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The Zero-Point-Average Structure of Bicyclo[3.1.0]hexane as Determined by Electron Diffraction and Microwave Spectroscopy[1a]

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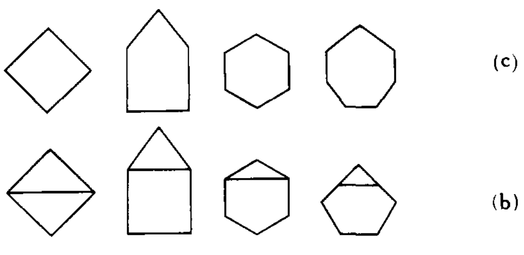
Abstract: The structure of bicyclo[3.1.0]hexane has been determined by a combined analysis of electron diffraction and microwave spectroscopic data. The molecule was observed to prefer the boat conformation with flap angles of 70.6° (1.1) and 25.2° (2.8) for the cyclopropane and cyclopentane moieties, respectively. On the basis of calculated vibrational amplitudes and a combined analysis including microwave rotational constants, the average C–C bond length, 1.524 (3) Å, was resolved into three distinct distances: C_1–C_5 = 1.454 (9) Å, C_1–C_6 = 1.515 (8) Å, and C_1–C_2, C_2–C_3 = 1.543 (4) Å. Although the bridge bond (C_1–C_5) appears to be quite short for a single bond, the bond lengths for the remaining bonds in the three- and five-membered rings are comparable to the corresponding parameters reported for cyclopropane (1.512 Å) and cyclopentane (1.546 Å).

Introduction

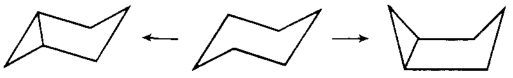
It is interesting to speculate on the structural changes which arise from the introduction of a 1–3 intraannular C–C bond in the cyclic systems **1c**–**4c**. Of particular interest are the conformational differences between the resulting bicyclo[*n*.1.0]alkanes, **1b**–**4b**, and their cyclic counterparts.



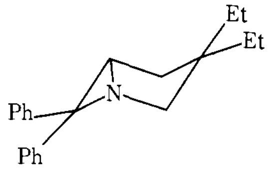
1 2 3 4

Precise comparisons, based on gas-phase structural data, are possible for the first two pairs: **1c**[2] with **1b**[3], and **2c**[4a] with **2b**.[4b] Structural data on **3c**[5] and **4b**[6] are also available; however, their respective analogs have not yet been investigated. Cycloheptane **4c**[7] is currently under investigation, and a comparison should be forthcoming for the fourth pair in this series. The purpose of this paper is to report on the structural parameters of **3b**, bicyclo[3.1.0]hexane (henceforth referred to as BCH).

In the case of the six-membered rings **3b** and **3c**, one might propose two possible conformations for the bicyclo compound, namely a chair and and a boat form. In view of the preferred conformation of cyclohexane, one might expect **3b′** to be the more stable form for BCH, and, in fact an early x-ray study of 3,3-diethyl-6,6-diphenyl-1-azabicyclo[3.1.0]hexane[8] (**5**) found this to be the case. More recently, Chiang and Bauer[9] have also found a preference for the chair conformation in the related compound Δ^6-bicyclo[3.2.0]heptane (**6**).



3b′ 3c 3b″



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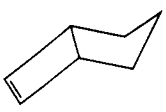

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Subsequent x-ray studies have shown, however, that several BCH derivatives, not substituted in the 3 and 6 positions, definitely prefer the boat conformation **3b″**.[10-13] The same conclusion has been reached for BCH itself on the basis of molecular mechanics calculations[14] and a recent microwave spectroscopic investigation.[15] In this latter study, however, a complete structural analysis was not possible since isotopic substitutions on the parent compound were not undertaken. We therefore felt that a combined microwave spectroscopic-electron diffraction investigation of BCH would be worthwhile in determining a precise geometry for this molecule. Such an

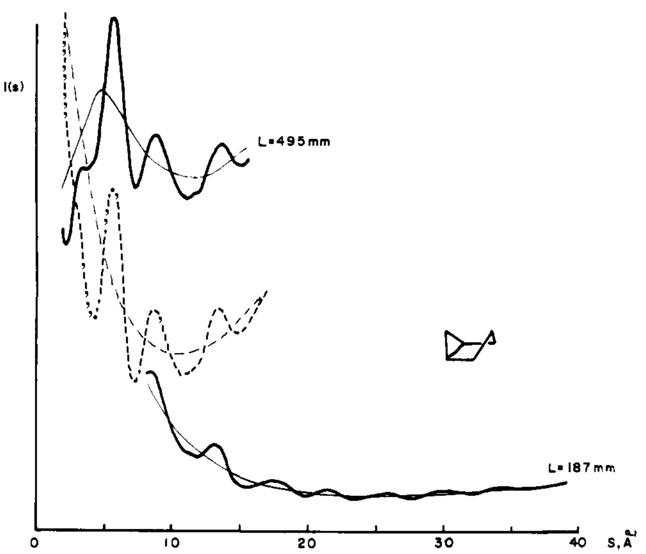


Figure 1. Experimental intensity curves and hand-drawn backgrounds for bicyclo[3.1.0]hexane. For the long camera length data (L = 495 mm) the two curves correspond to two different treatments of the experimental data as described in the text.

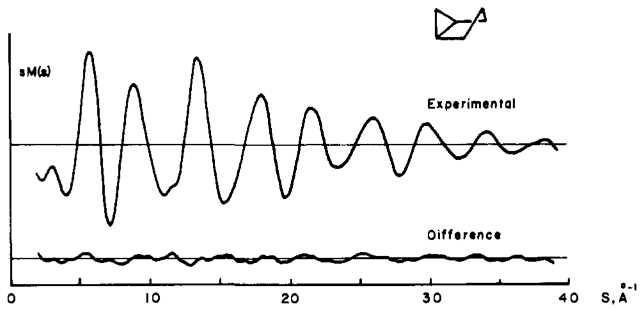


Figure 2. Levelled experimental intensity curve and error curve for best least-squares model shown in Table III.

analysis has recently been applied to the structure determination of the closely related compound cyclopentene oxide.[16]

Experimental Section

BCH was prepared according to the procedure of Rawson and Harrison[17] by reacting cyclopentene with $C_2H_2I_2$ in ether. Product verification was based on the mass spectrum of the resulting compound which exhibited a molecular ion peak corresponding to BCH, and the purity of the twice distilled product (99.4%) was determined by gas chromatography.

Diffraction patterns were recorded on the EG-100A gas-phase diffraction instrument at Moscow State University. The data were treated in the conventional manner[18] except that a method, devised by A. V. Golubinskii, was employed to determine the wavelength of the electron beam. Benzene calibration photographs were taken under conditions identical with those used for BCH, and the resulting diffraction patterns, based on an approximate value of λ, were subjected to a least-squares analysis. In this analysis the approximate wavelength was further refined by minimizing the function $\Sigma(sM(s)_{\text{exp}} - ksM(s)_{\text{calcd}})^2$ with respect to variations in λ while constraining the molecular geometry of benzene to its known structure.[19,20] It should be noted that although λ was the parameter varied in this procedure, one could equally well have varied L, the camera distance. The scale factor is strongly dependent on the $L\lambda$ product to the extent that L and λ are 100% correlated and cannot be determined simultaneously using the above technique. The choice of varying λ rather than L is based on a greater degree of confidence in the experimental determination of the nozzle-to-place distance. This procedure has been successfully applied to several other structural studies which have recently been carried out in our laboratory. Carbon disulfide has also been occasionally used as a calibration standard for some of these studies. While the amount of work is noticeably greater, we nevertheless feel that this additional effort is compensated for by an enhanced degree of reliability in the deduced structural parameters.

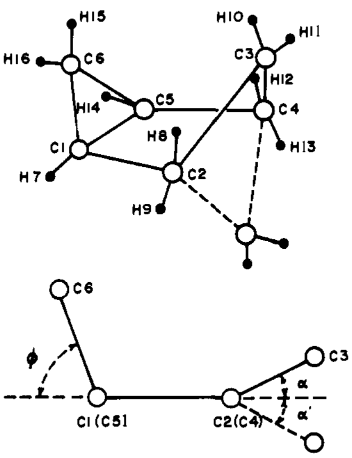


Figure 3. Molecular model of BCH and its projection. The chair conformation is illustrated by the dotted lines.

Four photographs for each nozzle-to-plate distance (49.5 and 18.7 cm) were used to cover the range from s = 2.0 to 16.0 Å^{-1} and from s = 8.2 to 39.2 Å^{-1}, respectively. Optical densities ranged from 0.06 to 0.09 for the long camera length plates, and from 0.32 to 0.56 for the short camera length plates.

Experimental intensities with hand-drawn backgrounds are shown in Figure 1. Initially, because of an error in our interpolation routine, we used unlevelled intensities for small s as shown by the solid lines in Figure 1. Later, after a good deal of the structural analysis had been completed, the interpolation program was corrected and a levelled intensity curve (shown as a dotted line in Figure 1) was employed for the remainder of the analysis.

Data Analysis

In the initial stages of analysis only the electron diffraction data (Figure 2) were employed. As is frequently the case with organic molecules of low symmetry, several simplifying assumptions had to be made in order to reduce the complexity of the model to a manageable number of parameters. The following constraints were imposed for all models investigated.

(1) The molecule was assumed to have C_s symmetry (see Figure 3).

(2) All C-H bond lengths were constrained to one average value.

(3) The methylene groups were assumed to have local C_{2v} symmetry. One average angular parameter was used to fix the geometry of the C_2, C_3, and C_4 methylene groups, and a second angular parameter was used for the C_6 methylene moiety.

(4) The position of the hydrogens bonded to C_1 and C_5 were initially located using the valence and dihedral angles found for cyclopentene oxide:[16] $\angle C_1C_5H$ = 129.0° and τ ($C_2C_1C_5H$) = 150.0°. In latter refinements which included the microwave data, however, these parameters were also varied.

Calculated vibrational amplitudes and shrinkage corrections were employed throughout the analysis. In these calculations the Urey-Bradley force field of Schachtschneider and Snyder[21] was used. Table I lists the force constants used and the parameters calculated.

The requirement of C_s symmetry for BCH leads to the possibility of four distinct C-C single bond lengths. Since all of these distances occur collectively under one peak of the radial distribution curve (Figure 4), they are difficult, if not impossible, to resolve without additional experimental information. Calculated vibrational amplitudes are quite helpful in this respect; however, one should always remember that

Table I. Molecular Force Field for BCH and Calculated Vibrational Parameters[a]

$K_{C\text{-}C}$ = 2.229 mdyn Å^{-1}	H_{CCC} = 0.687 mdyn Å
$K_{C\text{-}H_t}$ = 3.936 mdyn Å^{-1}	H_{CCH_s} = 0.329 mdyn Å
$K_{C\text{-}H_s}$ = 4.023 mdyn Å^{-1}	H_{CCH_t} = 0.317 mdyn Å
$F_{C\cdot\cdot C}$ = 0.324 mdyn Å^{-1}	H_{HCH} = 0.523 mdyn Å
$F_{C\cdot\cdot H}$ = 0.548 mdyn Å^{-1}	H_{τ} = 0.078 mdyn Å
$F_{H\cdot\cdot H}$ = 0.046 mdyn Å^{-1}	

Distance[b]	$l_{ij} \times 10^4$	$K_{ij} \times 10^4$	$r_\alpha(0) - r_\alpha(300)$
C-H$_{av}$	792	228	0.0058
C$_1$-C$_5$	514	29	0.0006
C$_1$-C$_6$	512	43	0.0015
C$_1$-C$_2$	519	44	0.0016
C$_2$-C$_3$	520	97	0.0058
C$_1$· ·C$_3$	644	29	
C$_2$· ·C$_5$	620	19	
C$_1$· ·C$_4$	620	18	
C$_2$· ·C$_6$	738	27	
C$_3$· ·C$_6$	1293	12	
C· ·H$_{gem}$ (av)	1055	221	

	B_0,[c] MHz	$B_z - B_0$, MHz
A	5542.96	+3.84
B	4236.82	+1.02
C	3127.04	−0.75

[a] Force constants taken from ref 21. [b] Amplitudes shown are for major peaks in the radial distribution curve. [c] B_0 rotational constants taken from 15.

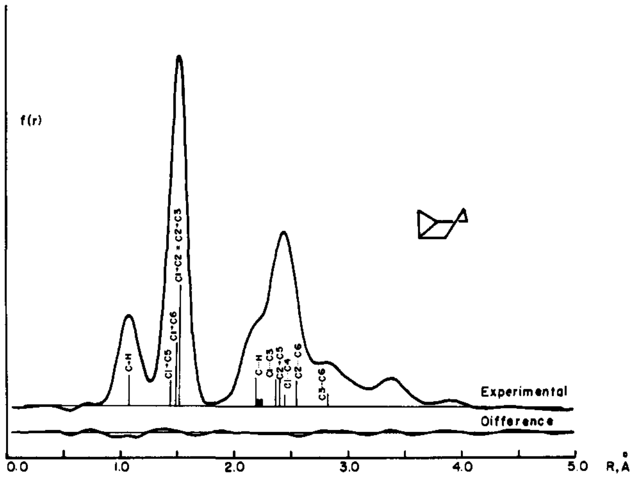


Figure 4. Experimental radial distribution curve and error curve for the best least-squares model shown in Table III.

Table II. Simplified Model of Bicyclo[3.1.0]hexane with Average C-C Bond Distance[a]

Parameter	r_g, Å; angles, deg	Parameter	r_g, Å; angles, deg
C-C$_{av}$	1.524 (3)	α	26.4 (3.0)
C-H$_{av}$	1.109 (6)	ϕ	70.6 (1.5)
∠C$_2$C$_3$C$_4$	104.2 (2.0)	R	0.155
∠HC$_3$H	104.1 (6.0)		

[a] Uncertainties shown in parentheses are 3σ values.

when they are used in the analysis the results obtained are conditionally predicated upon the unknown precision of these calculated parameters. In any event the inclusion of such calculated parameters is undoubtedly better than a simultaneous least-squares refinement of both the amplitude and distance parameters which are known to be highly correlated.

The strategy which was adopted for the analysis of the experimental data consisted of the following four steps: (1) a simplified model based on an average C-C bond length was refined as an initial approximation to the structure; (2) a model based on a mixture of boat and chair conformations was tested in an attempt to see whether an equilibrium mixture could be ruled out on the basis of the diffraction data alone; (3) various models based on nonequivalence of C-C distances were refined and subjected to statistical hypothesis testing procedures; (4) the models arrived at in step 3 were further subjected to a combined analysis employing both the electron diffraction data and the microwave rotational constants.

1. Simplified Model Employing One Average C-C Distance. The first model which was analyzed can be described in terms of the following six parameters: the average C-C and C-H bond lengths, the ∠C$_2$C$_3$C$_4$ valence angle, an average ∠HCH valence angle for the methylenes in the five-membered ring, and the two flap angles α and φ shown in Figure 3. The ∠HC$_6$H angle was constrained to 115°, the value for cyclopropane.[22]

Several refinements based on different starting values of the angular parameters, ∠C$_2$C$_3$C$_4$ (103-107°), α (25-33°), and φ (63-77°) were tried. These values were either transferred from similar reported structures,[10-13,15,16] or estimated from inspection of the experimental radial distribution curve (Figure 4). The results of this preliminary analysis are shown in Table II. While this model is crudely representative of the average structure of the molecule, it nevertheless has several shortcomings. In particular, the agreement in the C-C region of the radial distribution curve was rather poor. As one might expect the agreement could be improved by increasing the vibrational amplitude for the C-C distance, but the large value required to improve the fit only served as an additional indication of some rather large splittings among the various different C-C distances present in the molecule.

2. Determination of the Conformational Ratio for Boat and Chair. Even as we began our analysis there was no doubt concerning the preferred conformation of BCH. Infrared,[23] Raman,[24] and microwave spectroscopic[15] studies all agreed that the predominant form of the molecule in the gas phase was the boat conformation. Nevertheless, we decided to attempt an analysis of our data in terms of a conformational mixture in order to test the sensitivity of the electron diffraction technique to the presence of a second conformation.

Special geometrical subroutines were incorporated into the analysis programs which permitted the refinement of a model composed of a mixture of two conformations identical in all respects except for the flap angle α. This latter parameter was refined as two separate parameters α and α' corresponding to the boat and chair conformations, respectively.

Initial refinement of the conformational ratio led to a value of 75 ± 10% for the mole fraction of the boat form. At a later stage of refinement this analysis was repeated with more refined geometrical parameters, and in the final analysis, varying only α, α', φ, and the conformational ratio, a value of 98 ± 5% was obtained for the mole fraction of the boat form. It is somewhat gratifying to find that electron diffraction alone is capable of unambiguously assigning the correct conformation of BCH. In all subsequent analyses the mole fraction of the boat conformation was assumed to be 100%.

3. Nonequivalence of the C-C Bond Lengths. As previously mentioned C_s symmetry for BCH permits the existence of four distinct C-C bonds. Any attempt to resolve the splittings in these parameters must proceed in several stages by the successive relaxation of constraints. For example, one possible two-parameter model would result from the assumption that all of the bond lengths in the three-membered ring have one average value while the remaining bond lengths for the five-membered ring have a second average value. This, however,

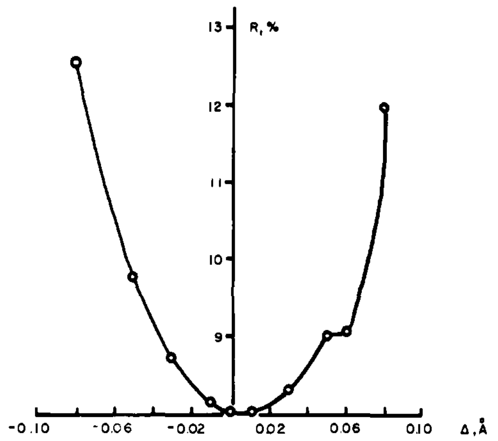


Figure 5. Plot of *R* factor as a function of nonequivalence between the C_1–C_2 and C_2–C_3 bond distances for BCH.

represents only one two-parameter possibility; several others also exist in addition to a number of three-parameter models. From all of the possible two- and three-parameter models, the following were selected for more detailed analysis:

(1) C_1–C_6 = C_1–C_5 and C_1–C_2 = C_2–C_3
(2) C_1–C_6 and C_1–C_5 = C_1–C_2 = C_2–C_3
(3) C_1–C_6 = C_1–C_5 = C_1–C_2 and C_2–C_3
(4) C_1–C_6, C_1–C_5 and C_1–C_2 = C_2–C_3
(5) C_1–C_2, C_2–C_3 and C_1–C_6 = C_1–C_5

Little or no improvement was obtained when least-squares refinement of the two-parameter models 1-3 was attempted, so we therefore turned our attention to the three-parameter models 4 and 5.

Despite the many choices of starting parameters tested, initial attempts to refine model 4 failed to converge and, accordingly, model 5 was first analyzed in more detail. Depending on the starting values chosen for the C_1–C_5 bond length, two resulting structures were obtained with "short" (1.46 Å) and "long" (1.53 Å) C_1–C_5 distances. *R* factors for these two models were found to be 0.150 and 0.152, respectively. At this point in the analysis, the initial background was improved and an attempt was made to refine a model based on all four C–C distances. Least-squares refinements of this model also failed to converge.

In a final attempt to resolve the question of nonequivalence, before proceeding to a combined analysis including rotational constants, it was decided to manually explore the shape of the error surface in the vicinity of the two minima obtained for model 5. This was done by setting C_1–C_2 = C_2–C_3 + Δ and refining the other structural parameters for fixed values of Δ. The results of this analysis are illustrated in Figure 5. The minimum value of *R* (0.080) occurred at Δ = 0.005 Å corresponding to a model with a "short" C_1–C_5 bond length. The peculiar feature exhibited by the response function in the vicinity of Δ = 0.05 Å was found to be due to the transition from the "short" C_1–C_5 model to the "long" C_1–C_5 model as mentioned above. The 1% difference in *R* factors between these two points, however, was found to be significant at the 99.5% confidence level according to the Hamilton criterion.[25]

The net result of this analysis was to indicate a near degeneracy between the C_1–C_2 and C_2–C_3 distances which led us to again consider further refinements of the three-parameter model previously referred to as model 4. With the improved starting values obtained from this intermediate analysis, we were now able to obtain convergence for this model and the results for our analysis of model 4 are indicated in Table III. At this point we felt that we had extracted the maximum amount of information from the diffraction data and therefore proceeded to a combined analysis including both the diffraction data and microwave rotational constants.

Table III. Structural Parameters for Bicyclo[3.1.0]hexane Obtained from Analysis of Diffraction Data Alone[a]

Parameter	r_g Å; ϕ_a, deg	r_g, Å; ϕ_α, deg
C_1–C_6	1.520 (11)	1.517 (10)
C_1–C_5	1.455 (10)	1.465 (10)
C_1–C_2 C_2–C_3	1.549 (5)	1.539 (4)
C–H	1.108 (5)	1.109 (5)
$\angle C_2C_3C_4$	107.5 (1.4)	108.0 (1.3)
$\angle HC_3H$	109.8 (4.5)	110.4 (4.5)
$\angle HC_6H$	105.8 (10.5)	105.4 (10.1)
α	25.0 (4.8)	23.8 (4.6)
ϕ	69.6 (1.5)	71.4 (1.4)
$\angle C_5C_1H$	129.0 (··)	
$\tau(C_4C_5C_1H)$	150.0 (··)	
R factor	0.079	0.078

[a] Uncertainties shown in parentheses are 3σ values.

4. Combined Analysis of Diffraction and Spectroscopic Data. In order to determine a structure by the combined analysis of electron diffraction and microwave spectroscopic data, one must simultaneously refine an r_α structure at temperature *T*, which is the basis for comparision with the electron diffraction data, and an r_α structure at absolute zero which is used to compare with the B_z rotational constants.[26] The differences between $r_\alpha(T)$ and $r_\alpha(0)$ depend on changes in the anharmonicities of bond stretchings and mean-square perpendicular vibrational amplitudes at the two temperatures. Calculated values of $r_\alpha(0) - r_\alpha(T)$ based upon the harmonic force field of Schachtschneider and Snyder as well as the $B_z - B_0$ corrections to the observed rotational constants are shown in Table I. In calculating the anharmonic portion of the $r_\alpha(0) - r_\alpha(T)$ corrections Morse anharmonicity parameters of 2.0 and 2.5 $Å^{-1}$ were assumed for C–C and C–H bonded distances, respectively. Also during the least-squares analysis the rotational constants were given a weight 500 times the value assigned to an individual electron diffraction data point. This is roughly in accord with the relative magnitudes in residuals allowing for as much as a 100% error in the $B_z - B_0$ corrections.

Four models were analyzed using the combination of electron diffraction and microwave spectroscopic data. The single average C–C bond length model gave essentially identical results to the structure listed in Table II. In addition models 1, 2, and 4 were subjected to further analysis using the combined data sets.

Essentially the same comments can be made with regard to the combined analysis as were previously made concerning the analysis of the diffraction data alone. The two-parameter models showed little improvement relative to the one parameter model while the model containing three different C–C bond lengths (model 4) gave an excellent fit to both the electron diffraction and microwave spectroscopic data. On the basis of Hamilton's *R* factor test,[25] it was possible to reject the other three models in preference to model 4 at the 99.5% confidence level.

We also found that the addition of the rotational constants to the data set permitted the variation of the $\angle C_1C_6H$ valence angle and the two parameters associated with the placement of the tertiary hydrogens, $\tau(C_4C_5C_1H)$ and $\angle C_5C_1H$, although the uncertainties in these three parameters were quite large.

The results of the combined analysis are shown in Table IV along with a comparison of the observed and calculated rotational constants. It should be noted that a slightly different parameterization was used in the combined analysis than was used in the analysis of the diffraction data alone. The $\angle C_5C_1C_2$ valence angle was used instead of the $\angle C_2C_3C_4$ angle, and for the methylene groups the $\angle CCH$ angles rather than the $\angle HCH$ angles were used. The agreement between the results shown

Table IV. Structural Parameters for BCH Obtained from Combined Analysis[a]

Parameter	r_g, Å; ϕ_α, deg[b]	r_z, Å
C_1-C_6	1.515 (8)	1.511
C_1-C_5	1.454 (9)	1.449
$\left.\begin{matrix}C_1-C_2\\C_2-C_3\end{matrix}\right\}$	1.543 (4)	1.541
$C-H_{av}$	1.100 (6)	1.084
$\angle C_5C_1C_2$	109.8 (4)	
$\angle CCH_{av}$[c]	110.2 (1.1)	
$\angle C_1C_6H$	128.2 (3.7)	
α	25.2 (2.8)	
ϕ	70.6 (1.1)	
$\angle C_5C_1H$	125.8 (6.4)	
$\tau(C_4C_5C_1H)$	147.1 (10.1)	
R	0.077	

	B_z (obsd), MHz	B_z (calcd), MHz
A	5546.79	5546.92
B	4237.84	4237.95
C	3126.89	3126.38

[a] Uncertainties shown are 3σ values. [b] Angles have been corrected for shrinkage effects. [c] Average value for the methylenes of the five-membered ring.

in Table III and those shown in Table IV is excellent, indicating that the calibration of the electron diffraction data is very good. Parenthetically, it should also be pointed out that these two analyses were carried out in two separate laboratories using two separate analysis programs.

As a last step in the analysis it was decided to test the sensitivity of the observed splittings in the C-C distances to variations in the C-C vibrational amplitude. The three C-C vibrational amplitudes were combined into one amplitude parameter, and several least-squares analyses were run for various values of this constrained parameter ranging from 0.044 to 0.058 Å. The observed variations in the r_α distances as a function of the average C-C vibrational amplitude are displayed in Figure 6. It is interesting to note that the magnitude of the amplitude has a negligible effect on the size of the average C-C bond length and only affects the size of the splittings. It was found from this analysis that for a variation of ±0.002 Å of the average amplitude about its calculated value (0.0517 Å) the C-C bond lengths remain within the uncertainties quoted in Table IV. Since the uncertainty in the average calculated amplitude is probably quite a bit less than ±0.002 Å, we feel pretty confident that the splittings obtained are reliable within the quoted uncertainties.

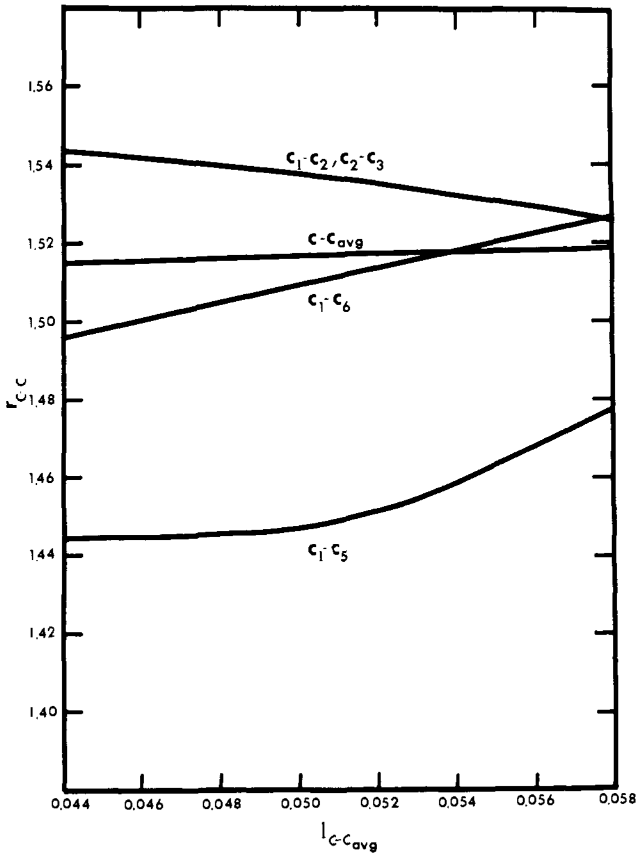
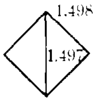


Figure 6. Dependence of the r_z distances for BCH on variations in the average C-C vibrational amplitude.

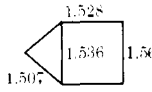
Discussion

The separation of nearly degenerate distances which occur in bicyclic hydrocarbons is a difficult problem when the analysis is based solely on electron diffraction data. The difficulty is effectively dramatized by the large differences between the electron diffraction r_g structures obtained for bicyclo[2.1.0]pentane[27] and bicyclo[2.1.1]hexane,[28] and the subsequently reported r_s structures obtained by microwave spectroscopy.[4b,29] We firmly believe, however, that the resolving power of electron diffraction is significantly enhanced by including spectroscopic data in the form of calculated vibrational amplitudes and microwave rotational constants as was done in the present paper.

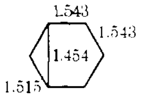
The bond of greatest interest in BCH is the C_1-C_5 bridge bond. Since bicyclic systems are formed by the fusion of two single cycloalkanes, one might expect the bridge bonds to be intermediate in length when compared with the bond lengths of the two monocyclic constituents. Bond lengths for the simple cycloalkanes as summarized by Kuchitsu[2b] are: C_3H_6 1.512 Å; C_4H_8 1.555 Å; C_5H_{10} 1.546 Å; and C_6H_{12} 1.536 Å. Of the bicyclic molecules studied to date, only bicyclo[2.1.0]pentane (**2b**) appears to exhibit this simplistic behavior. For the other fused rings (**1b**, **3b**, and **7**) the relationship of the bridge bond length to the bond lengths of the simple cycloalkanes is obviously more complex. In fact, BCH and its isomer bicyclo[2.2.0]hexane[30] are found to be extreme cases in which the bridge bond is the *shortest* and the *longest* distance in the molecule, respectively. Obviously such cases cannot simply be rationalized in terms of a model involving competition of the fused rings tending to form a bridge bond of intermediate length.



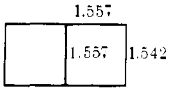
1b



2b



3b



7b

The C_1-C_5 bond length, which was predicted to have a normal cyclopropane value of 1.512 Å,[22] was in fact found to be substantially shorter (1.454 ± 0.009 Å). This observed value is much closer to the bridge bond length found in benzvalene (1.452 Å[31] and 1.442 Å[32]); however, in this latter case the shortened bridge bond length has been attributed to an enhanced p character not found in BCH. The more symmetrical nortricyclene,[33] which may be thought of as BCH bridged by a methylene group at the 3 and 6 positions, exhibits a normal cyclopropane distance of 1.515 Å; however, in this case all of the bonds in the three-membered ring are equivalent by symmetry.

The other C-C bond lengths in BCH are in excellent agreement with the simple cycloalkanes. The C_1-C_6 bond length (1.515 ± 0.008 Å) is in excellent agreement with the value for cyclopropane (1.512 Å),[22] and the C_1C_2, C_2C_3 av-

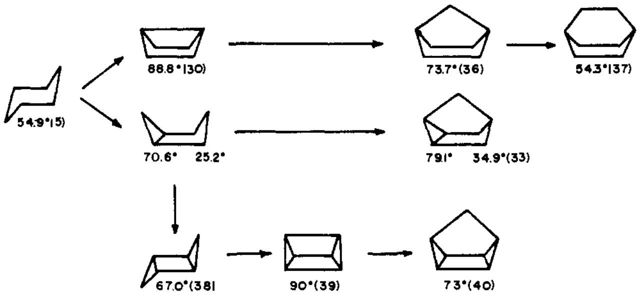


Figure 7. Conformation of six-membered fragments in hydrocarbons studied in the gas phase. Dihedral angles shown are either taken from the literature or calculated from the reported parameters. The numbers in parentheses correspond to literature references.

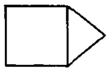
erage bond lengths (1.543 ± 0.004 Å) agree favorably with the reported value for cyclopentane (1.546 Å).[4a] BCH has been the subject of three spectroscopic studies.[15,23,24] While all three investigations agreed that only one conformer was present in the gas phase, only the microwave investigation[15] offered conclusive evidence that the preferred conformation was the boat form. It is interesting to note that this same conclusion was arrived at independently on the basis of the electron diffraction data.

The stability of the boat conformation for BCH and other bicyclo[2.1.0]hexanes containing heteroatoms has been rationalized in terms of a smaller Pitzer strain relative to the chair conformation.[34] In the case of BCH, however, there is a destabilizing effect which arises from the interaction of the methylene groups in the 3 and 6 positions. When this interaction is strong, as in the case of 3,3-diethyl-6,6-diphenyl-1-azabicyclo[3.1.0]hexane,[8] the chair form is preferred.

Boat conformations in cyclohexanoid moieties are quite frequently found in bicyclic and polycyclic hydrocarbons as illustrated in Figure 7. It is quite interesting to note, however, that BCH is the only one of these hydrocarbon species which assumes the boat conformation without any bridging across the 3 and 6 positions.

Table V compares the flap angles for BCH with those obtained for a series of related compounds. It is found that the flap angle ϕ for BCH (70.6 ± 1.1°) is very similar to the values obtained for bicyclo[2.1.0]pentane[4b] (67.26°) and bicyclo[3.1.0]heptane[6] (71.0°) while the flap angle α (25.2 ± 2.8°) agrees well with the quoted values for cyclopentene oxide[16] (27.7°), cyclopentene[35] (28.8°), and bicyclo[3.1.1]heptane[48] (27.0°).

As noted above, the cyclopentane portion of BCH bears a striking resemblance to the conformation of cyclopentene.[35] The present investigation offers further support to the popular belief that bicyclic systems containing a three-membered ring are conformationally similar to the analogous cycloalkenes. In both cases, the conformation is dominated by an increased rigidity against torsion about the bond is question. Shown below are two series of compounds which have been studied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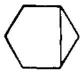
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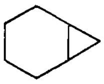
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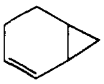
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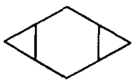
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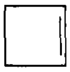
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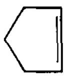
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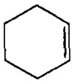
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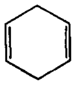
45a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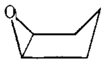
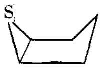
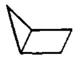
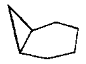
in the gas phase and which illustrate this hypothesis. In all cases, except perhaps the last pair of compounds, the conformation of the olefinic ring is similar to the corresponding bicyclic system. In the derivative of tricyclo[5.1.0.0^{3,5}]octane[42] the central six-membered ring was found to be planar while for 1,4-cyclohexadiene contradictory electron diffraction structures have been reported. Oberhammer and Bauer[45a] have reported a boat conformation, but Dallinga and Toneman[45b] concluded that the molecule is planar. Calculations by Allinger and Sprague[46] indicate that the molecule is planar on the average but has a large amplitude of inversion between the two equivalent boat forms.

Table V. Comparison of Dihedral Angles (deg) in BCH with Similar Parameters in Related Molecules

Molecule	φ	α	Ref	Method
	70.6 63.0	25.2 38.0	This work 15	ED SP
	75.3 64.0	27.7 40.0	16 49	ED SP
	60–70	30	47	SP
	58.34		2	SP
	67.25		4	SP
	71.0		6	ED
		28.8	35	ED
	68.65	27.0	48	ED

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Supplementary Material Available: A tabulation of the experimental data, correlation, and error matricies (4 pp). Ordering information is given on any current masthead page.

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Application of Linear Dichroism to the Analysis of Electronic Absorption Spectra of Biphenyl, Fluorene, 9,9′-Spirobifluorene, and [6.6]Vespirene. Interpretation of the Circular Dichroism Spectrum of [6.6]Vespirene

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Abstract: The electronic absorption spectra of biphenyl and three of its derivatives, fluorene, 9,9′-spirobifluorene, and [6.6]-vespirene, are separated into bands of different polarizations by the technique of linear dichroism in stretched polyethylene films. A semiempirical analysis of the polarization resolved spectra leads to a reassignment of part of the observed transitions. The circular dichroism of [6.6]vespirene is interpreted in terms of a dipole–dipole interaction mechanism based on the present polarization data.

The chiral derivatives of 9,9′-spirobifluorene synthesized by Prelog and Haas are interesting model compounds for the study of optical activity.[2a] Comprehensive circular dichroic studies of some vespirenes (see Figures 13 and 14) and other related chiral compounds have been carried out in order to elucidate the mechanism of optical rotation in this type of molecules and to determine their absolute configurations from chiroptical properties.[2a,b] Both the PPP-CI method[2b] and the exciton model[2a] led to results which could not account for the longest-wavelength band observed in the vespirene CD spectrum, and spiroconjugation was invoked as an additional important mechanism of interaction in the distorted spirobifluorene system. Since the exciton-type interaction implies a well defined relationship between the direction of polarization of a certain transition and the sign of its Cotton effect,[2a] an experimental determination of these polarization directions could, eventually, help to elucidate the question of how important are the contributions of other interaction mechanisms to the optical activity of chiral spirobifluorene compounds.

The present work deals with the application of linear dichroism (LD) of molecules oriented in stretched polyethylene films to this problem. Our treatment comprises four compounds, representing successive stages in the evolution of the basic biphenyl chromophoric system. It is noteworthy that much previous work, mostly theoretical, has already been published about biphenyl and fluorene. However, our experimental results show that part of the absorption bands observed in the spectra of these compounds were not given correct assignments. Employing the LD data as a basis for a semiempirical spectral analysis, a thorough understanding of the properties of chromophoric systems is achieved.

Results and Discussion

1. Biphenyl. Molecular Orientation in the Stretched Film. The linear dichroic spectrum of biphenyl and its calculated dichroic ratio,[3] $d_0 = \mathrm{OD}_\parallel/\mathrm{OD}_\perp$, as a function of wavelength are shown in Figure 1. The separation of this spectrum into bands of different polarizations relative to molecular coordinates necessitates the previous knowledge of the orientation of biphenyl molecules in the film.

Elongated, rod-like molecules exhibit a uniaxial orientation, being uniformly distributed in respect to the rotation about their longitudinal molecular axes. These axes have preferred orientation parallel to the stretching direction of the film.[4] A molecular distribution of this type may be described by a single orientational parameter, f, which is related both to the dichroic ratio, d_0, and to the polarization direction of the electronic