

ethylene sites, and that the subsequent ethylene adsorption displaces the adsorbed H₂, but this seems unlikely. Secondly, the ethylene sites are not related to the color centers. The latter are bleached very rapidly by the addition of H₂ (and D₂), and yet the C₂H₄ subsequently adsorbs as normal. Furthermore,

if the ethylene is added first, color still remains in the sample, and subsequent addition of H₂, after removing the gaseous C₂H₄, bleaches all the color. Finally, none of the unpaired electrons which are observed in the e.s.r. spectrum are related to the sites responsible for C₂H₄ chemisorption.

[CONTRIBUTION NO. 1229 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY, BLOOMINGTON, INDIANA]

The Molecular Structure of 1,3,5-Cycloheptatriene in the Vapor Phase as Determined by the Sector Electron Diffraction Method

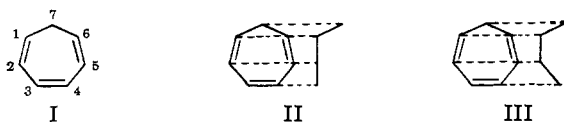
BY MARIT TRÆTTEBERG¹

RECEIVED FEBRUARY 10, 1964

The sector electron diffraction method was used to determine the molecular structure of 1,3,5-cycloheptatriene in the vapor phase. The molecule possesses C_s symmetry, and the most important observed structural results are as follows (for numbering of the atoms, see Fig. 5): $r_g(\text{C}_1-\text{C}_2)$ (assumed equal to $r_g(\text{C}_3-\text{C}_4)$) = 1.356, $r_g(\text{C}_2-\text{C}_3)$ = 1.446, $r_g(\text{C}_6-\text{C}_7)$ = 1.505, $r_g(\text{C}_1-\text{C}_6)$ = 2.511, $r_g(\text{C}_2-\text{C}_5)$ = 2.792, $r_g(\text{C}_3-\text{C}_4)$ = 2.424, $r_g(\text{C}_2-\text{C}_7)$ = 2.501, $r_g(\text{C}_1-\text{C}_3)$ = 2.510, $r_g(\text{C}_1-\text{C}_5)$ = 2.975, $r_g(\text{C}_3-\text{C}_7)$ = 3.064, $r_g(\text{C}_1-\text{C}_4)$ = 3.116, $r_g(\text{C}_1-\text{H}_1)$ = 1.095, $r_g(\text{C}_7-\text{H}_7)$ = 1.106 Å.; $l_m(\text{C}_1-\text{C}_2)$ = 0.044, $l_m(\text{C}_2-\text{C}_3)$ = 0.047, $l_m(\text{C}_6-\text{C}_7)$ = 0.050, $l_m(\text{C}_1-\text{H}_1)$ = 0.083, $l_m(\text{C}_7-\text{H}_7)$ = 0.085 Å.; $\angle \text{C}_1\text{C}_2\text{C}_3$ = 127.2°, $\angle \text{C}_2\text{C}_3\text{C}_4$ = 119.8°, $\angle \text{C}_5\text{C}_6\text{C}_7$ = 121.8°. The molecule exists in a boat conformation with the methylene group and the opposite carbon-carbon double bond bent out of the plane determined by the carbon atoms 1, 2, 5, and 6. The methylene group is tilted 36.5° away from that plane, and the angle between the planes determined by the carbon atoms 1, 2, 5, 6 and 2, 3, 4, 5 is found to be 40.5°. The estimated standard deviations of the molecular parameters are listed in Table I.

I. Introduction

During the last decade the molecular structure of 1,3,5-cycloheptatriene (CHT) has attracted interest from many scientists in different fields of research. But, so far an unambiguous over-all structure determination of this molecule has not been reported.



Three possible structural conformations of the carbon skeleton in the seven-membered carbon ring system are shown above (models I-III). Model I with planar carbon skeleton possesses C_{2v} symmetry, while the other two models belong to the point group C_s.

On the basis of the n.m.r. spectrum of CHT, Doering, *et al.*,^{2a} in 1956 suggested a pseudo-aromatic structure for the molecule with a planar carbon skeleton. The supposed aromatic structure is reflected in their use of the name tropilidene for CHT.

In 1958 Abel, *et al.*,^{2b} suggested from n.m.r. and vibrational spectra that the six carbon atoms in CHT, other than the methylene group, must be very nearly in the same plane, and that the six π -electrons form a delocalized system which bypasses the methylene group.

Dunitz and Pauling³ found from X-ray analysis that CHT in crystalline C₇H₈Mo(CO)₃ has a nonplanar structure and that the methylenic carbon atom does not lie in the plane of the conjugated system. The close similarity between limited regions of the infrared spectra of the complex and of the free CHT makes these

authors suppose that C_s symmetry also holds for the free molecule.

Evans and Lord⁴ have studied the infrared and Raman spectra of CHT and have satisfactorily interpreted the spectra in terms of C_{2v} symmetry (model I). They admit, however, that a slight displacement of the methylene group out of the ring plane is possible, as the selection rules would not be sensitive enough to make such a slight departure apparent.

Recently La Lau and De Ruyter⁵ reported an investigation of the vibrational spectra of CHT in order to determine the molecular symmetry. A comparative study⁶ of the infrared spectra of CHT and 7-D-CHT showed that the methylenic hydrogen atoms occupy geometrically nonequivalent positions, and the authors therefore concluded that the methylene group is tilted out of the plane of the conjugated system.

It should also be mentioned that Davis and Tulinsky⁷ have studied the molecular structure of thujic acid by X-ray crystallography. They found that the CHT ring in this molecule assumes a boat conformation (model III), with the methylene group and the C₃-C₄ double bond tilted 49.7 and 23.7° away from the plane determined by the carbon atoms 1, 2, 5, and 6.

It can be assumed that the energy of the π -electron system will decrease rapidly as the distance between carbon atoms 1 and 6 is decreased and that it will increase if the ring is puckered. These two factors are closely connected with the strain energy of the molecule, since decreasing the distance between carbon atoms 1 and 6 increases the strain, especially on $\angle \text{C}_5\text{C}_6\text{C}_7$ and on $\angle \text{C}_1\text{C}_2\text{C}_6$, and tends to force carbon atom 7 away from the plane of the adjacent double bonds. This would twist the π -orbitals of carbon atoms 1 and 6 out of parallelism of the other π -orbitals in the molecule and there-

(1) (a) The author wishes to thank the United States Air Force Office of Scientific Research for financial assistance; (b) on leave of absence from Norges Laererhogskole, Trondheim, Norway.

(2) (a) W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain, and R. B. Williams, *J. Am. Chem. Soc.*, **78**, 5448 (1956); (b) E. W. Abel, M. A. Bennett, and G. Wilkinson, *Proc. Chem. Soc.*, 152 (1958).

(3) J. D. Dunitz and P. Pauling, *Helv. Chim. Acta*, **43**, 2188 (1960).

(4) M. V. Evans and R. C. Lord, *J. Am. Chem. Soc.*, **82**, 1876 (1960).

(5) C. La Lau and H. De Ruyter, *Spectrochim. Acta*, **19**, 1550 (1963).

(6) K. Conrow, *J. Am. Chem. Soc.*, **83**, 2958 (1961).

(7) R. E. Davis and A. Tulinsky, *Tetrahedron Letters*, **19**, 839 (1962).

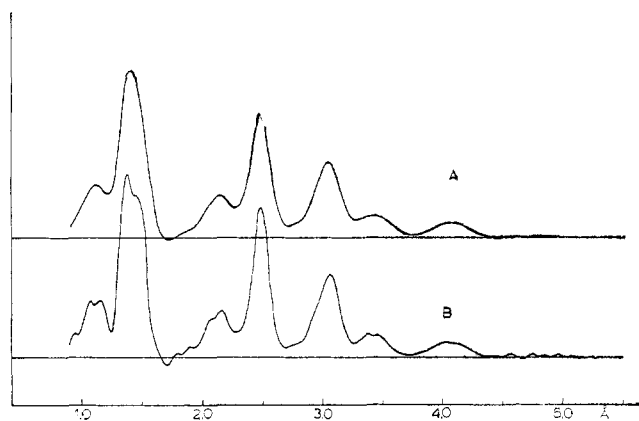


Fig. 1.—Experimental radial distribution functions for 1,3,5-cycloheptatriene: A, damping constant $b = 0.0009$; B, $b = 0$

by decrease the resonance energy. Thus there must be a balance between strain and resonance stabilization, and the equilibrium structure can be decided only by examining the carbon-carbon distances in the molecule.

II. Electron Diffraction Determination

The molecular structure of 1,3,5-cycloheptatriene was determined by the sector electron diffraction method, using a modified s^3 sector. The electron diffraction diagrams were made by cand. real. Arne Almenningen at Oslo University, Oslo, Norway. The distances between the scattering point and the photographic plate were 478.10 and 191.95 mm., covering s -ranges of 1.25–20 and 7.5–47.5 \AA^{-1} , respectively. The photometer curves of four single plates were studied for each nozzle-to-plate distance. They were read off at intervals of $\Delta s = 0.25 \text{\AA}^{-1}$, and the usual corrections were made for the effect of the photographic emulsion, for the use of plane photographic plates, and for the accurate shape of the sector.⁸

Two main methods exist for calculating radial distribution functions. In the following they will be referred to as the American-Japanese^{9,10} and Norwegian⁸ methods, respectively. In order to make a comparative study of the two methods, the experimental intensities were treated according to both schemes. The methods especially deviate in the way the electron-electron scattering correction is carried out, and while the Norwegian scheme subtracts the background scattering to yield the molecular intensity function on an arbitrary scale, the American-Japanese scheme calculates the molecular scattering according to the formula $M(s) = I(s)/B(s) - 1$, where $I(s)$ is the total intensity function and $B(s)$ is the background scattering. For further details concerning the two methods, see ref. 8–10. The molecular parameters determined from the two different sets of radial distribution curves agreed to better than $\pm 0.0002 \text{\AA}$, and in the following no distinction will be made between parameters obtained from the two sets.

In CHT it is expected that there will be at least three significantly different carbon-carbon bond distances. From the experimental radial distribution curve shown in Fig. 1A (damping constant $b = 0.0009$), it is seen that all the C-C bond distances appear in one unre-

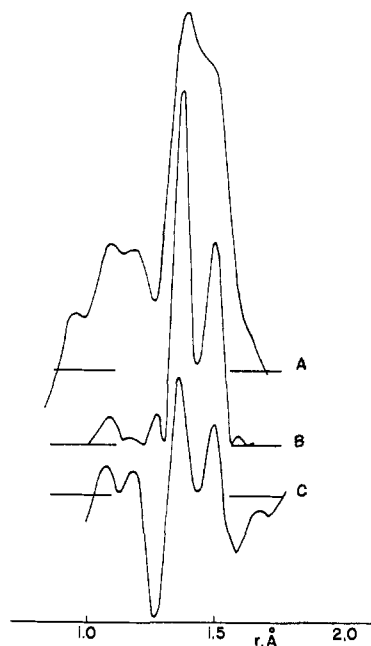


Fig. 2.—Undamped radial distribution function and power spectra for 1,3,5-cycloheptatriene: A, undamped radial distribution function; B, squared Fourier sine transform of modified intensities, using $\sqrt{2}\lambda e^{-\lambda(s_{\max}-s)}$ as modification function, $\lambda = 0.03$; C, diagonal power spectrum, $\lambda = 0.03$.

solved peak at 1.40 \AA , and it is accordingly very difficult to make a precise determination of the individual C-C bond lengths from the R.D. curves: Experience shows that a least-squares fit of three closely spaced distances appearing in one peak on the R.D. curve gives unreliable results. On an undamped R.D. curve (Fig. 1B), the resolution of the peak in question is slightly better, but as this curve is considerably affected by series termination errors, the resolution into individual carbon-carbon contributions would probably also give unreliable results.

Simultaneously with this structure investigation of CHT, a study of auto- and cross-correlation functions and corresponding power spectra applied to electron diffraction data was carried out in this laboratory.¹¹

These studies show that the power spectra of short-interval autocorrelation functions and other related functions are able to give a far better resolution of contributions from closely spaced distances than are the usual R.D. functions. This is clearly demonstrated in Fig. 2 which shows the usual undamped R.D. function (A), a sharpened radial distribution function (B), and the diagonal power spectrum (C) of CHT. All curves are based on the same experimental molecular intensity function.

The molecular parameters are not determined directly from the different power spectra or related functions: Preliminary parameters obtained from these functions are used in a zeroth-order molecular model, and the parameters are varied until the best possible fit is obtained between theoretical and experimental power spectra (or related functions).

The different power spectra are discussed in ref. 11, but, to give a better understanding of the method, the sharpened radial distribution function is treated in more detail here.

(8) A. Almenningen, O. Bastiansen, and L. Fernholt, *Kgl. Norske Videnskab. Selskabs Skrifter*, No. 3 (1958).

(9) R. A. Bonham and L. S. Bartell, *J. Chem. Phys.*, **31**, 702 (1959).

(10) Y. Morino and E. Hirota, *ibid.*, **28**, 185 (1958).

(11) M. Traetteberg and R. A. Bonham, *ibid.*, in press.

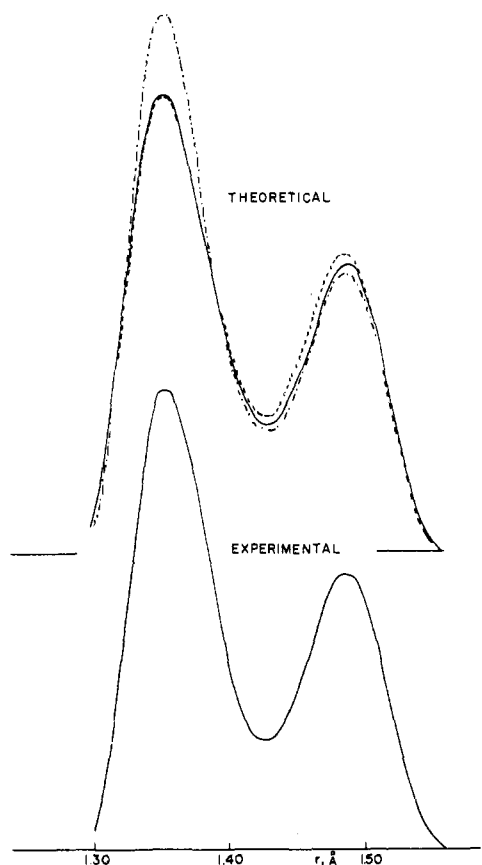


Fig. 3.—Experimental and theoretical sharpened radial distribution functions for 1,3,5-cycloheptatriene, $\lambda = 0.03$: -----, the effect of changing $r_g(C_1-C_7)$ from 1.505 to 1.503 Å.; - - - - -, the effect of changing $l_m(C_1-C_2)$ from 0.042 to 0.040 Å.

According to the folding theorem¹² the power spectrum of an autocorrelation function is equal to the sum of the square of the Fourier sine transform and the square of the Fourier cosine transform of the basic function. The definitions of the correlation functions and power spectra imply integration over infinite intervals, and in order to apply these functions to experimental data which are limited to a certain range of the variable, the experimental function is multiplied by an antidamping function so that the modified function assumes the value zero for negative values of the variable.

It is found that in the square of the Fourier sine transform of an antidamped molecular intensity function (in the following called a sharpened radial distribution function) the individual peaks are somewhat sharper than in the power spectrum based on a short-interval autocorrelation function.

According to the definition of the sharpened R.D. function, it is computed as the square of the sine transform of the modified molecular intensity function, where $sM(s)$ is modified by multiplication with a function of type $g(s) = \sqrt{2\lambda} \exp[-\lambda(s_{\max} - s)]$. The mathematical expression for the Fourier sine transform of the function $G(s) = sM(s) \cdot g(s)$ shows that each internuclear distance in the molecule contributes with a Gaussian function that is sharpened up by multiplication with a cosine function whose maximum value coincides with the maximum of the Gaussian peak. The amount of sharpening is determined by the period of the cosine function which again is a function of λ .

(12) See ref. 11 for references.

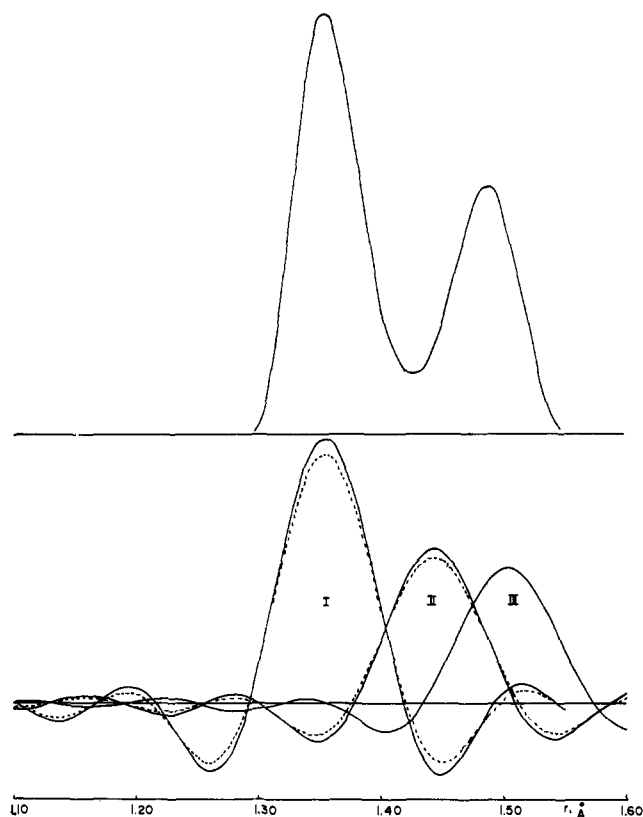


Fig. 4.—Theoretical sharpened R.D. function: I, II, and III show the Fourier sine transforms of the modified intensity contributions from the C_1-C_2 , C_2-C_3 , and C_1-C_7 distances, respectively (modification function $g(s) = \sqrt{2\lambda} e^{-\lambda(s_{\max}-s)}$, $\lambda = 0.03$); - - - shows the effect of increasing r.m.s. amplitudes by 0.002 Å.

An increase in λ leads to an increased sharpening effect. Experience shows that $\lambda = 0.03-0.04$ is a practical value for determining closely spaced bond distances.

The theoretical sharpened R.D. function is very sensitive to changes in the molecular parameters. Figure 3 shows the contributions to the sharpened R.D. function of CHT from the carbon-carbon bond distances. It also shows the effect of changing one of the distance parameters by 0.002 Å. and one of the root-mean-square amplitudes by 0.002 Å.

To illustrate how the sharpened R.D. function is composed and how it is possible to predict which changes in the molecular parameters have to be made to get the best possible fit between experimental and theoretical functions, the Fourier sine transform of $G(s)$ for each of the individual C-C contributions are shown in Fig. 4. It is also indicated how small changes in the vibrational parameters will influence the individual contributions, while changes in the distance parameters obviously will shift the different peaks along the r -scale.

In connection with the investigation of correlation functions and power spectra,¹¹ an error analysis was carried out to study how random errors in the molecular intensity function will influence the different $f(r)$ functions that might be calculated from it.

The parameters that gave the best fit between experimental and theoretical sharpened R.D. functions were the following: $r_g(C_1-C_2)$ (assumed equal to $r_g(C_3-C_4)$) = 1.356, $l_m(C_1-C_2)$ = 0.044, $r_g(C_2-C_3)$ = 1.446, $l_m(C_2-C_3)$ = 0.047, $r_g(C_6-C_7)$ = 1.505, $l_m(C_6-C_7)$ =

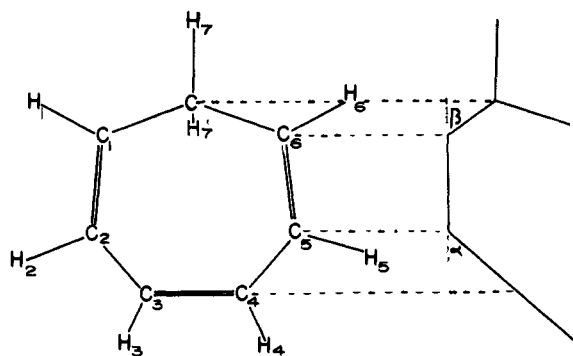


Fig. 5.—Molecular model for 1,3,5-cycloheptatriene.

0.050 Å.¹³ The experimental R.D. function, diagonal power spectrum and autocorrelation power spectrum were compared with the same theoretical functions based on the parameters determined from the sharpened R.D. function. The correspondence between experimental and theoretical functions was very satisfactory for all the different $\hat{f}(r)$ functions.

From the parameters given above it is seen that the carbon-carbon double bond distance in CHT is about 0.02 Å. larger than the C=C bond distance in ethylene,¹⁴ and that the single bond distance between trigonally hybridized carbon atoms is decreased by about 0.034 Å. compared to the same type of bond distance in butadiene.^{15,16} There is therefore a high degree of delocalization of π -electrons in the CHT molecule, and at this stage of the investigation the three double bond distances were believed to be in the same plane.

By careful studies of the radial distribution function, however, it became clear that the experimental carbon-carbon nonbonded distances were not compatible with model I or model II, and the only possibility left was model III, where the molecule has a boat conformation with the methylene group and the opposite C=C bond tilted away from the plane determined by the two other double bonds.

Before an estimate of the molecule's deviation from planarity can be given, the distances between the carbon atoms 1 and 6 and the carbon atoms 2 and 5 have to be determined. These two nonbonded C-C distances are very important as far as a structure determination is concerned, as nearly all the other nonbonded distances in the molecule are direct functions of them. Neither of these two C-C distances is resolved in the R.D. function (see Fig. 8).

A rough estimate of the possible magnitude of the distance C₂-C₅ combined with a study of the R.D. function limited this distance to the region 2.70-2.80 Å. It is harder to get any direct information about the C₁-C₆ distance from the R.D. function, and any distance in the region 2.35-2.65 Å. is compatible with the R.D. function as far as the C₁-C₆ distance itself is concerned.

(13) The notation r_g corresponds to $r_g(0)$ in Bartell's notation; see L. S. Bartell, *J. Chem. Phys.*, **23**, 1219 (1955). The root-mean-square amplitude of vibration l_m is defined as $l_m^2 = \int_0^\infty dr(r - r_m)^2 P(r) / \int_0^\infty dr P(r)$, where $P(r)$ denotes the probability distribution function and r_m the maximum position of the peak in question.

(14) L. S. Bartell and R. A. Boham, *ibid.*, **27**, 1414 (1957); **31**, 400 (1959).

(15) A. Almennigen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, **12**, 1221 (1959).

(16) D. J. Marais, N. Sheppard, and B. P. Stoicheff, *Tetrahedron*, **17**, 163 (1962).

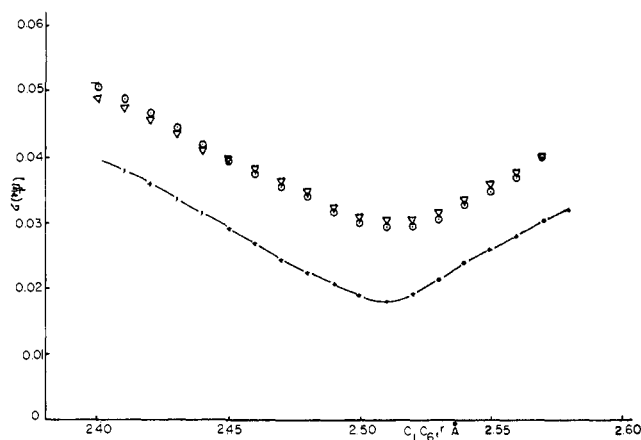


Fig. 6.—Standard deviation between experimental and theoretical R.D. functions as a function of the C₁-C₆ distance, when the C₂-C₅ distance is fixed at 2.79 Å. $\angle\alpha$ and $\angle\beta$ are determined from the C₁-C₃ and C₂-C₇ distances, respectively: + + +, "most probable" $\angle\alpha$ and $\angle\beta$ (assumption: $r_g(\text{C}_1-\text{C}_3) = r_g(\text{C}_2-\text{C}_7)$); $\circ\circ\circ$, largest possible $\angle\alpha$, smallest possible $\angle\beta$; $\nabla\nabla\nabla$, smallest possible $\angle\alpha$, largest possible $\angle\beta$.

The distances in question were established by determining the minimum standard deviation between the experimental R.D. function and a series of theoretical R.D. functions in the region 2.3-3.2 Å. In the theoretical models distance C₁-C₆ and distance C₂-C₅ were varied systematically within the estimated limits given above in intervals of $\Delta r = 0.01$ Å. The angles α and β (see Fig. 5) for each model were determined from the

TABLE I

1,3,5-CYCLOHEPTAENE. INTERNUCLEAR DISTANCES, BOND ANGLES, AND ESTIMATED STANDARD DEVIATIONS FOR THE EXPERIMENTALLY DETERMINED MOLECULAR PARAMETERS

Distance	$r_g(0)$, Å.	$\Delta r_g(0)$, Å.	l_m , Å.	Δl_m , Å.
C ₁ -C ₂	1.356	±0.005	0.044	±0.005
C ₂ -C ₃	1.446	±0.007	0.047	±0.007
C ₆ -C ₇	1.505	±0.007	0.050	±0.007
C ₁ -C ₆	2.511	±0.015	0.060 ^a	
C ₂ -C ₅	2.792	±0.015	0.070 ^a	
C ₁ -H ₁	1.095	±0.010	0.083	±0.010
C ₇ -H ₇	1.106	±0.010	0.085	±0.010
C ₂ -C ₄	2.424		0.055	
C ₂ -C ₇	2.501		0.055	
C ₁ -C ₃	2.510		0.055	
C ₁ -C ₅	2.975		0.058	
C ₃ -C ₇	3.064		0.060	
C ₁ -C ₄	3.116		0.060	

$$\angle\alpha = 40.5 \pm 2^\circ$$

$$\angle\beta = 36.5 \pm 2^\circ$$

$$\angle\text{H}_1\text{C}_1\text{C}_2 = 120 \pm 2^\circ$$

$$\angle\text{H}_2\text{C}_2\text{C}_1 = 120 \pm 2^\circ$$

$$\angle\text{H}_3\text{C}_3\text{C}_4 = 120 \pm 2^\circ$$

$$\angle\text{H}_7\text{C}_7\text{H}_7' = 109 \pm 3^\circ$$

$$\angle\text{C}_1\text{C}_2\text{C}_3 = 127.2^\circ$$

$$\angle\text{C}_2\text{C}_3\text{C}_4 = 119.8^\circ$$

$$\angle\text{C}_5\text{C}_6\text{C}_7 = 121.8^\circ$$

^a Assumed value.

peak at 2.48 Å. on the experimental R.D. function, after subtraction of the theoretical contributions from the two distances of type C₂-C₄ and the distance C₁-C₆. The small half-width of the remaining peak at 2.48 Å. indicated that the difference in magnitude between the distances C₂-C₇ and C₁-C₃ is very small. These two distances determine the deviation from planarity, as $\angle\alpha$ is determined from distance C₁-C₃ and $\angle\beta$ is determined from distance C₂-C₇, using the carbon-carbon

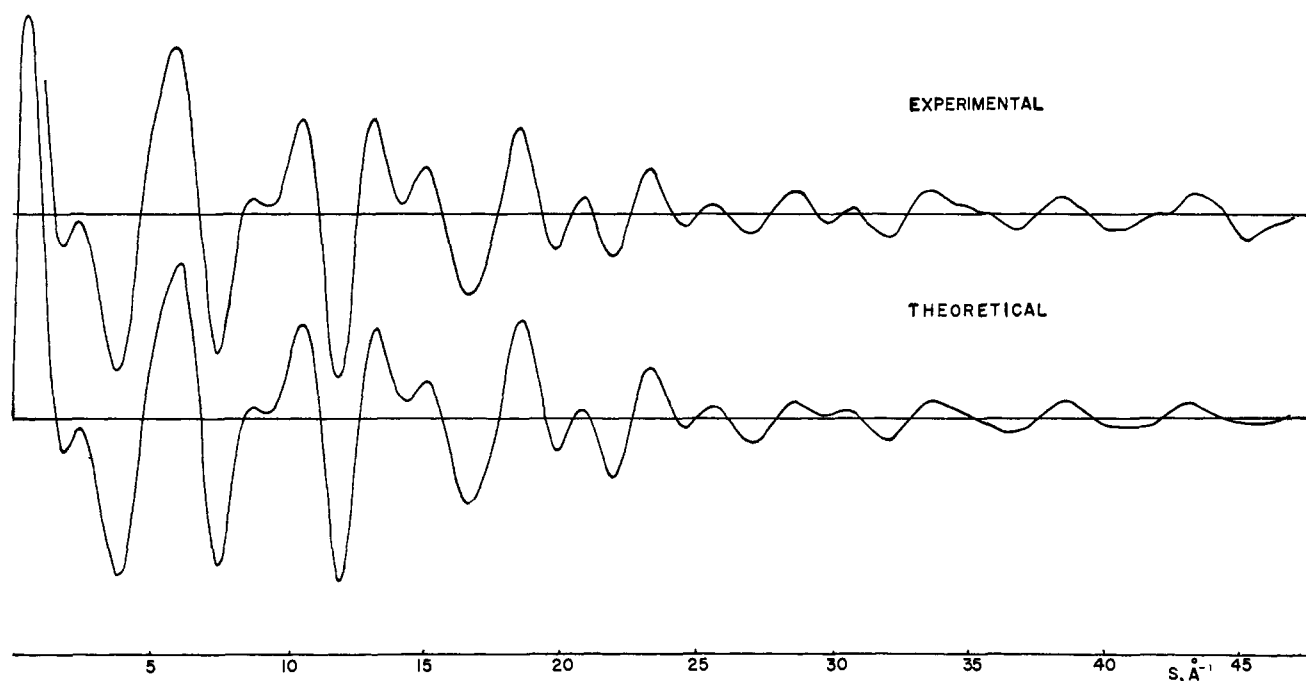


Fig. 7.—Experimental and theoretical molecular intensity functions for 1,3,5-cycloheptatriene.

bond distance parameters listed in Table I. For each combination of C_1-C_6 and C_2-C_5 distances, three possible values of the angles α and β were calculated, namely (1) the "most probable" values of $\angle\alpha$ and $\angle\beta$ [$r_g(C_2-C_7) = r_g(C_1-C_3)$], (2) the smallest possible $\angle\alpha$ combined with the largest possible $\angle\beta$, and (3) the largest possible $\angle\alpha$ combined with the smallest possible $\angle\beta$. The distances $C_1-C_6 = 2.511$ and $C_2-C_5 = 2.792$ Å. gave the smallest standard deviation between experimental and theoretical R.D. functions. Figure 6 shows the standard deviations plotted as a function of distance C_1-C_6 , while the distance C_2-C_5 is fixed at 2.79 Å. By inspecting the three standard deviation functions for the three possible combinations of $\angle\alpha$ and $\angle\beta$ in Fig. 6, it is seen that they are in accordance with the assumption that the distances C_1-C_3 and C_2-C_7 are very close in magnitude. The individual theoretical R.D. functions for parameters corresponding to values near the minimum of the standard deviation function were compared with the experimental R.D. function to assure that the determined parameters actually led to a better fit between experimental and theoretical R.D. functions.

The same procedure was used to determine the deviations from planarity in CHT. $\angle\alpha$ and $\angle\beta$ were varied systematically in the regions 38 to 42° and 34 to 40°, respectively, in intervals of 0.5°, while the distances C_1-C_6 and C_2-C_5 were given the values determined above. For all possible angle combinations the theoretical molecular models and R.D. functions were computed, and the minimum standard deviation between experimental and theoretical R.D. functions in the region 2.3–3.2 Å. was obtained for $\angle\alpha = 40.5$ and $\angle\beta = 36.5$ °. The theoretical R.D. function is quite sensitive to changes in $\angle\alpha$ and $\angle\beta$, and by comparing the theoretical R.D. functions calculated from values of the angles near the minimum in the standard deviation function with the experimental R.D. function, it was established that the values obtained for the angles actually led to a better over-all fit.

The positions of the hydrogen atoms were determined from the R.D. function by examining the CH nonbonded peaks together with the C-H bond-distance peak. The average distance between the hydrogen atoms and the trigonally hybridized carbon atoms was found to be 1.095 Å. and the C-H bond distance in the methylene group was found to be 1.106 Å. The experimental data indicate that the hydrogen atoms 1, 2, 5, and 6 are bent out of the plane given by the adjacent carbon atoms and that they are tilted in the opposite direction of the methylene group. No attempt was made to determine the angle between the tilted C-H bond distances and the plane determined by the carbon atoms 1, 2, 5, and 6.

III. Results

The results of the final analysis for all the measured molecular parameters are given in Table I, which also lists the carbon-carbon internuclear distances and bond angles that were calculated from the molecular parameter values. The quoted error limits include estimates of experimental errors due to the various measured quantities and uncertainties in the observed parameters due to random errors in the molecular intensity function. They do not include possible errors from application of the kinematic scattering theory.

The experimental and theoretical molecular intensity functions are shown in Fig. 7, while Fig. 8 shows the experimental and theoretical radial distribution functions (damping constant $b = 0.0009$). The two theoretical functions shown in Fig. 7 and Fig. 8 are based on the final molecular parameters for CHT, as listed in Table I. Fig. 5 shows the molecular model for 1,3,5-cycloheptatriene along with the numbering of the atoms in the molecule.

IV. Discussion

The results from this investigation are in disagreement with most of the structure determinations of CHT reported earlier.²⁻⁷ It is shown here that the molecule exists in a boat conformation, while nearly all the pre-

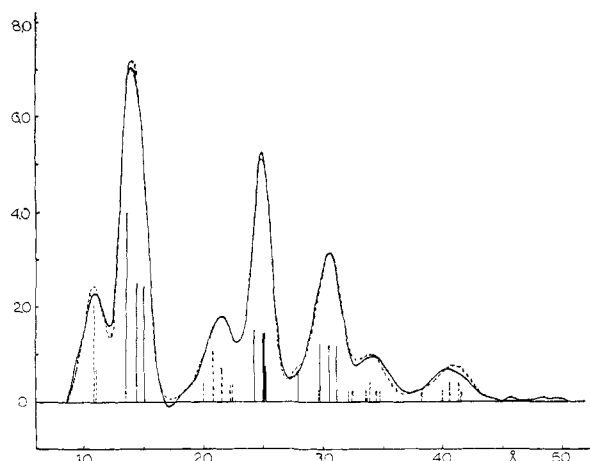


Fig. 8.—Experimental (—) and theoretical (---) radial distribution functions (damping constant $b = 0.0009$) for 1,3,5-cycloheptatriene. The solid and dotted bars represent relative contributions from C—C and C—H distances, respectively.

vious investigators have concluded that the six trigonally hybridized carbon atoms are approximately in the same plane. But in many of the reports this is an assumption rather than a result based on experimental evidence.

The present results are essentially in agreement with the report of Davis, *et al.*,⁷ on the molecular structure of thujic acid. They concluded that the CHT ring in that molecule assumes a boat conformation, and although their results for $\angle \alpha$ (23.7°) and $\angle \beta$ (49.7°) deviate considerably from the values obtained in the present study, that might be explained by the fact that in thujic acid the CHT ring is a part of a larger molecule.

It is natural to compare the molecular structure of CHT with that of 1,3,5,7-cyclooctatetraene (COT). Electron diffraction studies¹⁷ show that COT exists in a boat form with long and short carbon-carbon bond distances alternating along the carbon ring system. The C—C distances are given as $r_m(1)$ (C=C) = 1.334 Å. and $r_m(1)$ (C—C) = 1.462 Å. The double bond distance does not deviate significantly from the corresponding distance in ethylene,¹⁴ while the single bond distance is about 0.02 Å. shorter than would be expected if there were no π -electron delocalization. This is a remarkable result and attempts have been made to find a reasonable explanation¹⁸ of the observed bond lengths.

If the carbon skeleton in COT were planar, the trigonal angles would have to be increased from 120° to 135° . Following the same line of reasoning for CHT,

(17) O. Bastiansen, K. Hedberg, and L. Hedberg, *J. Chem. Phys.*, **27**, 1311 (1957).

(18) See, for example, O. Bastiansen and M. Traetteberg, *Tetrahedron*, **17**, 147 (1962).

it is found that in this molecule all the trigonal angles have to be increased by about 8° if the six trigonally hybridized carbon atoms should remain in the same plane. The angles between neighboring trigonally hybridized carbon atoms in CHT are 120° within the error limits of the method except $\angle C_1C_2C_3$, and the resonance energy gained by a planar arrangement of the six sp^2 carbon atoms is therefore smaller than the energy required to increase all the trigonal angles by 8° .

C
The angle between the two -C $\begin{matrix} \diagup \\ \diagdown \end{matrix}$ planes in COT corre-
H

sponds to $\angle \alpha$ in CHT and is found to be approximately 42.3° . The angles between neighboring p-orbitals is therefore somewhat larger in COT than in CHT. But on the other side, the COT molecule has a π -electron system going around the carbon ring system, while in CHT it is interrupted by the methylene group.

It is hard to understand why the C—C bond distances in CHT indicate a considerable amount of π -electron delocalization, while no such effect is found in COT. Simultaneous reinvestigations of the molecular structures of COT and 1,3-butadiene are, however, being planned at Oslo University, and a further comparison of the resonance effects in CHT and COT will be postponed until the results from the reinvestigation of COT are available.

The resonance energy for CHT in the gas phase was first reported by Kistiakowsky¹⁹ in 1939 to be 6.7 kcal./mole, and this result was confirmed by later investigations.²⁰ The reported resonance energy is based on a reference standard equal to three times the heat of hydrogenation of cycloheptene, and the order of magnitude is in agreement with the expected resonance energy of the molecular structure of CHT reported in this work.

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