In chlorocyclopropane[13] the carbon skeletal structure is an equilateral triangle with C–C bond lengths of 1.514 Å. In cyclopropanone the C_1–C_2 and C_1–C_3 bond length of 1.475 Å is smaller than the other cyclopropanes previously measured, but agrees well with the C–C bond lengths of the strained-ring compounds ethylene oxide (C–C = 1.472 Å) and ethylene sulfide (C–C = 1.492 Å).[14] The C–O bond length of 1.191 Å is approximately the same as formaldehyde.[15] The long C_2–C_3 bond length coupled with the shorter C_1–C_2 and C_1–C_3 bonds lengths (1.475 Å) would seem to suggest that cyclopropanone contains one especially weak carbon–carbon bond. This long bond is the one which is broken in reactions between cyclopropanone or substituted cyclopropanones with dienes such as furan to give cycloadducts.[16–23] The lengthening of the C_2–C_3 bond is also in agreement with the work of Scharpen and Laurie on cyclobutanone.[7] In cyclobutanone, the $C_2C_1C_4$ angle (C_1 bonding to the oxygen atom) of 93.1 ± 0.3° might indicate that the carbonyl bonding in the molecule is tending to enlarge the $C_2C_1C_4$ angle, making the C_2–C_4 distance larger than expected. This would be analogous to cyclopropanone, where the C_2–C_1–C_3 angle is 64° 36′, but the effect is not as acute. It is also interesting to note the angle of 29 ± 2° for the HCH plane angle with the C_2–C_3 axis.

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The Molecular Structure of Cyclohexene

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Abstract: The molecular structure of cyclohexene in the vapor phase has been determined by electron diffraction. The molecule has C_2 symmetry, in the half-chair conformation, in agreement with other studies of cyclohexene and of its derivatives. The geometrical parameters, obtained by least-squares analysis of the reduced molecular intensity pattern, are: $C_1{=}C_2 = 1.335 \pm 0.003$ Å, $C_2{-}C_3 = 1.504 \pm 0.006$ Å, $C_3{-}C_4 = 1.515 \pm 0.020$ Å, $C_4{-}C_5 = 1.550 \pm 0.040$ Å, $C{-}H = 1.093 \pm 0.015$ Å; $\angle C_2C_1C_6 = 123.5°$, $\angle C_1C_6C_5 = 121.1°$, $\angle C_3C_4C_5 = 111.0°$.

More than a quarter of a century ago Lister[1] proposed a half-chair conformation for cyclohexene on the basis of his measurements of the heats of bromination of cyclic olefins. Later Pitzer, *et al.*,[2] calculated the energy for different conformations and concluded that the most stable conformation was indeed the half-chair form (C_2 symmetry), to the extent of 2.7 kcal/mol lower than the half-boat configuration. Subsequently other theoretical calculations on the conformation of cyclohexene[3–5] were published; all of them concluded that the lower energy form has C_2 symmetry and the energy difference is about twice the above value. Since there has been no experimental determination of the molecular structure of cyclohexene, this investigation was deemed necessary.

Experimental Section

The purified sample of cyclohexene was kept at −30°. Sectored electron diffraction patterns were taken with our new apparatus under the following conditions: high-voltage beams (70 kV) at sample-to-plate distances of 262.4 and 129.4 mm. An additional set was obtained at low voltage (25 kV), with $L = 262.4$ mm. Diffraction patterns were recorded using several exposure times on 4 × 5 in. Kodak process plates; magnesium oxide patterns were recorded concurrently to establish the scale factor. The gas patterns were microphotometered with a double-beam Jarrell-Ash microdensitomer interfaced with a digital recorder. The procedure for data reduction has been described previously.[6]

Analysis and Results

The total experimental intensity curves for the three sets of data along with the refined background are plotted in Figure 1. The reduced experimental molecular intensity curve and that calculated for the best model are compared in Figure 2; the difference curve is also shown. The refined radial distribution curve and the difference

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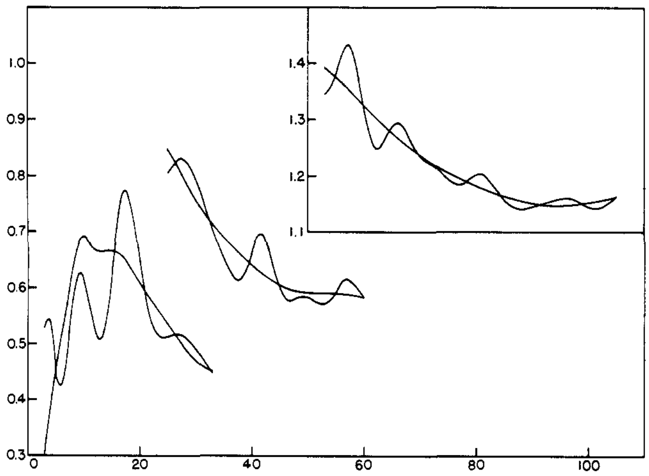

Figure 1. The experimental intensity and the refined background for cyclohexene.

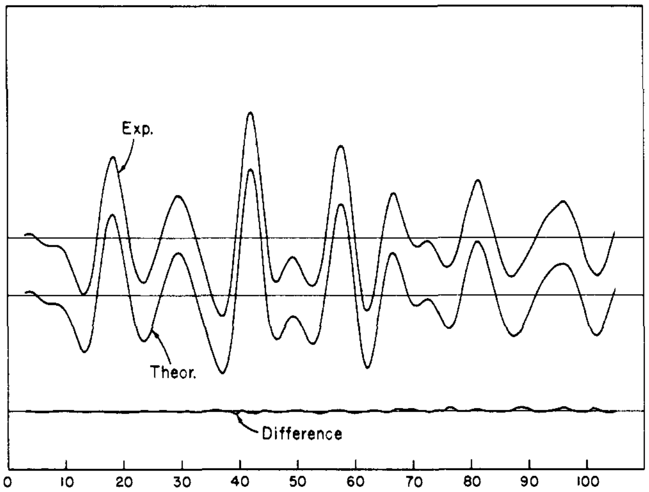

Figure 2. Experimental and theoretical molecular intensity curves for cyclohexene. The lower oscillating curve is the difference between the reduced molecular scattering and that calculated for the best model.

between that and the best theoretical radial distribution curves for half-chair and half-boat forms are shown in Figure 3. Both models were tested extensively with various combinations of bond distances and bond angles. None of the half-boat models could be brought into agreement with the experimental data. The C_2 symmetry conformation was defined as follows: carbon atoms 1, 2, 3, 6 (refer to Figure 6) and hydrogen atoms 7, 8 are coplanar (in the xy plane). The x axis is coincident with the C_1–C_2 bond and the y axis is in the plane of C_1, C_2, C_3, C_6 and perpendicular to x axis; C_5 is situated below the xy plane while C_4 is above the plane. The following parameters determine the geometry of the molecule: C_1–C_2, C_2–C_3, C_3–C_4, C_4–C_5, C_1–H_7, C_3–H_9, α, δ, γ. The angle α is that between C_1–C_6 and the x axis, δ is $\angle H_7C_1C_2$, and γ is the angle C_5–C_6 makes with the z axis. Polar coordinates were introduced to locate the positions of hydrogen atoms attached to C_3, C_4, C_5, and C_6. η,σ, and θ,ξ define H_{14} and H_{13}; τ,ρ and ψ,ϕ define H_{16} and H_{15}. (For definition of these angles, see Figure 4.)

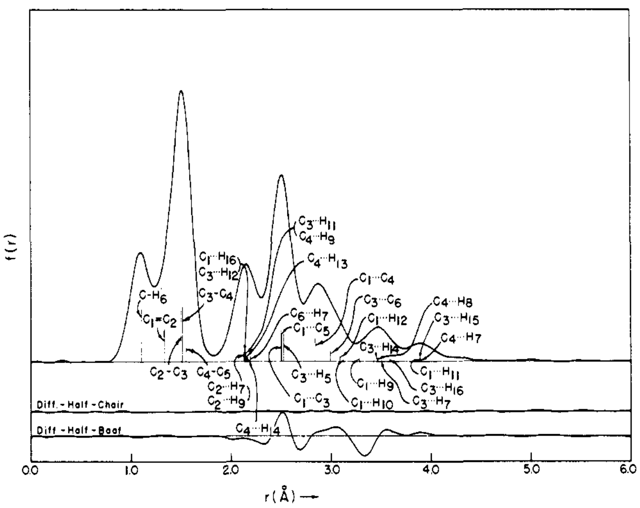

Figure 3. Radial distribution curve for cyclohexene. The lower oscillating curve is the difference between the experimental and theoretical radial distribution functions.

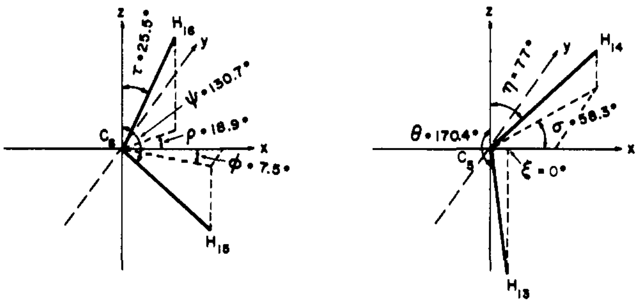

Figure 4. The polar coordinates for H_{13}, H_{14}, H_{15}, and H_{16}.

A least-squares analysis has been applied to the experimental intensity. The calculation converged after 15 cycles. Values for all the geometric parameters and for l_{12}, l_{35}, l_{56} were allowed to vary, except C–H, α, and ξ, which were constrained. The parameters and l_{ij}'s which gave the smallest residuals and errors are listed in Table I. The atomic coordinates obtained from the least-squares analysis are listed in Table II. The error matrix is reproduced in Table III. The diagonal elements are the standard deviations for the corresponding parameters, while the off-diagonal elements are measures of the correlations between parameters. As expected, there are significant correlations between several of the angles which locate the hydrogen atoms.

In the radial distribution curve the first peak at 1.093 Å is due to the bonded C–H distances. The second at 1.518 Å is the superposition of all bonded C–C distances, *i.e.*, C_1–C_2 = 1.335 Å, C_1–C_6 = 1.504 Å, C_3–C_4 = 1.515 Å, and C_4–C_5 = 1.550 Å. The third peak, at 2.14 Å, consists of nine nonbonded C···H and H···H distances. The nonbonded C···C distances $C_1\cdots C_3$ = 2.501 Å, $C_1\cdots C_5$ = 2.505 Å, $C_3\cdots C_5$ = 2.526 Å, and nine other nonbonded H···H distances compose the fourth peak. The fifth peak is produced by $C_1\cdots C_4$ = 2.845 Å, $C_3\cdots C_6$ = 2.993 Å, six different nonbonded C···H, and two H···H distances. The remaining peaks are due to more distant C···H and H···H nonbonded

Table I. Geometrical Structure Parameters and Internuclear Distances in Cyclohexene

	r_{ij}, Å	l_{ij}, Å
$C_1{=}C_2$	1.335 ± 0.003[b]	0.048 ± 0.002
C_1—C_6, C_2—C_3	1.504 ± 0.006	0.063 ± 0.010
C_3—C_4, C_5—C_6	1.515 ± 0.020	0.057 ± 0.010
C_4—C_5	1.550 ± 0.040	0.049 ± 0.006
C—H_{av}	1.093 ± 0.015	0.078 ± 0.008
	γ[a] 104.0 ± 0.7	τ 25.7 ± 2.5
	δ 122 ± 5	ρ 18 ± 5
	ψ 129 ± 6	η 76 ± 7
	ϕ 8 ± 5	σ 59 ± 8
		θ 170.0 ± 1.0
	Nonbonded C···C Distances[c]	
		l_{ij} (est)
$C_1 \cdots C_3$, $C_2 \cdots C_6$	2.501	0.061
$C_1 \cdots C_4$, $C_2 \cdots C_5$	2.845	0.085
$C_1 \cdots C_5$, $C_2 \cdots C_4$	2.505	0.085
$C_3 \cdots C_6$	2.993	0.080
$C_3 \cdots C_5$, $C_4 \cdots C_6$	2.526	0.070

[a] Angles in degrees. [b] The error limits cited here are three times the magnitudes of the σ_{ii}'s in Table III. [c] All nonbonded distances were calculated from the geometrical parameters and are given in ångströms.

Table II. Cartesian Coordinates from Least-Squares Analyses

	x	y	z
1	0.6672	0.0	0.0
2	−0.6672	0.0	0.0
3	−1.4966	1.2544	0.0
4	−0.6823	2.4779	0.3673
5	0.6823	2.4779	−0.3673
6	1.4966	1.2544	0.0
7	1.2553	−0.9213	0.0
8	−1.2553	−0.9213	0.0
9	−2.3347	1.1369	0.6917
10	−1.9468	1.4004	−0.9852
11	−1.2339	3.3827	0.0993
12	−0.4950	2.4779	1.4441
13	0.4950	2.4779	−1.4441
14	1.2339	3.3827	−0.0993
15	2.3347	1.1369	−0.6917
16	1.9468	1.4004	0.9852

distances. The locations of these distances are indicated by vertical lines, 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 corresponding distance between atoms of atomic numbers Z_i and Z_j. The structure and magnitudes of the bonded distances and angles in cyclohexene are shown in Figure 5.

Discussion

In cyclohexene, as shown in Figure 5, the twofold axis intercepts the centers of the $C_1{=}C_2$ and C_4—C_5 bonds. The conformation of this molecule agrees very well with that calculated by Bucourt, *et al.*[5] (refer to Figure 6, notation of Bucourt). As mentioned in the introduction, the energy difference between the two conformations was estimated to be 4.33 kcal/mol by Allinger, *et al.*[4] The half-chair conformation of cyclohexene was indicated by its infrared and Raman spectra,[7] and it is consistent with the Raman spectrum of 4,5-dichlorocyclohexene,[8] X-ray diffraction studies of pentachlorocyclohexene,[9] and electron diffraction results for 3,4,5,6-tetrachlorocyclohexene.[10] A half-chair conformation is also present in cyclohexene oxide.[11,12]

Table III. Error Matrix for Cyclohexene[a]

	$C_1{=}C_2$	C_2—C_3	C_3—C_4	C_4—C_5	γ	δ	ψ	ϕ	τ	ρ	η	σ	θ	l_{12}	l_{16}	l_{45}
$C_1{=}C_2$	0.0012															
C_2—C_3	−0.0007	0.0023														
C_3—C_4	0.0023	0.0019	0.0076													
C_4—C_5	−0.0025	−0.0043	−0.0105	0.0157												
γ	−0.0041	−0.0181	−0.0373	0.0595	0.2454											
δ	−0.0233	−0.0476	−0.1029	0.1592	0.6476	2.1709										
ψ	−0.0307	−0.0411	−0.0743	0.0991	0.2998	0.4390	2.5657									
ϕ	0.0371	0.0364	0.0770	−0.0888	−0.1482	0.6354	−2.1565	2.2726								
τ	0.0112	0.0270	0.0680	−0.1034	−0.4314	−1.3016	0.2804	−0.5384	1.0517							
ρ	0.0245	−0.0128	0.0908	−0.1199	−0.4601	−1.3802	1.0081	−0.9558	1.1894	2.2282						
η	−0.0353	−0.0453	−0.0922	0.1273	0.4356	1.3226	2.4019	−1.9999	−0.7339	0.7414	2.4873					
σ	0.0279	0.0721	0.1129	−0.1851	−0.7783	−2.5242	0.7624	0.1567	1.3849	1.1097	−1.4708	3.9660				
θ	−0.0108	0.0198	−0.0225	−0.0111	−0.0941	0.2248	−0.4345	0.3101	−0.2972	−0.5791	−0.3601	0.3215	0.3571			
l_{12}	0.0001	0.0008	0.0019	−0.0030	−0.0121	−0.0293	−0.0120	0.0100	0.0212	0.0254	−0.0165	0.0341	0.0030	0.0011		
l_{16}	0.0010	0.0028	0.0057	−0.0090	−0.0355	−0.0917	−0.0562	0.0480	0.0609	0.0671	−0.0701	0.1098	0.0151	0.0019	0.0054	
l_{45}	0.0015	−0.0010	0.0036	−0.0040	−0.0070	−0.0396	−0.0404	0.0448	0.0171	0.0340	−0.0518	0.0374	−0.0168	−0.0009	0.0012	0.0030

[a] Units for distances in ångströms; for angles in degrees. $\sigma_{ij} = \mathrm{sgn}[(BJ^{-1})_{ij}][|([B]^{-1})_{ij}|\chi_R/(n_q - n_p)]^{1/2}$; $[B] \equiv [J]^t[w][J]$, where χ_R is the sum of the squares of the residuals, n_q is the number of observations (105, at integral q's), n_p is the number of variable parameters (16), $[J]$ is the Jacobian matrix, and $[w]$ is the weight matrix. $w = \exp[-w_1(q_1 - q)]$ for $q < q_1 = 15$; $w = 1$ for $q_1 < q < q_2$; $w = \exp[-w_2(q - q_2)]$ for $q > q_2 = 95$; w_1 and w_2 is adjusted so that $w(q_{min}) = 0.1$, $w(q_{max}) = 0.25$.

The question arose whether the *relative* stabilities of the conformations and heats of formation of cyclohexene, cyclohexane, and cyclohexadiene are correctly predicted by one of the currently used empirical prescrip-

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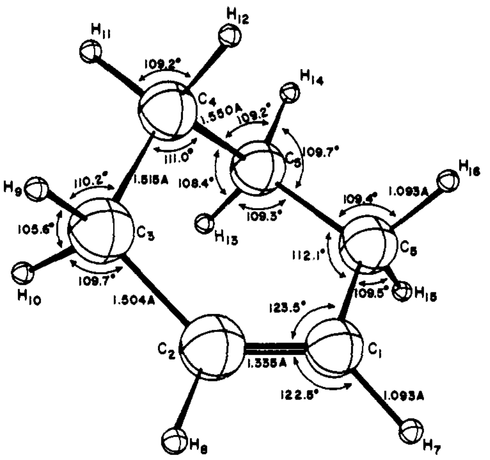


Figure 5. The structure of cyclohexene.

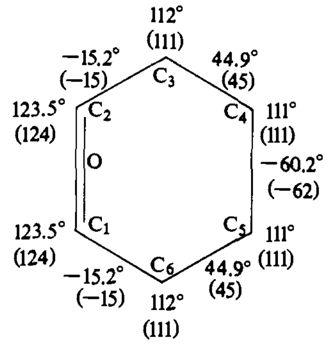
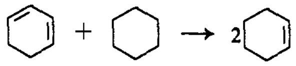


Figure 6. Comparison of the experimental and theoretical conformations of cyclohexene. The values in parentheses were calculated by Bucourt, *et al.*[5] The values at the corners of the hexagon refer to CCC angles while those at the centers of each bonds refer to the dihedral angles for the adjacent CC bonds; for example, the value −15.2° at C_2C_3 is the angle between the planes of $C_1C_2C_3$ and $C_4C_3C_2$, etc.

tions for estimating strain energies. We selected for this test the procedure by Bartell, *et al.*[13] The results of this calculation, closely similar to that performed for the cyclohexadienes,[14] are summarized in Table IV. What appears to be a more successful prescription[4] has not yet been extended to the cyclodienes. The heats of formation of cyclohexene[15] ($\Delta H_{f3} = -1.72$ kcal/mol), cyclohexane[15] ($\Delta H_{f2} = -29.43$ kcal/mol), and cyclohexadiene[16] ($\Delta H_{f1} = 24.17$ kcal/mol) were combined for the hypothetical reaction 1. One obtains for the heat of reaction $\delta(\Delta H_f) = 2\Delta H_{f3} - \Delta H_{f2} - \Delta H_{f1} = 1.82$ kcal/mol. On the other hand, one may estimate the quantity, δE, which is comparable to $\delta(\Delta H_f)$, from the "strain energies" of cyclohexene ($E_3 = 191.57$ kcal/mol), cyclohexane ($E_2 = 224.95$ kcal/mol), and cyclohexadiene

Table IV. Strain Energy for Half-Chair, Half-Boat, and Planar Conformations of Cyclohexene (in kcal/mol)

	Half-chair	Half-boat	Planar
Bond stretching	65.18	65.18	65.18
Angle bending	0.66	6.22	5.32
Torsional	3.24	9.85	7.83
Nonbonded interactions	122.49	127.79	128.76
Total	191.57	209.04	207.09
Strain Energy for Cyclohexane and 1,3-Cyclohexadiene			
Bond stretching	86.81	49.98	
Angle bending	0.65	0.11	
Torsional	1.59	3.26	
Nonbonded interactions	135.90	99.46	
Total	224.95	152.81	



(1)

($E_1 = 152.81$ kcal/mol), all calculated according to Bartell's scheme: $\delta E = 2E_3 - E_2 - E_1 = 5.38$ kcal/mol. In the above calculations we note that the same number of single and double bonds are present in the reactions and products and assumed that (a) the butadiene resonance in cyclohexadiene is negligible and (b) that the number of single bonds adjacent to double bonds, etc., is essentially equivalent. To this approximation the quantities $\delta(\Delta H_f)$ and δE check each other.

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