

# The Molecular Structures of Bicyclo[3.2.0]heptane and $\Delta^6$ -Bicyclo[3.2.0]heptene. An Electron-diffraction Study of Gaseous $C_7H_{12}$ and Molecular Mechanics Calculations on $C_7H_{12}$ and $C_7H_{10}$

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The electron-diffraction data of the title compound at room temperature are consistent with molecules predominately in an *endo* (boat) conformation of  $C_s$ -symmetry, with flap angles of  $65.0(3)^\circ$  [for C6 (C7)] and  $38.8(5)^\circ$  [for C3] and  $r_a$  (C-C) average of  $155.0(2)$  pm. The C-C bonds are shorter in the five-membered ring than in the four-membered ring. This is consistent with results of molecular mechanics calculations (Allinger's MM2) which also show that the bridge bond is the longest bond in the molecule. Significant amounts of a second conformer were not detected, but the co-existence of an *exo* form as indicated by the MM2-results (10 %) cannot be completely ruled out. The data are consistent with a planar four-membered ring and the MM2-results gave only slight puckering ( $2^\circ$ ) for the *endo* form as compared to  $24^\circ$  for the less favoured *exo* conformer which thus conforms to the trends established by the structure of related compounds.

Concurrent MM2-calculations also favour the *endo* form (99 % at room temperature) of bicyclo[3.2.0]heptene.

Some years ago the crystal structures of two derivatives of bicyclo[3.2.0]heptane were reported.<sup>1</sup> The five-membered rings of the molecules were found to have the *endo* conformation. Considering that the unsubstituted heptene analogue ( $\Delta^6$ -bicyclo[3.2.0]heptene) was reported to exist in the *exo* form (*i.e.* a chair conformation) in the gas phase, as determined by electron diffraction,<sup>2</sup> it was of interest to make a conformational study of the unsubstituted bicycloheptane. For this molecule a conformational preference of the *endo* (boat) form over the *exo* (chair) form by about  $6-10$  kJ mol<sup>-1</sup> ( $1.4-2.4$  kcal mol<sup>-1</sup>) was indicated by molecular mechanics calculations.<sup>1</sup>

It should be noted that several related bicyclohydrocarbons exist predominately in the *endo* form as summarized elsewhere.<sup>3,4</sup> Also, the result of the electron-diffraction study of bicycloheptene has been seriously questioned, particularly with regard to unreasonable structural features such as C-C-C angles in the five-membered ring of  $86.7^\circ$ , and on grounds of spectroscopic evidence.<sup>5,6</sup> It was said that in the absence of the electron-diffraction results the microwave data would have been interpreted unequivocally in terms of the boat form,<sup>5</sup> and also low frequency infrared and Raman data clearly favoured the boat form as it was concluded that any second conformer is at least 19.5

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$\text{kJ mol}^{-1}$  [ $4 \text{ kcal mol}^{-1}$ ] energetically less favoured.<sup>6</sup>

This paper primarily reports the results of a gas-phase electron-diffraction study of bicyclo[3.2.0]heptane. It was initiated as a natural extension of the structural and conformational study started by molecular mechanics calculations.<sup>1,7</sup> The results of these calculations have to some extent been incorporated in the analysis of the electron-diffraction data, and they are therefore briefly described in the present paper. Pending conclusive experimental clarification on the contrasting structural results for  $\Delta^6$ -bicyclo[3.2.0]heptene we also present molecular mechanics results for this molecule as obtained in calculations performed concurrently with those for the title compound.<sup>7</sup>

## MOLECULAR MECHANICS CALCULATIONS

Several sets of molecular mechanics calculations have been performed,<sup>1,7</sup> but only the results obtained by Allingers MM2 program<sup>8</sup> are quoted in the present paper.

$\Delta^6$ -Bicyclo[3.2.0]heptene. It was shown that the *exo* form is less stable by  $11.50 \text{ kJ mol}^{-1}$  [ $2.75 \text{ kcal mol}^{-1}$ ] than the *endo* form, indicating that the gas at room temperature contains 99 % of the *endo* (boat) form. This result is in contrast to the electron-diffraction result and agrees, although not on the magnitude of the energy difference, with the spectroscopic data<sup>5,6</sup> discussed above.

The rotational constants calculated from the atomic coordinates obtained, which are available upon request, are for the *endo* form:  $A=4429.7$ ,

Table 1. Molecular mechanics results of the *endo* (favoured) and the *exo* forms of bicyclo[3.2.0]heptene and bicyclo[3.2.0]heptane, represented by parameters of models with  $C_s$  molecular symmetry. See text for the assumed approximations and actual deviations from  $C_s$ -symmetry.

	Bicyclo[3.2.0]heptene		Bicyclo[3.2.0]heptane <sup>b</sup>	
	<i>endo</i>	<i>exo</i>	<i>endo</i>	<i>exo</i>
Geometrical parameters <sup>a</sup>				
C( $sp^2$ )-H	110.2	110.2	—	—
C( $sp^3$ )-H (average)	111.6	111.6	111.6	111.6
C1-C2	153.00	153.04	153.20	153.20
C2-C3	153.65	153.53	153.53	153.58
C1-C5	157.14	157.45	155.42	155.71
C1-C7	151.79	151.66	154.66	154.70
C6-C7	133.91	133.97	154.31	154.55
$\angle(\text{H-C-H})_{\text{pent}}$	108.3	108.3	108.2	108.2
$\angle(\text{H-C-H})_{\text{but}}$	—	—	112.2	112.2
$\angle(\text{C6-C7-H17})$	133.8	133.8	—	—
$\angle(\text{C5-C1-H8})$	115.7	113.5	114.2	112.6
$\theta(\text{C4-C5-C1-H8})$	131.5	128.9	129.0	126.0
$\angle(\text{C5-C1-C2})$	106.1	106.0	106.2	105.7
$\alpha$	65.1	63.7	63.2	61.5
$\beta$	36.2	-39.2	37.0	-42.0
Dependent angles				
$\angle(\text{C2-C1-C7})$	115.1	116.5	115.7	117.4
$\angle(\text{C1-C2-C3})$	105.0	103.8	104.9	103.9
$\angle(\text{C2-C3-C4})$	103.9	104.0	103.4	102.0
Mol fractions (293 K)				
$x$	0.99	0.01	0.90	0.10

<sup>a</sup> Distances in pm and angles in degrees. See Fig. 2 for numbering of the atoms. The flap angles are:  $\alpha=180-\phi(\text{C6-C1}\cdots\text{C5-C4})$  and  $\beta=180-\phi(\text{C3-C2}\cdots\text{C4-C5})$ ;  $\beta$  is defined positive for the *endo* (boat) form and negative for the *exo*(chair) form. <sup>b</sup> See Fig. 1 for deviations from  $C_s$  symmetry and actual parameter values.

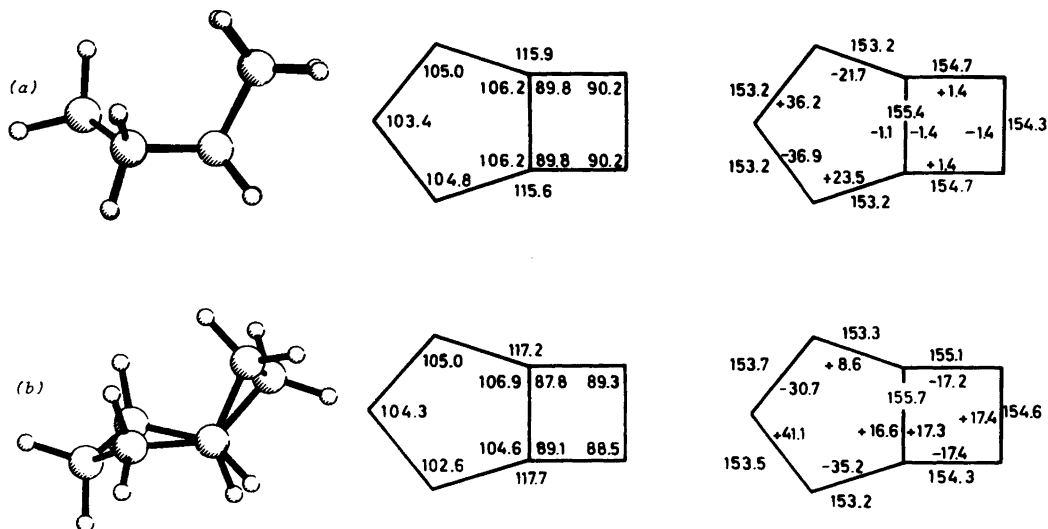


Fig. 1. Results of molecular mechanics calculations for bicyclo[3.2.0]heptane for the *endo* (a) and the *exo* (b) forms: The molecules viewed along the bridge bonds; and calculated valence angles, torsional angles and bond lengths for the carbon skeletons.

$B=3088.3$  and  $C=2382.0$  MHz; and for the *exo* form:  $A=4948.8$ ,  $B=2867.3$  and  $C=2137.3$  MHz. Comparisons with the experimental values:<sup>5</sup>  $A_0=4419.20$ ,  $B=3080.16$  and  $C_0=2375.33$  MHz reveal that the structure calculated for the *endo* form is in remarkably good agreement with the experimental results, the discrepancies corresponding to a scale inconsistency of 0.2–0.3 % in the rotational constants.

The coordinates suggest that  $C_s$  molecular symmetry should be adopted for both forms. Assuming  $C_{2v}$  local symmetry for the methylene groups, thus disregarding calculated tilts of about  $2.5^\circ$  between the bisectors of the H–C–H and C–C–C angles, and using average values for the H–C–H angles and for the C( $sp^3$ )–H bonds, the coordinates are fairly well represented by the fourteen geometrical parameters of  $C_s$ -models given in Table 1.

The approximate structure of the preferred *endo* conformer is not in good agreement with that proposed on the basis of experimental rotational constants alone. This has, for example,  $\alpha=71.2$  and  $\beta=22.6^\circ$ , but the determination was said to be hampered by severe correlation between  $\alpha$  and  $\beta$ .<sup>5</sup>

The structural parameters given for the less favoured *exo* form are in poor agreement with

those of the *exo* conformer, favoured in the electron-diffraction study, in which both flap angles are rather large,  $\alpha=76.0$  and  $\beta=-65.0^\circ$ .

In conclusion, it appears that the evidence against the structural results of the electron-diffraction study is substantial and they could represent a false minimum in the refinement. In the absence of new experimental results from an electron-diffraction reinvestigation and/or a microwave study using more complete isotopic substitution we believe that the result of the present calculation is the most reliable available for gaseous  $\Delta^6$ -bicyclo[3.2.0]heptene.

**Bicyclo[3.2.0]heptane.** The final calculations for this compound<sup>7</sup> also favoured the *endo* (boat) form. The energy difference between the two conformers of  $5.5 \text{ kJ mol}^{-1}$  [ $1.3 \text{ kcal mol}^{-1}$ ] is less than for the corresponding heptene and it suggests that the gas at 293 K contains 10 % of the *exo* (chair) form as a minor conformer.

The calculated structures for the two conformers are depicted in Fig. 1. The corresponding atomic coordinates are available upon request. In contrast to the *exo* form it is seen that the *endo* conformer is close to possessing overall  $C_s$  molecular symmetry. For this form the C–C–C–C dihedral angles ( $\theta$ ) of the four-membered ring are in the range  $1.1$ – $1.4^\circ$  and the

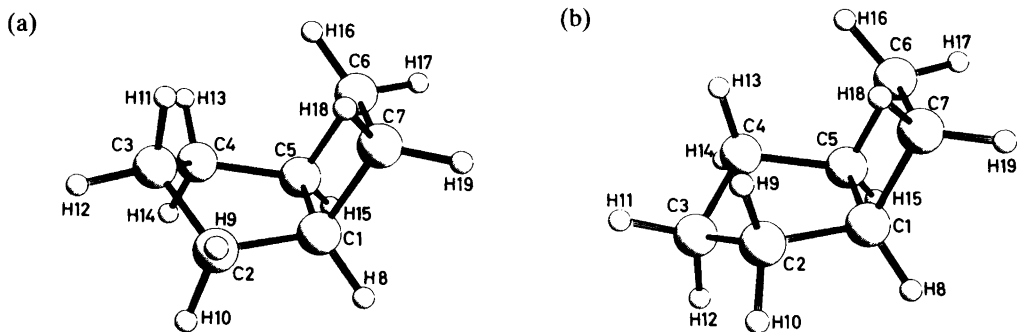


Fig. 2. Molecular models of  $C_s$ -symmetry for the *endo* (a) and *exo* (b) conformers of bicyclo[3.2.0]heptane; and numbering of the atoms.

difference between "symmetry related"  $\angle(C-C-C)$  and  $\theta(C-C-C-C)$  values of the five-membered ring are slight, compared to substantial differences for the *exo* form which has torsional angles in the four-membered ring of about  $17^\circ$ . However, both forms were approximated to models with  $C_s$  symmetry. Additionally, average values were used for the C-H bond lengths and for H-C-H valence angles for the five-membered ring,  $\angle(H-C-H)_5$ , and of the four-membered ring,  $\angle(H-C-H)_4$ . Finally local  $C_{2v}$  symmetry for the methylene groups was introduced thus neglecting tilts which according to the calculations could be  $1-3^\circ$  in the planes perpendicular to the corresponding C-C-C planes. Each of the two  $C_s$ -models is then described by thirteen geometrical parameters as defined in Table 1. The parameter values which give the best representation of the calculated atomic coordinates within the constraints described are listed in Table 1. It is seen that the flap angles ( $\alpha$  and  $\beta$ ) of  $63.2$  and  $37.0^\circ$  for the *endo* form and  $61.5$  and  $-42.0^\circ$  for the *exo* form are similar to the corresponding angles calculated for the analogous heptene (Table 1).

The values in Table 1 for bicycloheptane reveal that the C-C bonds are longer and the H-C-H angles wider in the four-membered ring than in the five-membered ring. This is consistent with experimental average values for such types of structural parameters as they are said to be  $155.5$  and  $153.4$  pm, and  $114$  and  $109.5^\circ$ , respectively.<sup>9</sup> The longest bond in both forms is that common to the fused rings,  $r(C1-C5)=155.4-155.7$  pm which appears to be in agreement with the situation in bicyclo[2.2.0]hexane which has fused

four-membered rings.<sup>10</sup>

The difference of the two forms with respect to the puckering of the four-membered ring is remarkable. The torsional angles given in Fig. 1 correspond to puckering angles ( $\phi$ ) of about  $2^\circ$  (*endo*) and  $24^\circ$  (*exo*). The MM2 program is said to give satisfactory reproduction of the puckering for cyclobutane<sup>8</sup>:  $\phi$  is  $28.4^\circ$  as compared to for example  $24.1^\circ$  determined by *ab initio* MO-calculations and  $26^\circ$  given as the most recent experimental value.<sup>11</sup> It has been pointed out that  $\phi$  in bicyclic compounds decreases according to the strain invoked by the fusing ring:  $\phi=0^\circ$  in bicyclo[2.1.0]pentane,<sup>12</sup> and  $\phi=11.5^\circ$  in bicyclo[2.2.0]hexane,<sup>10</sup> whereas it is said that the similarity of the structural parameters of the four-membered rings in *cis* and *trans* bicyclo[4.2.0]octane to those of cyclobutane and its nonfused derivatives, suggest that the strain is accommodated by the more flexible six-membered ring.<sup>13</sup> Thus the flexible *exo* form conforms to the established trend with a  $\phi$ -value intermediate to those encountered for the bicyclic hexane and octane, whereas the favoured *endo* form has an essentially planar four-membered ring with eclipsing neighbouring C-H bonds.

In all the calculations performed<sup>1,7</sup> the *endo* form of bicyclo[3.2.0]heptane has been favoured with an energy preference of  $5.5$  to  $10$  kJ mol<sup>-1</sup> where the lowest energy difference refers to the MM2 calculations. Such calculations have also been used in a conformational study of bicyclo[3.3.1]nonane and they appear to yield conformational compositions which are consistent with results of electron-diffraction studies of the gas at  $338$  and  $673$  K.<sup>14</sup>

Table 2. Weighting functions, correlation parameters and scale factors.<sup>a</sup>

Camera height mm	Wave-length pm	$\Delta s$ nm <sup>-1</sup>	$s_{\min}$	$sw_1$	$sw_2$	$s_{\max}$	Correlation parameter		Scale factor	
							<i>endo</i>	<i>exo</i>	<i>endo</i>	<i>exo</i>
128.3	5.815	4	60	70	300	324	0.239	0.298	0.734(8)	0.703(17)
286.3	5.788	2	20	50	120	140	0.481	0.486	0.774(10)	0.675(20)

<sup>a</sup> See Ref. 20 for definitions.

## ELECTRON DIFFRACTION

**Experimental.** Bicyclo[3.2.0]heptane was prepared according to literature procedures<sup>15</sup> and the electron-diffraction data were recorded on Kodak Electron Image plates using the Cornell/Edinburgh diffraction apparatus<sup>16,17</sup> with nozzle-to-plate distances of 128 and 286 mm. The sample and nozzle were maintained at room temperature during the exposures. The accelerating voltage was about 44 kV and the electron wavelength was calibrated against diffraction patterns of gaseous benzene [ $r_s(\text{C}-\text{C})=139.7$  pm] recorded immediately before and after the sample plates. The optical densities of three and four plates for the short and long camera distances, respectively, were recorded using the Joyce-Loebl Microdensitometer 6 at S.E.R.C. Laboratory, Daresbury.<sup>18</sup>

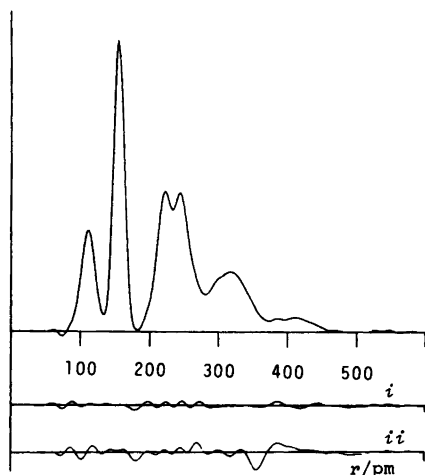


Fig. 3. Experimental molecular scattering intensities for nozzle-to-plate distances of (a) 128 and (b) 286 mm; and the corresponding final weighted difference curves according to the parameter values in Table 4 for the (i) *endo* and (ii) *exo* form of bicyclo[3.2.0]heptane.

**Data reduction and analysis procedure.** The data reduction was carried out using established programs<sup>17</sup> which at the final stages include an automatic background correction based on spline functions. Least-squares refinement program described previously<sup>19</sup> was used in the structure analysis. The data ranges and the parameters of the off-diagonal weighting functions are presented in Table 2 together with the scale factors and correlation parameters of the final results. The complex scattering factors of Schäfer *et al.*<sup>20</sup> were used and all calculations were carried out on an ICL 2972 computer. The experimental molecular intensities and the corresponding radial distribution curves are shown in Figs. 3 and 4, respectively.

**Vibrational amplitude quantities.** Root-mean-square amplitudes of vibration and perpendicular amplitude correction coefficients (*u*- and *K*-values) for the two *C<sub>s</sub>*-models of the molecule were calculated using a normal coordinate computer program originally written by R. L. Hilderbrandt<sup>21</sup> and atomic coordinates corresponding to the *C<sub>s</sub>*-structures estimated from the molecular mechanics results (*cf.* Table 1). The calculations were based on the Urey-Bradley force field for hydrocarbons given by Schachtsneider and Snyder.<sup>22</sup> Table 3 lists the force constants and the *u*- and *K*-values associated with the more important interatomic distances. An alternative Urey-Bradley force field discussed in a study of manxane,<sup>23</sup> gave similar results, but the chosen force field (Table 3) is as used in an electron-diffraction investigation of the related bicyclo[3.1.0]hexane.<sup>4</sup> A full list of the calculated *u*- and *K*-values for 293 and 0 K is available upon request.

**Structure refinements and results.** The initial analysis suggested that an *endo* form of *C<sub>s</sub>*-symmetry could represent the electron-diffraction data of bicyclo[3.2.0]heptane rather well, in contrast to the corresponding *exo* form.

The interpretation of the radial distribution curve (Fig. 4) was fairly straight forward, but as reflected in the distance values given in Table 3,

Table 3. Urey-Bradley force field for bicyclo[3.2.0]heptane and root-mean-square amplitudes of vibration ( $u$ ) and perpendicular amplitude correction terms ( $K$ ) calculated for the *endo* and *exo* forms of  $C_s$ -symmetry at  $T=298$  K.<sup>a</sup>

$K(C-C)$	223	$F(C\cdots C)$	32	$H(CCC)$	0.69	$H(CCH_t)$	0.32
$K(C-H_t)$	394	$F(C\cdots H)$	55	$H_t$	0.078	$H(CCH_s)$	0.33
$K(C-H_s)$	402	$F(H\cdots H)$	5			$H(HCH)$	0.52

Atom pair <sup>b</sup>	<i>endo</i>			<i>exo</i>		
	$r$	$u$	$K$	$r$	$u$	$K$
C-H <sup>c</sup>	111.6	7.94	1.84	111.6	7.93	1.81
C1-C2	153.2	5.27	0.42	153.2	5.28	0.41
C2-C3	153.5	5.23	0.52	153.6	5.23	0.50
C1-C5	155.4	5.41	0.29	155.7	5.43	0.27
C1-C7	154.7	5.28	0.43	154.7	5.26	0.41
C6-C7	154.3	5.23	0.78	154.6	5.23	0.75
C1-H9 <sup>c</sup>	219.4	10.50	1.26	219.7	10.49	1.23
C1-H18 <sup>c</sup>	223.6	10.45	1.31	223.6	10.44	1.27
C3-H9 <sup>c</sup>	219.7	10.49	1.35	220.1	10.49	1.32
C2-H11 <sup>c</sup>	220.2	10.48	1.39	220.7	10.47	1.33
C6-H18 <sup>c</sup>	223.3	10.44	1.67	223.5	10.44	1.62
C2-H8	225.5	10.20	0.94	224.1	10.26	0.92
C7-H8	222.1	10.42	0.93	224.0	10.36	0.92
C5-H8	225.5	10.48	0.82	223.7	10.57	0.79
C1-C6	218.9	6.34	0.35	219.1	6.32	0.33
C1-C4	246.8	8.08	0.15	246.2	7.99	0.16
C1-C3	243.1	7.08	0.24	241.6	7.21	0.23
C2-C4	240.9	6.92	0.31	238.6	7.03	0.32
C2-C7	260.7	7.38	0.35	263.1	7.31	0.37
C4-C7	324.2	8.79	0.11	325.7	9.49	0.11
C3-C7	313.5	11.23	0.15	363.6	7.76	0.12
C1-H11	288.8	14.46	0.82	340.1	10.33	0.77
C1-H12	339.7	10.45	0.80	282.8	14.65	0.80
C1-H13	337.3	11.15	0.66	301.7	14.39	0.69
C1-H14	304.8	14.71	0.69	338.4	11.13	0.67
C1-H16 <sup>c</sup>	296.0	11.42	1.01	296.2	11.37	0.98
C2-H13	337.8	10.15	0.85	279.1	15.13	0.84
C2-H14	286.1	15.01	0.84	337.6	10.09	0.86
C2-H15	332.2	12.33	0.45	328.4	11.88	0.47
C2-H16	360.8	17.62	0.53	363.0	18.39	0.53
C2-H17	422.8	10.78	0.54	423.9	11.03	0.51
C2-H18	347.0	11.82	0.91	349.1	11.78	0.88
C2-H19	268.0	14.99	1.09	271.8	14.81	1.15
C3-H8	341.1	10.39	0.53	305.4	13.25	0.53
C3-H16	306.4	20.46	0.72	386.5	16.19	0.56
C3-H17	420.9	13.10	0.55	457.5	11.08	0.51
C6-H8	295.7	11.29	0.69	295.8	11.35	0.66
C6-H9	377.5	16.00	0.47	337.2	18.80	0.51
C6-H10	412.9	11.77	0.49	422.2	11.80	0.47
C6-H11	302.4	21.89	0.59	446.4	13.22	0.48
C6-H12	422.5	13.28	0.56	426.9	13.37	0.46
C6-H13	278.1	15.45	0.97	267.0	14.78	1.06
C6-H14	355.0	10.71	0.82	335.4	12.37	0.92
H9-H10 <sup>c</sup>	180.8	12.94	2.35	180.8	12.94	2.28
H16-H17	185.2	12.68	2.45	185.2	12.67	2.41

<sup>a</sup> Force constants in  $\text{aJ nm}^{-2}$  ( $K$  and  $F$ ) and in  $\text{aJ rad}^{-2}$  ( $H$ ); distances ( $r$ ) and amplitudes ( $u$  and  $K$ ) in pm.  $1 \text{ aJ} = 1 \text{ mdyne } \text{\AA}$ . <sup>b</sup> See Fig. 2 for numbering of the atoms. Most  $\text{H}\cdots\text{H}$  values are omitted. <sup>c</sup> Average values are given for parameters that are symmetrically (by  $C_s$ -symmetry) different, but by additional constraints (see text) are assumed to be equal.

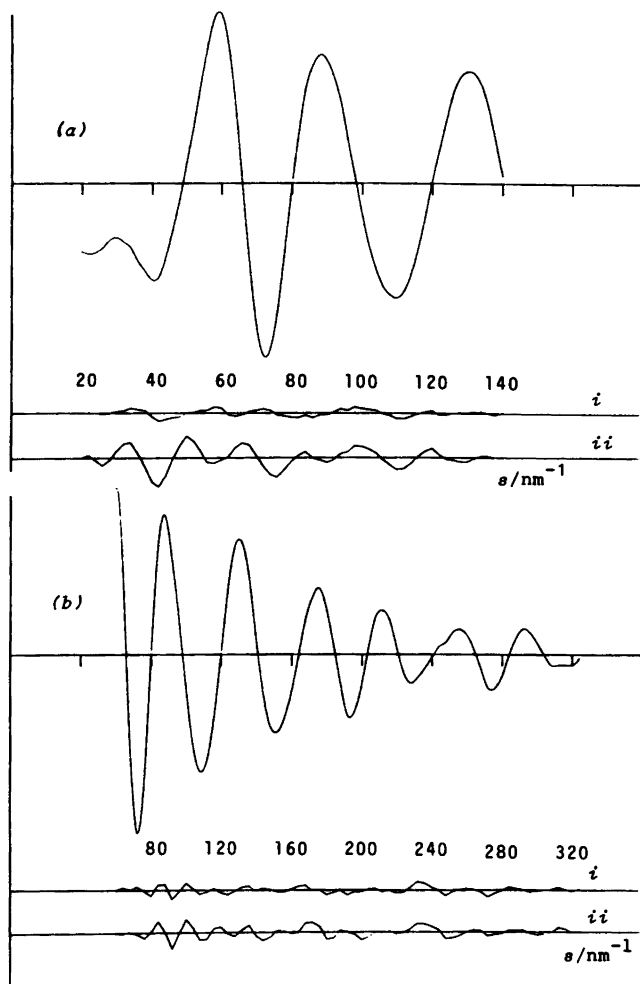


Fig. 4. Experimental radial distribution curve,  $P(r)/r$ , for bicyclo[3.2.0]heptane and difference curves corresponding to the intensities in Fig 3: (i) *endo* and (ii) *exo* form. Before Fourier inversion the data were multiplied by  $s \exp[-0.00015s^2]/(Z_C - f_C)$ .<sup>2</sup>

there are severe distance overlaps. The various C-H and C-C bonds account for the peaks at 110 and 154 pm respectively; and one-angle distances are the major contributors to the next peak which has double feature: C...H and C1...C6 (*i.e.* within the four-membered ring) at 220 pm and the remaining one-angle C...C distances at 240–260 pm. The C4...C7 and C3...C7 distances must then be contained in the next feature, but from about 300 pm there are also substantial contributions from C...H distances. The failure of the *exo* form to give a good representation of the data appears to be related

to the long C3...C6 (C7) distances at about 360 pm.

Refinements of both forms were carried out and the final molecular models were defined essentially as described in the preceding section and in Table 1. The two models are thus analogous, but for the sign of the flap angle  $\beta$ . Additional constraints to those previously given concern the relative magnitudes of the C-C bond lengths and the locations of the hydrogen atoms.

Only one C-C bond distance [ $r(\text{C1}-\text{C2})$ ] was kept as an independent parameter and the four

Table 4. Results of structural refinements of  $C_s$ -models (see text) for bicyclo[3.2.0]heptane based on electron-diffraction intensities.<sup>a</sup> Elements of the correlation matrices for the variables,  $p1$  to  $p5$  and  $u1$  to  $u5$ , are given in Table 5.

		<i>endo</i> [ $R_G=6.75\%$ ]		<i>exo</i> [ $R_G=14.09\%$ ]	
		Distances angles	Amplitudes	Distances angles	Amplitudes
Independent parameters ( $r_a$ , $\angle_a$ )					
$p1$	$r(C-H)$	109.8(2)		108.4(5)	
$p2$	$r(C1-C2)^b$	153.8(1)		153.7(1)	
$p3$	$\angle(C5-C1-C2)$	106.1(6)		105.8(3)	
$p4$	$\alpha$	65.0(3)		69.1(7)	
$p5$	$\beta$	38.8(5)		-40.3(24)	
	$\angle(H-C-H)_{pent}$	110.	fixed	110.0	fixed
	$\angle(H-C-H)_{but}$	114.		114.0	
	$\angle(C5-C1-H8)$	114.2		112.6	
	$\theta(C4-C5-C1-H8)$	129.0		126.0	
Interatomic distances ( $r_a$ ) <sup>c</sup> and amplitudes ( $u$ )					
$u1$	C-H	111.0(2)	7.9(2)	109.6(5)	7.8(5)
$u2$	C1-C2 <sup>b</sup>	154.0(1)	5.2(1)	154.0(1)	4.9(2)
	C2-C3 <sup>b</sup>	154.5(1)		154.4(1)	
	C5-C6 <sup>b</sup>	155.4(1)		155.3(1)	
	C1-C5 <sup>b</sup>	156.3(1)		156.5(1)	
	C6-C7 <sup>b</sup>	155.5(1)		155.6(1)	
	C1...H9	218.8(4)		217.7(4)	
	C1...H18	222.6(2)	221.6(4)		
	C3...H9	219.1(4)	218.2(4)		
	C2...H11	219.7(5)	11.0[u3]	218.8(4)	10.5[u3]
	C6...H18	222.7(2)	221.8(4)		
	C2-H8	225.1(4)	222.4(4)		
	C7-H8	223.6(3)	230.3(8)		
	C5-H8	224.8(2)	222.0(4)		
$u3$	C1-C6	219.9(1)	6.6(1)	219.9(2)	6.3(3)
$u4$	C1-C4	247.5(10)	7.5[fixed]	247.1(5)	9.0(9)
	C1-C3	243.5(20)	6.5[fixed]	243.1(19)	7.9[u4]
	C2-C4	241.3(30)	6.3[fixed]	240.1(15)	7.9[u4]
	C2-C7	259.4(4)	6.8[fixed]	253.4(10)	8.2[u4]
$u5$	C4-C7	323.2(9)	9.2(9)	318.3(9)	8.1[u13]
	C3-C7	308.8(13)	11.7[u5]	354.6(11)	7.8[fixed]
Dependent angles ( $\angle_a$ , $\theta_a$ )					
	$\angle(C1-C2-C3)$	104.5(12)		104.3(12)	
	$\angle(C2-C3-C4)$	102.9(18)		102.3(9)	
	$\angle(C2-C1-C7)$	114.0(2)		110.1(7)	
	$\theta(C5-C1-C2-C3)$	23.8(8)		24.8(12)	
	$\theta(C1-C2-C3-C4)$	38.4(7)		40.0(21)	
	$\theta(C7-C1-C2-C3)$	73.4(10)		120.5(13)	

<sup>a</sup> Distances and amplitudes in pm; angles in degrees. Values in parentheses are least-squares standard deviations which include correlation among the parameters, but not systematic uncertainties. See Fig. 2 for numbering of the atoms and Table 1 for definitions of  $\alpha$  and  $\beta$ . Dihedral angles are defined relative to zero for *syn* arrangements and are positive for counter clock-wise rotation. <sup>b</sup> The remaining C-C bond lengths are tied to C1-C2 ( $r_a$ ) according to the results of molecular mechanics calculations (Table 1). The standard deviation given is thus that of the average and not of the individual C-C bonds. <sup>c</sup> The remaining C...H (see Table 3 for approximate distance distribution and  $u$ -values) and H...H distances were included in the refinements but are omitted here.



Table 5. Elements of the correlation matrices ( $i, j$ :  $\rho_{ij}$  for  $|\rho_{ij}| > 40\%$ ) corresponding to the least-squares results given in Table 4 ( $p$ - and  $u$ -values) and Table 2 ( $k$ -values, *i.e.* scale factors).

<i>endo</i> form		<i>exo</i> form	
$p3, p4$ :	-45;	$p3, u5$ :	-75
$p4, u5$ :	44	$p4, p5$ :	42;
$u2, kl$ :	69	$p5, u4$ :	62
		$u2, kl$ :	70
		$u3, u4$ :	57;
		$p4, u4$ :	62
		$u3, kl$ :	41

remaining types of C–C bonds were given lengths relative to this bond as suggested by the MM2-calculations (Table 1). In the initial refinements, which were carried out prior to the MM2-calculations, it was found that for the *endo* form the best fit was obtained if the C–C bond lengths of the four-membered ring exceeded those of the five-membered ring by about 2 pm whereas for the *exo* form it appeared that the best fit was obtained where all C–C bonds were of equal length. It proved difficult to refine the parameters defining the positions of the hydrogens. With the exceptions of  $r(\text{C–H})$  they were maintained at fixed values which corresponded to the MM2-results for the H8(15) hydrogens (Table 1). For  $\angle(\text{H–C–H})$  110 and 114° were used respectively for the five- and four-membered ring as refinements had suggested that larger values than those predicted by the MM2-calculations were preferred.

For both models the parameter values deduced from the MM2 results were used as starting values in  $r_a$ -refinements in which the vibrational parameters were fixed at the calculated values (Table 3). However, several series of refinements established that the same minima were approached from several sets of starting values for the highly correlated flap angles ( $\alpha$  and  $\beta$ ). These sets included  $\alpha=76$  and  $\beta=-65^\circ$  which correspond to the disputed electron-diffraction structure for bicyclo[3.2.0]heptene, and for the *endo* form special attention was given to possible exchange of magnitudes for the C4...C7 and C3...C7 distances. Consecutive  $r_a$ -refinements and inclusion of some  $u$ -values in the refinements resulted in slightly improved fit to the data without significant shifts in the geometrical parameters. The final results for which  $R_G^{19}$  was 6.75 and 14.09 % [ $R_D$ : 4.53 and 11.11 %] respectively for the *endo* and *exo* forms are given in Table 4. Errors quoted are standard deviations obtained in the least-squares refinements, *i.e.* they are not augmented to account for systematic uncertainties. Elements of the correlation matrices for the final refinements are given in Table 5. The weighted differences in molecular scattering in-

tensities and the differences between experimental and theoretical radial distributions are included with the corresponding experimental curves in Figs. 3 and 4, respectively.

The possibility that the *exo* form may co-exist with the *endo* form as a minor conformer was considered. However,  $r_a$ -refinements for such compositions using the calculated  $u$ -values did not give improved fit to the data: the obtained  $R_G$  factors were: 7.28, 7.32, 7.47, 7.71 and 8.04 % for 100, 95, 90, 85 and 80 % of the *endo* form. It is also seen from Figs. 3 and 4 that the *endo* form represents the data rather well. In particular there are no obvious discrepancies for the 350–360 pm and 300–310 pm regions in which the C3...C6(7) distances for the *exo* and *endo* forms are found.

Possible deviations from  $C_s$ -symmetry have not been seriously considered in the present electron-diffraction investigation. In this respect it should be noted that the symmetrical *endo* form represents the data in an acceptable manner, and this may be used as evidence against substantial distortions. Small deviations from  $C_s$  symmetry as indicated by the molecular mechanism calculations are judged to be insignificant as far as the electron-diffraction data are concerned, as the complex distance overlaps would obscure attempt to determine the asymmetry parameters. Admitted, the  $C_s$ -model may introduce a bias against the *exo* form, which is substantially distorted according to the molecular mechanics results. However, by inspection of the distance distributions of the unsymmetrical form it is clear that the *exo* form could not be present as the major conformer nor in substantial amounts (*i.e.* more than 10 %).

## DISCUSSION

Although it may be argued that the molecular mechanics results have been incorporated in the interpretation of the electron-diffraction data, it appears that the two investigations agree that an *endo* form which only shows minor distortions

from  $C_s$ -symmetry is the major conformer of bicyclo[3.2.0]heptane at room temperature. The electron-diffraction data do not suggest the co-existence of a second conformer in significant amounts, but in view of the many assumptions and distance overlaps, a contribution of up to 10 % of the *exo* form, as indicated by the molecular mechanics calculations, cannot be completely ruled out. A puckering angle of  $16.4^\circ$  for the four-membered ring in bicyclo[3.2.0]heptane has been predicted from an empirical equation<sup>24</sup> and it is, as discussed previously, remarkable that the preferred form of bicyclo[3.2.0]heptane appears to be only insignificantly puckered. It is possible that substantial puckering would be in conflict with steric interactions between hydrogens across the rings, *i.e.* H11 of C3 and H16(18) of C6(7).

The flap angles obtained,  $\alpha=65.0(3)^\circ$  and  $\beta=38.8(5)^\circ$ , are respectively smaller and larger than those obtained for related compounds with fused three- and five-membered rings. For example in bicyclo[3.1.0]hexane<sup>4</sup>  $\alpha=70.6(11)^\circ$  and  $\beta=25.2(28)^\circ$  and the latter value is similar to that found for cyclopentene which has  $\beta=28.8(25)^\circ$ .<sup>25</sup> In the present investigation attempts to fit models with smaller  $\beta$ -values failed. The final structure has a bridgehead carbon angle [ $\angle(C2-C1-C7)$ ] of  $114.0^\circ$  compared with for example  $\angle(C2-C1-C6)=113.5(1.1)^\circ$  in bicyclo[2.2.0]hexane.<sup>10</sup>

In the preliminary analysis it was indicated that the bond lengths in the four-membered ring exceeded those of the five-membered ring by 2 pm, in agreement with the subsequent MM2 calculations and experimental average values.<sup>9</sup> Cyclobutane and cyclopentane have  $r_g$  (C-C) values of 155.1(3) [an earlier value is 154.8 pm]<sup>26</sup> and 154.6(1) pm,<sup>27</sup> respectively. The average C-C bond length of bicyclo[3.2.0]heptane is 154.9 pm (Table 4) as compared to 155.6 pm for bicyclo[2.2.0]hexane.<sup>10</sup>

The length of the transannular C-C bonds is of particular interest, and it has been stated that the bridgebond *cannot* simply be predicted in terms of a model involving competition from the fused rings, giving a bridgebond of intermediate length. In fact, it appears that the bridgebond is the longest C-C bond in bicyclo[2.2.0]hexane (157.7 pm) and in bicyclo[3.2.0]heptane (156.3 pm) according to an electron-diffraction study<sup>10</sup> and the present MM-calculations. For the former

molecule the bridgebond was resolved among three types of C-C bonds. In the present case there are five types of such distances and only 12.5 % of the C-C bond-peak area can be attributed to the transannular bond and any attempt to determine its length based on the electron-diffraction data alone was judged vain. Based primarily on electron-diffraction data very short bridgebonds have been assigned to bicyclo[3.1.0]hexane (145.4 pm)<sup>4</sup> and bicyclo[2.1.0]pentane (143.9 pm).<sup>28</sup> Although agreeing on the average C-C bond length for these compounds a recent *ab initio* Mo-study has questioned the reported relative magnitudes of the C-C bonds for these two compounds.<sup>29</sup> The calculated values for the bridgebonds were 150.9 and 152.9 pm for the hexane and pentane, respectively, and for the latter this is in better agreement with structural results obtained from microwave data.<sup>30</sup>

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