

Table III. A Summary of Bond Distances and Bond Angles ( $\phi$ ) in Isocyanates and Isothiocyanates

	Bond distance, Å					$\phi$ , deg.	Ref
	Si-N	C-N	N=C	C=O	C=S		
HNCO			1.207 $\pm$ 0.01	1.171 $\pm$ 0.01		128.1 $\pm$ 0.5	1
HNCS			1.216 $\pm$ 0.002		1.561 $\pm$ 0.002	130.25 $\pm$ 0.25	2
DNCS			1.216 $\pm$ 0.002		1.561 $\pm$ 0.002	132.25 $\pm$ 0.25	2
H <sub>3</sub> CNCO		1.47	1.19 $\pm$ 0.03	1.18 $\pm$ 0.03		125° $\pm$ 5	3
		(assumed)					
H <sub>3</sub> CNCS		1.47	1.22		1.56	142	4
H <sub>3</sub> SiNCS	1.714 $\pm$ 0.010		1.211 $\pm$ 0.010		1.560 (assumed)	180	10
(CH <sub>3</sub> ) <sub>3</sub> SiNCO	1.76 $\pm$ 0.02		1.20 $\pm$ 0.01	1.18 $\pm$ 0.01		150 $\pm$ 3°	<i>a</i>
(CH <sub>3</sub> ) <sub>3</sub> SiNCS	1.78 $\pm$ 0.02		1.18 $\pm$ 0.01		1.56 $\pm$ 0.01	154 $\pm$ 2	<i>a</i>
Si(NCO) <sub>4</sub>						180	12, 13
Si(NCS) <sub>4</sub>							

<sup>a</sup> Present work.

paper, to 1.714 Å in H<sub>3</sub>SiNCS, to approximately 1.65 Å in the Cl<sub>*n*</sub>Si(NCO)<sub>4-*n*</sub> sequence.<sup>19</sup> The sensitivity of the Si-N bond distance to the nature of the groups attached to the silicon strongly argues for the assumption that the Si-N bond is more complex than  $\sigma^2$  derived from an (sp<sup>3</sup>) hybrid. The length of the bond appears to increase with increasing electron release by the substituent groups. In turn, the types of orbitals which determine the Si-N bond affect the Si-N-C bond angle. Ebsworth,<sup>20</sup> in summarizing the chemical and some of the physical properties of

silylamines, calls attention to the apparent multiple-bond character of Si-N linkages.

**Acknowledgments.** K. Kimura wishes to thank Professor Y. Morino of Tokyo University for helpful discussions. This work was supported in part by grants from: Office of Naval Research [Contract Nonr-401(41)], and Materials Science Center (Advanced Research Projects Agency). Samples of the two compounds studied were generously given to us by Professor G. S. Forbes and were prepared as described by Forbes and Anderson.<sup>21</sup>

(19) Manuscript in preparation.

(20) E. A. V. Ebsworth, "Volatile Silicon Compounds," The Macmillan Co., New York, N. Y., 1963, Chapter 5.

(21) G. S. Forbes and H. H. Anderson, *J. Am. Chem. Soc.*, **70**, 1222 (1948), and previous publications. For a tabular summary of physical constants, refer to T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1952, p 476 ff.

## Structures of C<sub>7</sub>H<sub>10</sub> Valence Tautomers as Determined by Electron Diffraction

Joseph F. Chiang and S. H. Bauer

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York. Received September 16, 1965

**Abstract:** The structures of the valence tautomers 1,3-cycloheptadiene and  $\Delta^6$ -bicyclo[3.2.0]heptene have been investigated in the gaseous phase by electron diffraction. Both molecules possess C<sub>3</sub> symmetry. In 1,3-cycloheptadiene all but one of the carbon atoms are coplanar; the C atom at the apex is tilted 73° up from the plane.  $\Delta^6$ -Bicyclo[3.2.0]heptene is in a chair conformation. For the best models the bond lengths and the bond angles are as follows. For 1,3-cycloheptadiene the bond lengths (Å) are C<sub>1</sub>=C<sub>2</sub> = 1.35, C<sub>2</sub>-C<sub>3</sub> = 1.48, C<sub>1</sub>-C<sub>7</sub> = 1.54, C<sub>6</sub>-C<sub>7</sub> = 1.55, C<sub>1</sub>-H<sub>1</sub> = 1.09, and C<sub>7</sub>-H<sub>7</sub> = 1.11;  $\angle$ C<sub>3</sub>C<sub>2</sub>C<sub>1</sub> = 129° and  $\angle$ C<sub>1</sub>C<sub>7</sub>C<sub>6</sub> = 119°. For  $\Delta^6$ -bicyclo[3.2.0]-heptene C=C = 1.34, C-C = 1.56, C-H = 1.10 Å;  $\angle$ C<sub>2</sub>C<sub>1</sub>C<sub>2</sub> = 105.5°,  $\angle$ C<sub>1</sub>C<sub>2</sub>C<sub>3</sub> = 86.7°,  $\angle$ C<sub>3</sub>C<sub>1</sub>C<sub>2</sub> = 109.5°,  $\angle$ C<sub>2</sub>C<sub>3</sub>C<sub>4</sub> = 112.9°,  $\angle$ C<sub>6</sub>C<sub>7</sub>C<sub>1</sub> = 94.0°, and  $\angle$ C<sub>7</sub>C<sub>1</sub>C<sub>5</sub> = 86.0°.

The valence tautomers 1,3-cycloheptadiene and  $\Delta^6$ -bicyclo[3.2.0]heptene possess unexpected structural features. 1,3-Cycloheptadiene was first synthesized in 1901 by Willstätter.<sup>1</sup> Since then there have been many investigations of this compound. Friess<sup>2</sup> reported that it absorbs in the ultraviolet at  $\lambda_{\max}$  = 248 m $\mu$ , with log  $\epsilon$  = 3.87, independent of the solvent used. This was confirmed by Hafner and Rellensmann,<sup>3</sup> who

found that in *n*-hexane,  $\lambda_{\max}$  = 247.4 m $\mu$ , log  $\epsilon$  = 3.90. The spectrum shows a single broad band which is characteristic of conjugated cyclic dienes.<sup>4-6</sup> Raman spectra of 1,3-cycloheptadiene<sup>7</sup> were interpreted in terms of a *cis* configuration about the double bond in the ring.

(1) v. R. Willstätter, *Ann.*, **317**, 2041 (1901).

(2) P. Pesch and S. L. Friess, *J. Am. Chem. Soc.*, **72**, 5756 (1950).

(3) K. Hafner and W. Rellensmann, *Ber.*, **95**, 2567 (1962).

(4) C. B. Allsopp, *Proc. Roy. Soc. (London)*, **A143**, 618 (1939).

(5) V. Henn and L. W. Pickett, *J. Chem. Phys.*, **7**, 439 (1939).

(6) A. C. Cope and L. L. Estes, *J. Am. Chem. Soc.*, **72**, 1129 (1950).

(7) E. V. Sobolev, V. T. Aleksanyan, E. M. Milvitskaya, and M. A. Pryanishnikova, *J. Struct. Chem. (USSR)*, **4**, 169 (1963).

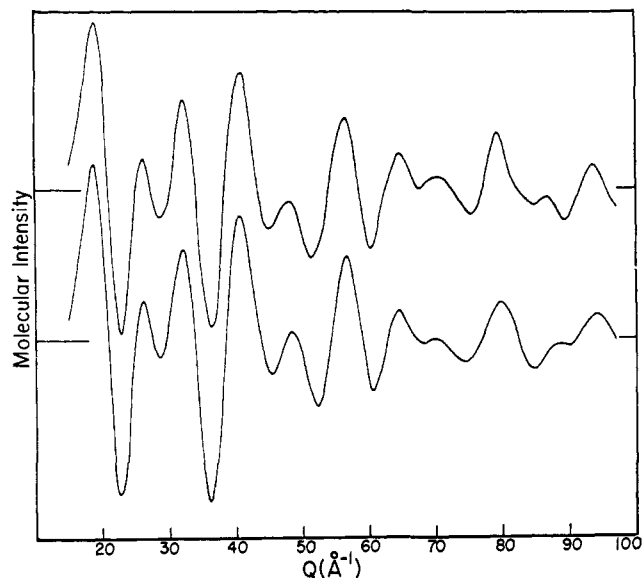


Figure 1. The reduced experimental molecular scattering curve of 1,3-cycloheptadiene and the molecular intensity calculated for the best model (Figure 10): upper curve, experimental; lower curve, theoretical.

The synthesis of  $\Delta^6$ -bicyclo[3.2.0]heptene was carried out by a photochemical transformation of 1,3-cycloheptadiene.<sup>8,9</sup> In the infrared the product shows absorptions at 3020, 1560, and 735  $\text{cm}^{-1}$ , which are characteristic of cyclobutene.<sup>8,10</sup> The presence of a cyclobutene ring in  $\Delta^6$ -bicyclo[3.2.0]heptene was demonstrated by ozonization<sup>8</sup> and by permanganate oxidation of the parent compound.<sup>9</sup> Both the chair and boat conformations have been proposed. Also, the mass spectra and the energetics of the fragmentation patterns have been compared for these tautomers.<sup>11</sup>

Electron diffraction studies were undertaken to establish the molecular geometries of this pair of isomers. For 1,3-cycloheptadiene the following conformations were considered in detail: planar, all but the apex atom planar, chair, and boat forms. Comparison of structures of the two tautomers with cycloheptatriene, cyclopentane, cyclobutene, and cyclobutane also proved instructive.

### Experimental Section

A sample of 1,3-cycloheptadiene was prepared by Dr. Y. Meinwald in this laboratory by a modification of the method of Pesch and Friess,<sup>2</sup> in which a Cope N-oxide pyrolysis (*cf.* Meinwald, *et al.*<sup>12</sup>) was substituted for the Hofmann elimination;  $\Delta^6$ -bicyclo[3.2.0]heptene was furnished by Dr. O. L. Chapman from the Department of Chemistry, Iowa State University, and was specified to be 95% pure (gas chromatography). Sector electron diffraction photographs were taken at 57 kv. The apparatus used has been described.<sup>13</sup> The samples were kept in a large glass bulb at an initial pressure of 0.1 mm. The bulb was heated by a hair dryer (with the nozzle at room temperature) and diffraction patterns were taken of the issuing vapor. Gold foil was used for calibration. The diffraction photographs were read with a Leeds and Northrup microphotometer; during scanning the plates were oscillated about

- (8) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 180 (1961).  
 (9) O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Am. Chem. Soc.*, **84**, 1220 (1962).  
 (10) R. C. Lord and D. G. Rea, *ibid.*, **79**, 2401 (1957).  
 (11) C. Lifshitz and S. H. Bauer, *J. Phys. Chem.*, **67**, 1629 (1963).  
 (12) J. Meinwald, D. W. Dicker, and N. Danieli, *J. Am. Chem. Soc.*, **82**, 4087 (1960).  
 (13) J. M. Hastings and S. H. Bauer, *J. Chem. Phys.*, **18**, 13 (1950).

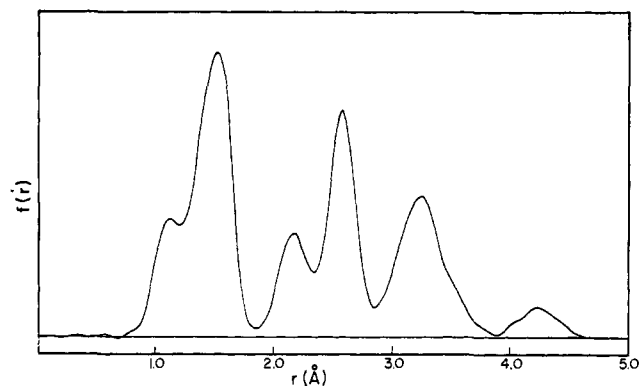


Figure 2. The refined radial distribution curve for 1,3-cycloheptadiene.

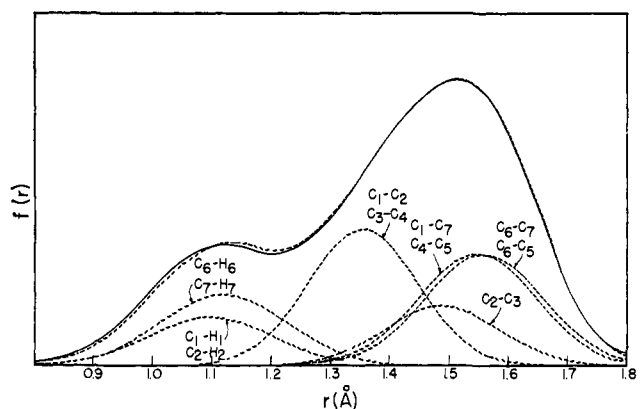


Figure 3. Detailed analysis of the 0.9–1.8-Å region of Figure 2.

their centers of diffraction in order to reduce fluctuations due to emulsion granularity.

The method for reduction of data has been described previously.<sup>14</sup>

### Analysis and Results

**1,3-Cycloheptadiene.** The reduced experimental and theoretical intensities,  $M_{0\text{exptl}}(q)$  and  $M_0(q)$ , are shown in Figure 1. The final refined radial distribution curve is shown in Figure 2, computed with a damping factor  $\gamma = 0.00024$ . A large variety of models were considered, based on planar and nonplanar conformations, using reasonable ranges for the bonded distances; these included the boat-like structure with  $C_2$  symmetry. The critical parameters proved to be the bond angles. None of the models considered fitted the radial distribution curve as well as the following. The first asymmetric peak at 1.516 Å is shown at an enlarged scale in Figure 3, resolved into six bonded interatomic distances; *i.e.*,  $C_1-H_1 = 1.09$ ,  $C_7-H_7 = 1.11$ ,  $C_1-C_2 = 1.35$ ,  $C_2-C_3 = 1.48$ ,  $C_1-C_7 = 1.54$ , and  $C_6-C_7 = 1.55$  Å (refer to Figure 10 for atom designations). The ratio of observed area to the theoretical area is 410/400. All the remaining peaks in the radial distribution curve other than those shown in Figure 3 are due to nonbonded distances. Figure 4 shows the second peak at 2.17 Å as resolved into five C-H distances:  $C_1-H_2 = 2.12$ ,  $C_2-H_3 = 2.13$ ,  $C_1-H_7 = 2.16$ ,  $C_7-H_1 = 2.19$ , and  $C_7-H_6 = 2.17$  Å. The third peak at 2.57 Å consists of nonbonded C-C distances:  $C_1-C_6 = 2.526$ ,  $C_5-C_7 = 2.537$ ,  $C_2-C_4 = 2.554$ , and  $C_2-C_7 = 2.61$  Å. The ratio of the observed area under these two peaks to

- (14) K. Kimura and S. H. Bauer, *ibid.*, **39**, 3172 (1963).

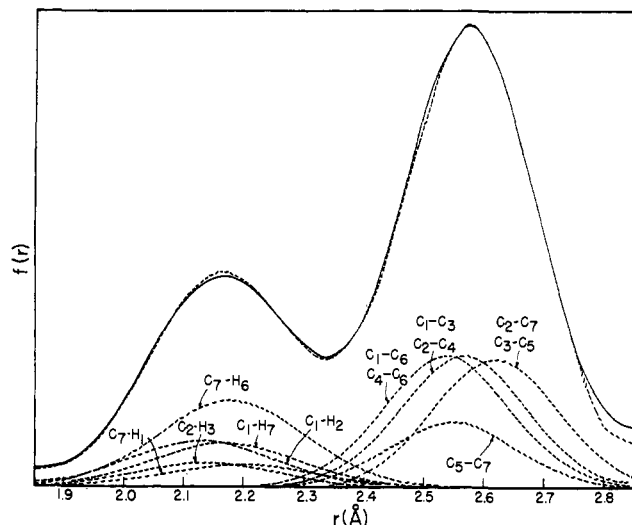


Figure 4. Detailed analysis of the 1.9-2.8-Å region of Figure 2.

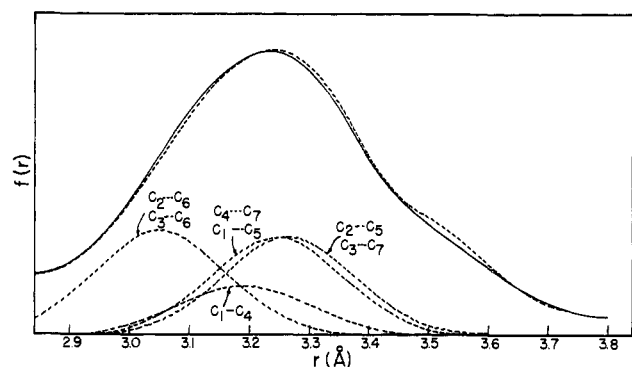


Figure 5. Detailed analysis of the 2.9-3.8-Å region of Figure 2.

the theoretical is 330/327. Figure 5 presents the resolution of the fourth peak into  $C_2-C_6 = 3.035$ ,  $C_1-C_4 = 3.178$ ,  $C_1-C_5 = 3.231$ , and  $C_2-C_5 = 3.25$  Å. The area ratio as defined before is 224/227. The indicated areas include all nonbonded C-H scattering, but the corresponding peaks for these numerous small contributions were not shown individually in Figures 4 and 5. The last small peak at 4.24 Å was assigned to seven different C-H distances. The area ratio is 86/90. The molecule has  $C_s$  symmetry, with the carbon skeleton planar except for the  $C_6$  atom. The various bond angles have the following values:  $\angle C_1 = \angle C_2 = 129 \pm 2^\circ$ ,  $\angle C_6 = \angle C_7 = 119 \pm 2^\circ$ . The plane of  $C_5C_6C_7$  makes an angle of  $73^\circ$  with the plane of the ring carbon atoms;  $\angle H_{61}C_6H_{62} = \angle H_{71}C_7H_{72} = 125^\circ$ .

The synthetic radial distribution curve for this model fits the experimental curve very well. Comparison of the experimental and theoretical intensities, as drawn in Figure 1, shows that they agree well except in the region  $q = 84$  to  $q = 90$ . In the experimental curve, the minimum at 89.5 is deeper than that at 84.5, but in the theoretical intensity curve the deeper minimum appears at 84.5 instead of 89.5. This may be due to the experimental error of the diffraction pattern at the very edge of the plate. The best structural parameters are summarized in Table I. The limits of error cited were estimated as roughly twice the maximum magnitudes

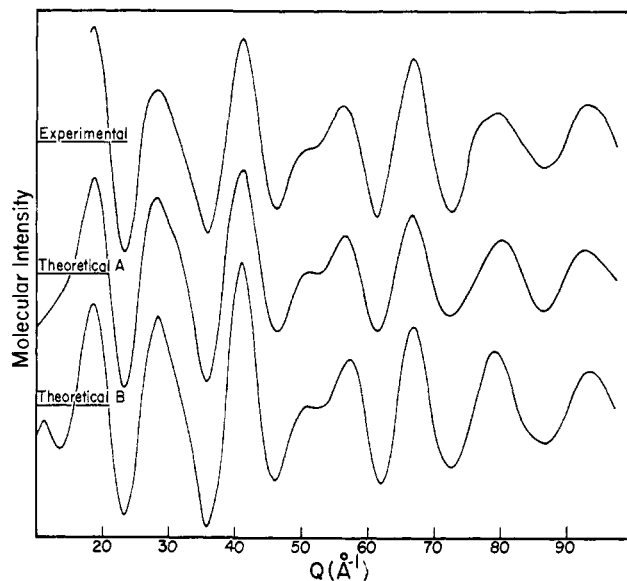


Figure 6. The reduced experimental molecular scattering curve of  $\Delta^6$ -bicyclo[3.2.0]heptene and molecular intensity curves calculated for (A) the chair conformation (see Figure 11), and (B) the best boat conformation.

of the shifts in peak positions which would not destroy an acceptable fit between the observed and calculated radial distribution curves.

Table I. Structure Parameters of 1,3-Cycloheptadiene<sup>a</sup>

Type	$r_{ij}$ , Å	$l_{ij}$ , Å
Bonded Interatomic Distances		
$C_1-C_2$	$1.35 \pm 0.01$	$0.055 \pm 0.005$
$C_2-C_3$	$1.48 \pm 0.01$	$0.060 \pm 0.005$
$C_1-C_7$	$1.54 \pm 0.01$	$0.065 \pm 0.005$
$C_6-C_7$	$1.55 \pm 0.01$	$0.065 \pm 0.005$
$C_1-H_1$	$1.09 \pm 0.02$	$0.085 \pm 0.01$
$C_2-H_2$		
$C_7-H_7$	$1.11 \pm 0.02$	$0.084 \pm 0.01$
$C_6-H_6$		
Nonbonded Interatomic Distances		
$C_2-C_7, C_3-C_5$	2.610	0.075
$C_1-C_3, C_2-C_4$	2.554	0.065
$C_1-C_6, C_4-C_6$	2.526	0.080
$C_5-C_7$	2.537	0.080
$C_2-C_6, C_3-C_7$	3.250	0.085
$C_2-C_6, C_3-C_6$	3.035	0.085
$C_1-C_4$	3.178	0.075
$C_4-C_7, C_1-C_5$	3.231	0.085
$C_2-H_3$	2.130	0.085
$C_3-H_2$		
$C_2-H_1, C_3-H_4$	2.120	0.095
$C_1-H_{71}, C_4-H_{51}$	2.160	0.090
$C_1-H_{72}, C_4-H_{52}$		
$C_7-H_1, C_5-H_4$	2.190	0.100
$C_7-H_6, C_5-H_6$	2.170	0.090
$C_6-H_7, C_6-H_5$		
$\angle C_1 = \angle C_2 = 129 \pm 2^\circ$		
$\angle C_6 = \angle C_7 = 119 \pm 2^\circ$		
$\angle ABC_6 = 107.2^\circ$		

<sup>a</sup> See Figure 10.

$\Delta^6$ -Bicyclo[3.2.0]heptene (BCH). The reduced  $M_{0\text{expt}}(q)$  function is plotted in Figure 6 along with the theoretical  $M_0(q)$  for the chair form (curve A) and a boat form (curve B). Both curves are similar except in the regions having maxima at  $q = 28$ ,  $q = 79$ ; i.e.,

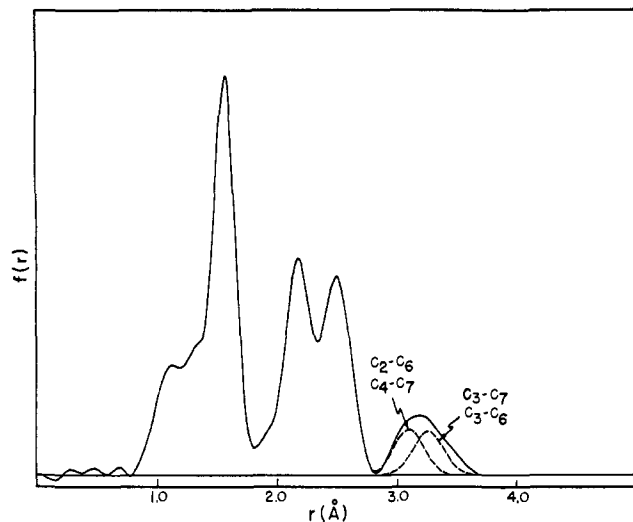


Figure 7. The refined radial distribution curve for  $\Delta^6$ -bicyclo-[3.2.0]heptene.

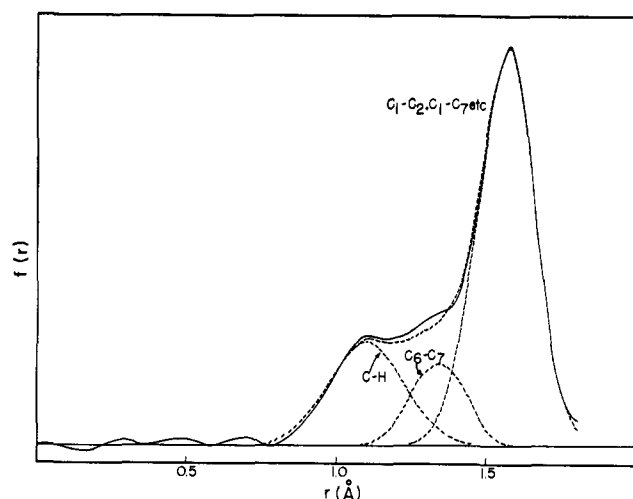


Figure 8. Detailed analysis of the 0.8-1.8-Å region of Figure 7.

the second and seventh maxima in curve A are broader than those in curve B and are closer to the experimental curve. These differences are barely distinctive enough to permit selection of the best model. More reliable criteria were obtained from the radial distribution curve as discussed below.

Figure 7 is a plot of the refined radial distribution function calculated with a damping factor  $\gamma = 0.00024$ . The first peak (Figure 8) is asymmetric and consists of three types of bonded distances: the direct C-H distances, C=C in the four-membered ring, and the C-C single bonds in the four- and five-membered rings.  $C_iH_i = 1.10$  Å with a mean amplitude 0.095; C=C = 1.34 Å, with a mean amplitude 0.040. This agrees very well with the approximate calculation of mean square amplitudes by Kimura.<sup>15</sup> The single bonded distance C-C = 1.56 Å has a mean amplitude 0.065. The ratio of the observed area to the theoretical area is 488/489. The second and third peaks (Figure 9) consist of ten nonbonded distances:  $C_7 \cdots C_5 = 2.127$ ,  $C_1 \cdots C_3 = 2.14$ ,  $C_2 \cdots H_3 = 2.19$ ,  $C_7 \cdots H_1 = 2.20$ ,  $C_7 \cdots H_6 = 2.24$ ,  $C_3 \cdots H_2 = 2.352$ ,  $C_1 \cdots H_7$

(15) K. Kimura and M. Kimura, *J. Chem. Phys.*, **25**, 362 (1956).

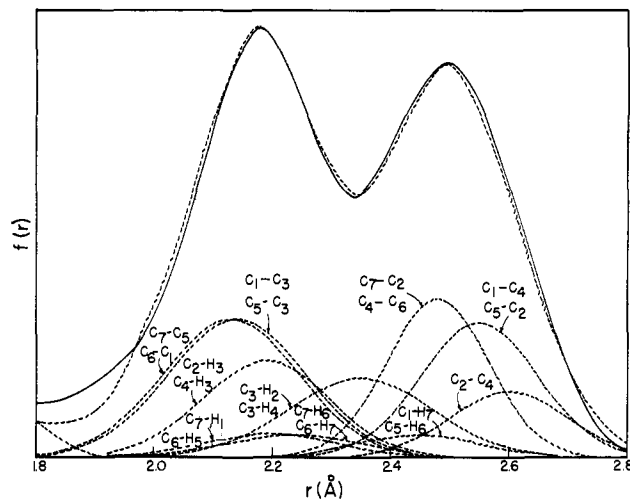


Figure 9. Detailed analysis of the 1.8-2.8-Å region of Figure 7.

$= 2.446$ ,  $C_7 \cdots C_2 = 2.48$ ,  $C_1 \cdots C_4 = 2.548$ , and  $C_2 \cdots C_4 = 2.60$  Å. The ratio of the observed area to the theoretical area under these two peaks is 382/393. The indicated areas include all nonbonded C-H scattering; however, the corresponding radial distribution peaks, being numerous and small, were not shown individually in Figure 9.

The chair configuration is in much better agreement with this radial distribution curve than is the boat form. In the latter, the  $C_3 \cdots C_7$  distance is 2.44 Å. This destroys the agreement in the regions of the third and fourth radial distribution peaks because the observed area under the third peak (at 2.49 Å) is larger than the theoretical area under the same peak; *i.e.*, the ratio of the observed area to the theoretical area is 186/251 under the third peak. If one changes  $C_3-C_7 = 2.44$  to 3.265 Å, the ratio of the observed area to the theoretical area is 186/192. This is the chair form. The third peak (at 3.18 Å) was assigned to the two nonbonded distances:  $C_4 \cdots C_7 = 3.10$  and  $C_3 \cdots C_7 = 3.265$  Å. This peak also favors the chair conformation. The ratio of the observed area to the theoretical area is 93/90.

The angle between the planes  $C_2C_3C_4$  and  $C_1C_2C_4C_5$  is  $115^\circ$ . The various bond angles have the following values:  $\angle C_1C_2C_3 = 86.7 \pm 0.3^\circ$ ;  $\angle C_4C_5C_6 = 105.5 \pm 0.3^\circ$ ;  $\angle C_2C_3C_4 = 112.9 \pm 0.3^\circ$ , and  $\angle C_5C_1C_2 = 109.5^\circ$ . A summary of structural parameters is given in Table II. The limits of error cited are approximately twice the magnitudes of allowable shifts in peak positions which do not destroy an acceptable fit between the calculated and observed radial distribution curves.

## Discussion

**1,3-Cycloheptadiene.** The structure of 1,3-cycloheptadiene as derived from this study is shown in Figure 10 ( $C_s$  symmetry). The carbon skeleton is coplanar except for the  $C_6$  atom which is tilted  $73^\circ$  up from the plane. The length of the double bond was found to be 1.35 Å, close to the double bond length in cycloheptatriene<sup>16</sup> (1.356 Å). The length of the single bond between the double bonds is 1.48 Å, which is nearly equal

(16) (a) S. S. Butcher, *ibid.*, **42**, 1830 (1965); (b) M. Traetteberg, *J. Am. Chem. Soc.*, **86**, 4265 (1964); (c) S. S. Butcher, *J. Chem. Phys.*, **42**, 1833 (1965); (d) F. A. L. Anet, *J. Am. Chem. Soc.*, **86**, 458 (1964).

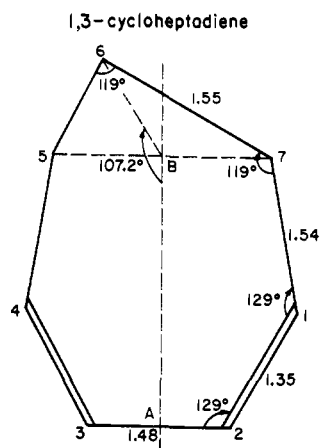


Figure 10. The structure of 1,3-cycloheptadiene ( $C_7$ ; planar, except for  $C_7$ ).

to that in 1,3-butadiene (1.483 Å). This can be explained either in terms of resonance interactions between the two  $\pi$  bonds, or to a radius contraction for  $sp^2$  bonding.

Table II. Structure Parameters of  $\Delta^6$ -Bicyclo[3.2.0]heptene<sup>a</sup>

Type	$r_{ij}$ , Å	$l_{ij}$ , Å
Bonded Interatomic Distances		
$C_1-H_1$	$1.10 \pm 0.02$	$0.095 \pm 0.005$
$C=C$	$1.34 \pm 0.01$	$0.040 \pm 0.005$
$C-C$	$1.56 \pm 0.01$	$0.065 \pm 0.005$
Nonbonded Interatomic Distances		
$C_7-C_5$	2.127	0.090
$C_1-C_3$	2.140	0.090
$C_2-H_{31}$	2.190	0.080
$C_7-H_1$	2.200	0.080
$C_7-H_6$	2.240	0.090
$C_3-H_{21}$	2.352	0.100
$C_1-H_7$	2.446	0.080
$C_2-C_7$	2.480	0.050
$C_1-C_4$	2.548	0.070
$C_3-C_4$	2.600	0.070
$C_4-C_7$	3.104	0.100
$C_3-C_7$	3.265	0.100
$\angle ABC_3 = 115 \pm 1^\circ$	$\angle C_5C_1C_2 = 109.5 \pm 0.7^\circ$	
$\angle C_1C_2C_3 = 86.7 \pm 0.3^\circ$	$\angle H_{31}C_3H_{22} = \angle H_{21}C_2H_{22} = 112.9 \pm 0.3^\circ$	
$\angle C_4C_5C_6 = 105.5 \pm 0.3^\circ$	$\angle C_1C_7C_6 = 94^\circ$	
$\angle C_2C_3C_4 = 112.9 \pm 0.3^\circ$	$\angle C_7C_1C_5 = 86^\circ$	
	$\angle DAB = 104^\circ$	

<sup>a</sup> See Figure 11.

The unexpected feature of the structure as found is the considerable angular strain, based on classic bond angles. If classic C-C-C bond angles were maintained, the ring could be closed with ease. This ring would have a configuration in which carbon atoms 7, 1, 2, 3, 4, 5 are not coplanar, but are closely packed in space (symmetry  $C_2$ ). This structure would not incorporate the conjugation energy present in planar 1,3-butadiene. Atoms 2, 3, 4, 5 could be coplanar, while atoms 3, 2, 1, 7 could be coplanar but the two planes would not be coincident. In addition, one of the hydrogen atoms on  $C_7$  would be brought very close to the  $\pi$  orbitals of  $C_4$ , and on the other side the hydrogen

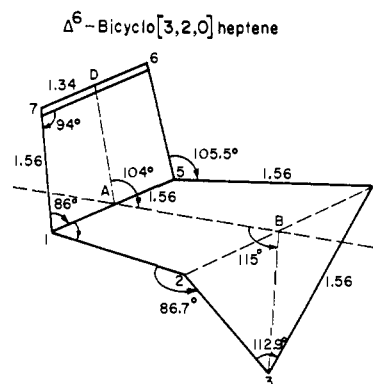


Figure 11. The structure of  $\Delta^6$ -bicyclo[3.2.0]heptene ( $C_7$ ; chair conformation).

atom attached to  $C_5$  would get very close to the  $\pi$  orbitals attached to  $C_1$ . It appears that nonbonding repulsion and the loss of conjugation more than compensate for the distortion energy (estimated at  $\approx 7$  kcal/mole) of the bond angles throughout the ring. Displacement of the methylene group at  $C_6$  from the plane not only reduces the magnitude of valence bond angle distortions at  $C_5$  and  $C_7$ , but also the nonbonded repulsion between the hydrogen atoms on adjacent carbons in the ring.

The nonplanar carbon skeletons of 1,3-cyclohexadiene and of cycloheptatriene present an interesting contrast with the almost planar conformation of 1,3-heptadiene. From partial microwave data Butcher<sup>16a</sup> estimated that in the hexadiene one ethylene group is rotated by  $17.5^\circ$  relative to the other about the single bond which connects them. The boat structure of cycloheptatriene has been established in an electron diffraction study<sup>16b</sup> and confirmed by a microwave analysis.<sup>16c</sup> Thus, it is evident that the minimum energy conformation is essentially determined by a balance between bond angle distortion and nonbonded repulsions; the influence of conjugation appears to be small. This conclusion is supported by the observed activation energy for ring inversion ( $6.3 \pm 0.5$  kcal/mole) reported by Anet<sup>16d</sup> for cycloheptatriene.

**$\Delta^6$ -Bicyclo[3.2.0]heptene.** The structure of  $\Delta^6$ -bicyclo[3.2.0]heptene (BCH) as derived from this study is shown in Figure 11. The molecule possesses  $C_2$  symmetry. A chair conformation is in best agreement with  $f(r)$  and intensity curves. Comparison of single and double bond lengths in the four-membered ring of BCH with cyclobutene<sup>17</sup> and cyclobutane<sup>18</sup> is made in Table III.

The expansion of bond lengths in the four-membered ring in BCH appears to be due to the attached five-membered ring. The latter apparently introduces strain in the cyclobutene portion, as noted by comparison with free cyclobutene and cyclopentane in which the bond length is 1.54 Å.<sup>19</sup> Whereas the bond angles in the cyclobutene ring in BCH are the same as those observed for the free cyclobutene, the carbon-carbon bond distances in the latter are approximately 0.02 Å shorter. It is the distortion of the exterior bond angle

(17) E. Goldish, K. Hedberg and V. Schomaker, *J. Am. Chem. Soc.*, **78**, 2714 (1956).

(18) J. D. Dunitz and V. Schomaker, *J. Chem. Phys.*, **20**, 1703 (1952).

(19) O. Hassel and H. Viervoll, *Tidsskr. Kjemi, Bergvesen*, **6**, 31 (1946).

**Table III.** Comparison of the Bond Lengths of Single and Double Bonds in Four- and Five-Membered Rings of BCH, Cyclobutene, Cyclobutane, and Cyclopentane

Compounds	Length, Å		Angle between single and double bond, deg
	Single bond	Double bond	
Four-membered ring in BCH	1.56 ± 0.01	1.34 ± 0.01	94 ± 0.5
Cyclobutene <sup>17</sup>	1.537 ± 0.01	1.325 ± 0.04	94 ± 0.8
Cyclobutane <sup>18</sup>	1.568 ± 0.02		
Five-Membered ring in BCH	1.56 ± 0.01		
Cyclopentane <sup>19</sup>	1.54 ± 0.02		
1,3-Cycloheptadiene	1.54 ± 0.01	1.35 ± 0.01	129
1,3,5-Cycloheptatriene <sup>16</sup>	1.505 ± 0.007	1.356 ± 0.005	127.2

which may be the cause for the destabilization and thus force a reduction in the bond overlap between adjacent carbons in the cyclobutene ring. It is evident that the bond directions, 1, 2 and 4, 5, must be on the same side of the cyclobutene ring. Further, to minimize nonbonding hydrogen atom repulsions—H<sub>7</sub> with H<sub>1</sub>, H<sub>6</sub> with H<sub>3</sub>—the chair conformation results. A quantitative analysis for the conformation which has the minimum energy has not been undertaken. This would require the assumption of specific potential functions for the interaction between hydrogen atoms and the lobes of the  $\pi$  bonds transannular to those hydrogen atoms. Since the total number of variables is large, a quantitative analysis is deferred for another investigation.

In considering the conformation of  $\Delta^6$ -bicyclo[3.2.0]heptene, boat and chair forms were proposed, but their relative thermodynamic stabilities are now known. In a similar compound, cyclohexane, the boat form has a higher energy by 6 kcal.<sup>20</sup> Barton<sup>21</sup> calculated the

energy difference between these boat and chair forms by using a semiempirical potential curve  $V(r) = ae^{-br}$ . The calculated values of free energy difference range from 1.31 to 6.85 kcal, depending on the choice of parameters. However, all the calculations show that the chair form has a greater stability than the boat form. If we assume that in BCH the boat form is only 3 kcal above the chair, and that the entropies of the two conformations are approximately equal, at 300°K, the concentration ratio (boat/chair) is expected to be about 10<sup>-2</sup>. However, it is doubtful that a concentration as high as 1:4 boat/chair could be detected in a mixture by electron diffraction.

**Acknowledgments.** The authors wish to thank Dr. O. L. Chapman for the sample of  $\Delta^6$ -bicyclo[3.2.0]heptene and Dr. Y. Meinwald for the sample of 1,3-cycloheptadiene used in this work. Grateful acknowledgment is made for support of this work by the Materials Science Center (ARPA). We acknowledge with thanks informative discussions with Dr. C. F. Wilcox of strain energy calculations for small ring hydrocarbons, and in particular, we thank Dr. Kenya Katada who took the photographs and started on the analysis of the 1,3-cycloheptadiene data.

(20) W. D. Dauben and K. S. Pitzer, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 1.

(21) D. H. R. Barton, *J. Chem. Soc.*, 340 (1949).