₄, H₆).

Table V. Error Matrix for 1,4-Dichloronorbornane

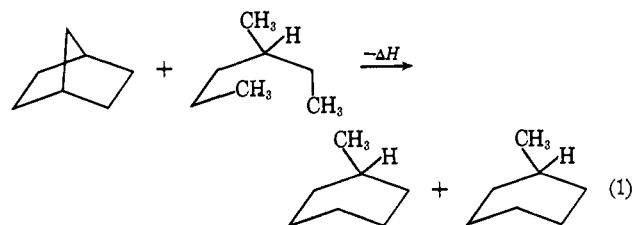
	C ₁ -C ₂	C ₁ -C ₇	C ₇ -C ₃	C-H	Bridge angle	Flap angle	∠HCH at C ₇	C-Cl	Cl...Cl	θ ₁	φ ₁	θ ₂	φ ₂	l ₁₂	l ₁₃	l _{C-H}	l _{C-Cl}	
C ₁ -C ₂	0.0035																	
C ₁ -C ₇	-0.0018	0.0053																
C ₇ -C ₃	-0.0034	-0.0082	0.0052															
C-H	0.0025	-0.0031	-0.0016	0.0070														
Bridge angle	0.0059	-0.0058	0.0085	0.0034	0.0087													
Flap angle	0.0050	-0.0025	-0.0053	0.0019	0.0080	0.0082												
∠HCH at C ₇	-0.0051	-0.0050	0.0046	0.0044	0.0045	-0.0078	0.0080											
C-Cl	-0.0027	0.0041	-0.0004	-0.0007	-0.0049	0.0021	-0.0036	0.0027										
Cl...Cl	-0.0037	0.0028	0.0034	-0.0027	-0.0048	-0.0057	0.0086	0.0028	0.0010									
θ ₁	-0.0052	-0.0028	0.0034	-0.0027	-0.0023	-0.0048	0.0086	-0.0012	0.0065	0.0093								
φ ₁	-0.0062	0.0056	0.0082	-0.0021	-0.0067	-0.0065	0.0038	0.0029	0.0042	0.0051	0.0075							
θ ₂	0.0074	-0.0040	-0.0096	-0.0059	0.0045	0.0034	0.0078	0.0018	-0.0094	0.0054	-0.0095	0.0105						
φ ₂	-0.0050	0.0075	-0.0021	-0.0010	-0.0082	-0.0064	-0.0056	0.0014	0.0056	0.0008	0.0022	-0.0052	0.0086					
l ₁₂	-0.0056	0.0065	0.0088	0.0020	-0.0072	-0.0073	0.0076	0.0028	0.0090	0.0056	-0.0054	-0.0073	0.0087	0.0030				
l ₁₃	0.0095	-0.0070	0.0090	-0.0036	0.0080	-0.0039	0.0039	-0.0082	-0.0050	0.0067	-0.0055	0.0059	-0.0051	0.0036	0.0021			
l _{C-H}	0.0031	-0.0055	-0.0037	0.0087	0.0015	0.0025	0.0050	-0.0051	0.0037	-0.0072	0.0056	0.0070	0.0034	-0.0061	0.0050	0.0010		
l _{C-Cl}	0.0023	0.0062	0.0030	-0.0051	0.0020	0.0011	0.0040	0.0063	0.0019	0.0031	0.0039	0.0035	0.0027	-0.0028	-0.0035	0.0028	0.0010	

Both norbornane and the 1,4-dichloride show a marked distortion of the bridgehead (C₁ and C₄) angles from tetrahedral values. This distortion can be gauged by comparing the sum of the three internal skeletal angles around the bridgehead atom (308° for norbornane and 313° for the dichloride) with the sum expected for a tetrahedral arrangement, 325°. An alternate, more easily visualized, means for quantifying this distortion is to compare the perpendicular distances of the bridgehead carbons above the plane defined by C₂, C₆ and C₇. For a tetrahedral arrangement, using an averaged C-C distance appropriate for these molecules, the perpendicular distance is 0.52 Å. The observed value for norbornane is 0.69 Å while in the dichloride it is 0.64 Å.

This manner of expressing the distortion also highlights the significant flattening of the bridgehead position in the dichloride relative to the parent unsubstituted norbornane. As has been suggested elsewhere⁶ the flattening accompanying substitution by two strongly electronegative atoms may be responsible in part for the relative difficulty in forming the monolithium derivative of the dichloride compared with the formation of the dilithium derivative of the parent.

The decrease in the internal skeletal angles of norbornane compared to tetrahedral values implies an increase in the p character of the orbitals of the bridgehead carbons used in forming the C₁-C₂, C₁-C₆, and C₁-C₇ bonds, and a corresponding increase in s character of the bridgehead orbital used to form the external bonds to hydrogen. These implied changes in hybridization are qualitatively consistent with the data and suggestions of Tori, *et al.*,¹² on the C¹³-H coupling constant for bridgehead C-H bonds of norbornane ($J = 142 \pm 2$ cps). The simple expression for relating fractional s character to coupling constant, %s = $J_{C^{13}-H}/500$, gives 28% for the external C₁ and C₄ orbitals. This is considerably less than the 48% which would be predicted were the orbitals constrained to lie along the lines of centers joining the C₁ atom to C₂, C₆, and C₇. Like in cyclopropane, however, "banana" bonds may be present so that the observed value is reasonable and our structure consistent with it.

The strain energy of norbornane has been estimated by Bedford, *et al.*,¹³ to be 18.5 ± 0.4 kcal/mole, by equating it to the enthalpy increment for the hypothetical reaction shown below. The magnitude was obtained from the measured heat of combustion of solid norbornane, a reasonable estimate of the heat of fusion of norbornane and literature values for the heats of formation of liquid methylcyclohexane and liquid 3-methylhexane.

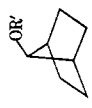
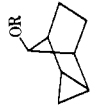
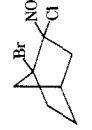
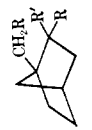
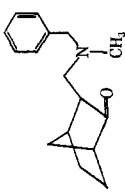


The identification of the norbornane strain with the enthalpy change for this reaction presumes that methyl-

(12) K. Tori, *et al.*, *Can. J. Chem.*, **41**, 3142 (1963).

(13) A. F. Bedford, *et al.*, *J. Chem. Soc.*, 3823 (1963).

Table VI. Comparison of Bond Angles (degrees) of Norbornane and Related Compounds

Compound	Norbornane									Longifolene ^b	
	This study	Morino, <i>et al.</i>	Berndt	Wilcox ^a	Kitaygorodsky ^a						
Bridge angle	96.0	93.2	96.3	94-96	92	96.0	97.0	95	93	94	93.5
Flap angle	108.0	113.0	...	109.0
$\angle C_2C_1C_6$	103.5	107.2	105.2	...	109.5	104	105	108	...	97	110.7
$\angle C_3C_4C_5$	103.5	107.2	105.2	...	109.5	107	107	114	...	103	108.9
$\angle C_1C_2C_3$	104.3	105.1	...	104	103	101	103	107	106	104	102.3
$\angle C_2C_3C_4$	104.3	105.1	...	104	103	104	103	100	103.5	103	102.9
Ref		5	4	6b	6a	7c	7c	7a	7b		7d

^a Calculated values. ^b A. F. Cesur and D. F. Grant, *Acta Cryst.*, **18**, 55 (1965).

cyclohexane and 3-methylhexane are devoid of strain. The group additivity corrections of the Franklin scheme for calculating heats of formation of organic materials¹⁴ suggests that molecules containing a cyclohexane ring have a small negative strain (stabilization) of about -0.5 kcal/mole. This lowers the apparent strain energy of norbornane to 17.5 kcal/mole. An additional correction should be made, since *n*-heptane rather than 3-methylhexane should be used for the reference compound. In this way one not only balances changes in bonds but also changes in the groups (CH, CH₂, CH₃) that accompany the relief of strain in norbornane. The additional correction raises the norbornane strain energy to 18.2 kcal/mole.

An alternate deduction of the strain energy of norbornane is to use the Franklin group additivity method to calculate the energy of a hypothetical strainless molecule containing five CH₂ groups and two CH groups. One then concludes that the strain in gaseous norbornane is $[4.8 + \Delta H_{\text{sub}}]$, which with a reasonable value, for the sublimation energy of 13 kcal/mole leads to 17.8 kcal/mole. The two estimates are in reasonably satisfactory accord. The maximum error in the strain energy appears to be less than ± 2 kcal/mole.

It is of considerable interest to compare this magnitude with a value calculated according to the scheme of Allinger,¹⁵ using the atomic coordinates obtained in this investigation. His procedure, and others closely related to it,¹⁶⁻²⁰ has been strikingly successful for estimating differences in the energies of conformational isomers. Calculation of the total "strain" of a single,

(14) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

(15) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. Tymiński, and F. A. VanCatledge, *J. Am. Chem. Soc.*, **90**, 1199 (1968). In the original version of this manuscript calculations were made using Allinger's first model [N. L. Allinger, *et al.*, *ibid.*, **89**, 4345 (1967)]. Because of major improvement in the prediction of strain energies of highly strained molecules afforded by the new model, the manuscript was revised. We thank Dr. Allinger for making a copy of his manuscript available to us prior to its publication.

(16) G. J. Gleicher and P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 582 (1967).

(17) J. B. Hendrickson, *ibid.*, **83**, 4537 (1961); **84**, 3355 (1962); **86**, 4854 (1964); **89**, 7036, 7043, 7047 (1967).

(18) K. B. Wiberg, *ibid.*, **87**, 1070 (1965).

(19) M. Bixon and S. Lifson, *Tetrahedron*, **23**, 769 (1967).

(20) It was our intention at the outset to include in this analysis the interesting scheme proposed by L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960); **47**, 3736 (1967). However, establishing the appropriate zero reference energies appears to be very tedious, and worthy of a separate detailed analysis.

highly distorted molecule like norbornane is, however, a more challenging test. In the Allinger scheme one assumes that the strain is the sum of bond stretching, angle bending, torsion, and nonbonded interaction contributions. Table VII lists values for each of these

Table VII. Contributions to the Strain Energy of Norbornane (kcal/mole) According to Allinger¹⁵

Bond stretching	3.85
Angle bending	7.47
Torsional	6.14 ^a
Nonbonded interactions	0.04
Total (uncorrected for reference state)	17.50
Correction for reference compounds	-0.38
Total strain	17.12

^a Of this total 1.45 kcal/mole arises from 1,4 nonbonded interactions.

for norbornane. Note that Allinger's scheme is based on reproducing internuclear distances as deduced from microwave data. To make this procedure compatible with r_g electron diffraction distances which are generally larger,²¹ an average increment of 0.006 Å was added to Allinger's r_{CC}^0 values. Allinger's second scheme¹⁵ differs from his first (and from others) in its use of a sigmoid relation for angles distorted by 0.5° or more, rather than the usual quadratic potential. This diminution of the effective bending force constant with increasing departure from the minimum leads to a striking drop in the angle bending strain.²² In Table VII, the 1,4 nonbonded interactions have been included as part of the torsional contribution. This allows direct comparison of the torsional contribution with that of other schemes.

The net value of 17.5 kcal/mole must be corrected for the residual strain left in the reference compounds used in eq 1. From the data given by Allinger on the alkanes one may estimate that *n*-heptane would have a calculated strain energy of 0.86 kcal/mole, so that with his value of 0.62 kcal/mole for *one* methylcyclohexane the calculated energy change for reaction 1 in the absence of

(21) D. R. Lide, Jr., *Tetrahedron*, **17**, 125 (1962); L. S. Bartell and D. A. Kohl, *J. Chem. Phys.*, **39**, 3097 (1963).

(22) For example, with a quadratic law and typical valence force constants the angle strain of norbornane is of the order of 16-19 kcal/mole. In Allinger's model (see Table VII), it drops to 7.5 kcal/mole. Schleyer's scheme¹⁶ leads to a total strain energy of 28 kcal/mole.

strain in norbornane is +0.38 kcal/mole. Subtracting this amount gives the total calculated strain of 17.1 kcal/mole for norbornane.²³

Although the calculated value for the energy is in striking agreement with that observed (17.8–18.2 kcal/mole), Allinger's deduction of the geometry of norbornane at minimum energy is regrettably in poor agreement with observation. While the angles he calculated²⁴ correspond fairly well to our measured ones, all the C–C internuclear distances are smaller by about 0.03 Å, even after adding the 0.006 Å for conversion to the microwave scale.²¹ Worse yet, the model calculation predicts $(C_2-C_3) \approx (C_1-C_2) > (C_1-C_7)$ while the observed distances decrease in the reverse order. Finally, Allinger found that his minimum energy structure had a strain energy of 12 kcal/mole; consequently, corre-

(23) This is not entirely correct since the calculated value is for a single linear conformation rather than for the mixture actually present in *n*-heptane, in terms of which the strain energy of norbornane is defined. Properly, the energy of any single species should be weighted over the energies of the different conformations accessible to the system. A calculated energy based on the single most stable species tends to be too negative, the more so as the number of accessible states increases. On the other hand, the parameters of the model have been selected to reproduce heats of isomerization such as that accompanying *n*-butane to isobutane, and thus indirectly the requisite weighting has already (but approximately) been included.

(24) N. L. Allinger, private communication.

spondence of the value calculated in this paper with the observed magnitude of (17.8–18.2) kcal/mole must be largely fortuitous. It appears that, despite the success of both of Allinger's models in calculating differences in conformational energies of flexible molecules, they do not satisfactorily reproduce the value or the character of strain present in norbornane.

The present analysis suggests a hierarchy of difficulties in testing theory against experiment. All of the strain models in use today appear to be successful in reproducing conformational energy differences. Less accurately, but still acceptably, is the applicability of the models in seeking the correct minimum energy structure. The least reliable results appear to be the calculated strain energies of highly distorted molecules.

Acknowledgments. The authors express their sincere thanks to the National Science Foundation, GP-4291, and the Material Science Center, ARPA-SD-68, for support of the work presented in this report. The structural study of these compounds was initiated by Dr. Mary E. Wilcox, who made preliminary analyses of the electron diffraction photographs. We also thank Dr. Robert K. Bohn for taking the second set of electron diffraction photographs on the Oslo apparatus and for providing us with copies of his reduced intensity scattering patterns.

Dielectric Dispersion and Chemical Relaxation

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Received January 3, 1968

Abstract: Starting from Debye's concept of dielectric dispersion, it is shown how chemical relaxation effects can contribute to the frequency dependence of dielectric permittivity. Since for rapidly orienting dipole molecules the chemical effect is nonlinear, it can be observed only if a very strong dc field is superimposed to the alternating field. The chemical-field effect could be identified for dimerization and association processes involving H-bond chelation. The dispersion range was found to be in the MHz region and thus clearly separated from the orientational relaxation in the microwave range. The magnitude of the chemical effect is very small and requires very sensitive methods of detection. The technique opens the possibility of studying the elementary steps of base pairing as involved in the information transfer in nucleic acids.

I. The Debye Curve of Dielectric Dispersion

Among Peter Debye's various achievements, the interpretation of the phenomena of electrical polarization stands up as a landmark in molecular physics. Actually, this subject intrigued him so much, that the only book he wrote¹ was dedicated to this field. It was especially the dynamic behavior of polar molecules on which he centered his interest.

The anomalous dispersion of the dielectric constant of certain substances was already observed by Drude² as early as 1895, but it was Debye³ who could show that this phenomenon was due to the existence of polar

molecules, which can be oriented by an electric field. The dielectric dispersion then can be explained by a delay of orientation due to the viscous motion of the molecular dipoles. The temporal delay can be characterized by a time constant τ_{or} . In an alternating field of the (angular) frequency ω ($\approx 1/\tau_{or}$), the polarization will lag behind the orienting field with a phase angle $\varphi = \arctan(\omega\tau_{or})$. At the same time the amplitude of the orientational polarization will decrease, and an energy loss will occur showing up as a contribution to electrical conductivity.

Both amplitude dispersion and energy loss can be described by a complex dielectric permittivity

$$\epsilon_0\epsilon_\omega + \frac{\epsilon_0\epsilon_{or}}{1 + j\omega\tau_{or}} \quad (1)$$

(1) P. Debye, "Polare Molekeln," S. Hirzel Verlag, Leipzig, 1929;

"Polar Molecules," New York, N. Y., 1929.

(2) P. Drude, *Z. Physik. Chem.*, **23**, 267 (1897).

(3) P. Debye, *Verhandl. Deut. Phys. Ges.*, **15**, 777 (1913).