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Microwave Structural and Mechanistic Study of Tricyclo[2.2.0.0^{2,6}]hexane

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Received October 11, 1974

Abstract: The microwave spectra of 11 isotopic species of tricyclo[2.2.0.0^{2,6}]hexane have been observed and analyzed. These data are sufficient for a complete structural determination by the r_s method. The internuclear distances are (in Å) C_1-C_2 = 1.513 ± 0.005, C_1-C_4 = 1.584 ± 0.005, C_2-C_3 = 1.523 ± 0.004, C_2-C_6 = 1.533 ± 0.008, C_3-C_4 = 1.549 ± 0.004, C_1-H_7 = 1.079 ± 0.002, C_2-H_8 = 1.081 ± 0.002, C_3-H_9 = 1.099 ± 0.004, C_3-H_{10} = 1.087 ± 0.005, C_4-H_{11} = 1.086 ± 0.002. The dipole moment has been determined by observation and analysis of the second-order Stark effect. The nonzero dipole moment components are $\mu_b = 0.090 \pm 0.01$ D and $\mu_c = 0.203 \pm 0.01$ D which yield a total dipole moment of 0.222 ± 0.01 D. In addition, the isotopic labeling experiments provide information about the reaction mechanism involved in the reduction of 5,6-dibromobicyclo[2.1.1]hex-2-ene with $LiAlH_4$ to form tricyclo[2.2.0.0^{2,6}]hexane. The reduction is a two-step process in which the initial step is the removal of the bromine exo to the double bond. Following the removal of each bromine, the molecule passes through a nonclassical cationic intermediate species before being reduced by the addition of a hydride ion.

In recent years there have been a number of microwave investigations of small polycyclic hydrocarbon molecules. Among those studied to date are bicyclo[1.1.0]butane,[1] 1-chlorobicyclo[1.1.1]pentane,[2] bicyclo[2.1.0]pentane,[3] tricyclo[3.1.0.0^{2,6}]hex-3-ene (benzvalene),[4a,4b] 4-chlorotricyclo-[2.2.1.0^{2,6}]heptane,[5] bicyclo[3.1.0]hexane,[6] and bicyclo-[2.2.0]hexa-2,5-diene (Dewar benzene).[7] The list of molecules of this type for which good structural data are available is quite small; however, the importance of experimentally determined structures for these molecules cannot be overemphasized since it is very difficult to predict good structures a priori. One of the goals of these studies is to further our understanding of the different types of bonds in the molecule and to correlate this with reactivity of different atom sites within the molecule.

In this work the microwave spectra of the normal species, five different monodeuterio species, four singly substituted ^{13}C enriched species, and a dideuterio species of tricyclo-[2.2.0.0^{2,6}]hexane (hereafter referred to simply as tricyclohexane) have been assigned. The data obtained are suffi-

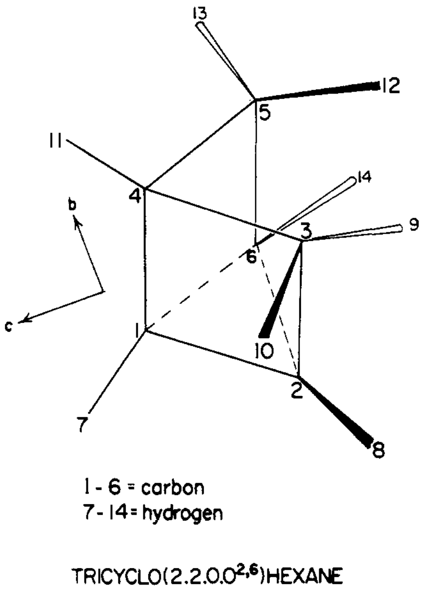


Figure 1. Tricyclo[2.2.0.0^{2,6}]hexane (C_6H_8) structure. Carbon atoms are labeled 1-6 and hydrogen atoms are labeled 7-14. The vectors labeled **b** and **c** show the approximate orientations of the *b* and *c* principal axes.

cient for a complete structural determination. In addition, the relative amounts of the different isotopic species in the product mixture have been determined. These results lead to information concerning the reaction mechanism involved in the reduction of 5,6-dibromobicyclo[2.1.1]hex-2-ene with $LiAlH_4$ to form tricyclohexane.

Experimental Section

Normal Species Tricyclohexane. The sample of the normal species of tricyclohexane was kindly provided by Professor Katz of Columbia University. The sample was purified by preparative GLC.

1-, 2-, and 3-*exo*- and 4-^{2}H Tricyclohexane.[8] A mixture of monodeuterio species was synthesized by the two-step sequence of Roth and Katz.[9] The first step involves the reaction of benzvalene[10] with 5% Br_2 in CCl_4 at 0°. From this one obtains 5,6-dibromobicyclo[2.1.1]hex-2-ene which is then reduced with $LiAlH_4$ in the second step to give tricyclohexane. In this particular case the benzvalene that was used consisted of a mixture of the monodeuterio isomers.[11] From relative intensity measurements[12] performed on microwave absorption lines of the monodeuterio benzvalene species the relative amounts of the different isomers were found to be: 1-^{2}H = 70%, 2-^{2}H = 17%, and 3-^{2}H = 13%. This starting mixture produced a mixture of four monodeuterio tricyclohexane isomers in the following percentages as determined by microwave relative intensity measurements: 1-^{2}H = 46%, 2-^{2}H = 17%, 3-*exo*-^{2}H = 26%, and 4-^{2}H = 12%. No 3-*endo*-^{2}H could be detected in the product mixture by microwave techniques.

1-, 2-, 3-, and 4-^{13}C Enriched Tricyclohexane. This synthesis was similar to the synthesis of the mixture of the monodeuterio species described above except that a mixture of monosubstituted ^{13}C species of benzvalene was used as the starting material. The previously reported synthesis[4b] of a mixture of ^{13}C isomers of benzvalene has been improved as follows. Carbon-13 enriched CH_3OH was prepared in 45% yield (1.46 g) from 20 g of 90% ^{13}C enriched $BaCO_3$.[4b,13,14] Purification of the $^{13}CH_3OH$ was accomplished by preparative GLC on a 3.7 m × 6.4 mm copper column packed with 50/80M Porapak Q, operated at 200° with 40 ml/min helium flow. Carbon-13 enriched CH_2Cl_2 was prepared by passing $^{13}CH_3OH$ vapor over a commercial molybdenum oxide-iron oxide catalyst in a stream of air at about 160° and 150 ml/min flow rate.[15-17] This procedure oxidized the $^{13}CH_3OH$ to $H^{13}CHO$ and H_2O. The $^{13}CH_3OH$ to $H^{13}CHO$ conversion was intermittently monitored by injecting samples of the flow stream into a gas chromatograph. A 1.5 m × 6.4 mm stainless steel column packed with 60/80M Carbosieve-B was used to separate H_2O, $H^{13}CHO$, and $^{13}CH_3OH$.[18] The effluent gas stream from the catalyst bed was maintained above 80° to keep the formaldehyde monomer from polymerizing. This stream was passed directly through a trap containing PCl_5 where the $H^{13}CHO$ was converted to $^{13}CH_2Cl_2$. After passing through the PCl_5, the gas stream was flowed through two traps maintained at approximately −126°. At the end of the reaction the contents of the traps were transferred under vacuum to a single tube which was subsequently used as a distillation pot. The contents were allowed to distill under vacuum through a series of three traps. The first trap was maintained at −45°, the second at −126°, and the third at −196°. A good deal of higher boiling material was collected in the first trap, $^{13}CH_2Cl_2$ in the second trap, and HCl in the third trap. Residual acidic material was removed by transferring the $^{13}CH_2Cl_2$ under vacuum into a tube containing some dilute NaOH solution. The contents were then subjected to a second distillation through cold traps. This time the first trap was maintained at −78° and the second trap was maintained at −196°. The $^{13}CH_2Cl_2$ was collected in the second trap and was used without further purification. The yield of $^{13}CH_2Cl_2$ from $^{13}CH_3OH$ was 51% (2.0 g). A mixture of the ^{13}C isomers of benzvalene was then prepared by incorporating the $^{13}CH_2Cl_2$ into the benzvalene ring as previously described.[4b] The relative percentages of the monosubstituted ^{13}C isomers of benzvalene were determined by microwave relative intensity measurements. The percentages were 1-^{13}C = 63%, 2-^{13}C = 23%, and 3-^{13}C = 13%. From this mixture all of the singly substituted ^{13}C species of tricyclohexane were obtained in the following relative amounts, again determined by relative intensity measurements on the microwave lines: 1-^{13}C = 48%, 2-^{13}C = 17%, 3-^{13}C = 26%, and 4-^{13}C = 9%.

3-*endo*-5-*endo*-Dideuteriotricyclohexane. A sample of 5,6-dibromobicyclo[2.1.1]hex-2-ene was reduced by the method of Roth and Katz[9] using $LiAlD_4$ instead of $LiAlH_4$. This resulted in only 3-*endo*-5-*endo*-dideuteriotricyclohexane as determined by microwave spectroscopy.

3-*endo*-Deuteriotricyclohexane. This synthesis was analogous to the previous one except that a mixture of $LiAlD_4$ and $LiAlH_4$ was used (approximately 1:1 ratio). The 3-endo compound results when the dibromo species has one bromine replaced by a hydrogen atom and the second by a deuterium atom. From this synthesis one actually gets a mixture of the normal species (attack by $LiAlH_4$ twice), the monodeuterio species (attack by $LiAlH_4$ once and $LiAlD_4$ once), and the dideuterio species (attack by $LiAlD_4$ twice).

Gas Chromatography of the Tricyclohexanes. At the end of the reaction sequence one has tricyclohexane in an ethereal solution. It was found that the best way to purify the sample was to subject it to preparative GLC. Initially a 4.6 m × 6.4 mm copper column packed with 10% $AgNO_3$ saturated benzyl cyanide on 45/60M Chromosorb-G was used;[9] however, the separating power of this column gradually diminished as large volumes of the ether solution were passed through it. A second column was prepared which was similar to the one described by Lemal and Shim when they reported the first synthesis of tricyclohexane.[19] This column was a 2.7 m × 6.4 mm copper column packed with 45/60M Chromosorb A coated with 10% UCON HB-50-2000. The benzyl cyanide column was operated at room temperature and the UCON Polar column was operated at 45°. Helium was used as the carrier gas in both cases.

Instrumental. The microwave studies were carried out using a Hewlett-Packard 8460 Microwave Spectrometer and a Hughes-Wilson spectrometer employing 100 kHz Stark modulation.[20]

Dipole moment measurements were performed using the Hewlett-Packard instrument. Only one Stark modulator and cell were used for the dipole measurements. The cell was calibrated using OCS. All voltage measurements were made with a digital voltmeter by recording the voltage at the ground-to-base monitor jack of the Stark modulator.

Relative Intensity Measurements. The relative intensity measurements were performed following the method of Esbitt and Wilson.[12] The microwave spectrum of benzvalene is intense and sparse so the relative intensity measurements were easily performed. The 2_{12}-3_{13} transition was used to determine the relative amounts of the deuterated isomers of benzvalene. Two determinations were performed and the results were averaged. The relative amounts of 1-^{2}H, 2-^{2}H, and 3-^{2}H were 70 ± 3, 17 ± 1, and 13 ± 2%, respec-

Table I. Rotational Transition Frequencies[a] in Tricyclohexane

Transition	Normal species		$1\text{-}^{13}C$		$2\text{-}^{13}C$		$3\text{-}^{13}C$		$4\text{-}^{13}C$	
	Obsd	Obsd − Calcd[b]	Obsd	Obsd − Calcd	Obsd	Obsd − Calcd	Obsd	Obsd − Calcd	Obsd	Obsd − Calcd
$0_{00}-1_{10}$	11,210.47	0.01								
$1_{01}-2_{11}$	21,723.27	0.02	21,499.33	0.03					21,598.01	0.03
$1_{10}-2_{20}$	22,665.63	0.02	22,382.03	0.03	22,472.51	0.02	22,459.94	0.03		
$1_{11}-2_{21}$	23,118.63	0.02	22,813.46	0.02	22,920.86	0.01	22,930.30	0.01	22,869.47	0.07
$2_{11}-3_{21}$	32,776.10	−0.01	32,424.30	0.01			32,361.53	0.01	32,555.70	0.03
$2_{02}-3_{12}$	32,801.95	−0.00	32,465.33	−0.02	32,546.64	−0.01	32,325.81	−0.01	32,635.05	−0.05
$2_{12}-3_{22}$	33,631.39	−0.01	33,234.54	−0.02			33,265.76	−0.01	33,350.55	0.02
$2_{20}-3_{30}$	34,460.81	−0.03	34,003.75	−0.01	34,159.73	−0.01	34,205.72	−0.01		
$2_{21}-3_{31}$	34,811.39	−0.02	34,343.52	0.00	34,510.77	−0.01	34,548.62	−0.01	34,417.82	−0.06
$1_{10}-2_{21}$	22,036.64	0.02								
$1_{11}-2_{20}$	23,747.62	0.01								
$1_{01}-2_{12}$	18,477.29	0.02								
$2_{12}-3_{03}$	26,285.98	−0.01			26,032.88	0.01			26,130.60	−0.01
$2_{02}-3_{13}$									26,382.55	0.00
$2_{21}-3_{30}$			34,622.48	−0.01						
$3_{13}-4_{04}$			34,594.71	−0.03	34,409.95	0.01				
$3_{03}-4_{14}$			34,656.58	0.03	34,475.47	−0.01	34,315.42	−0.01		

Transition	$1\text{-}^{2}H$		$2\text{-}^{2}H$		3-*endo*-^{2}H		3-*exo*-^{2}H		$4\text{-}^{2}H$		3-*endo*-5-*endo*-^{2}H	
	Obsd	Obsd − Calcd	Obsd	Obsd − Calcd	Obsd	Obsd − Calcd	Obsd	Obsd − Calcd	Obsd	Obsd − Calcd	Obsd	Obsd − Calcd
$1_{01}-2_{11}$	20,892.42	0.02	21,116.31	0.03	20,993.57	0.03	20,938.62	0.01	21,196.24	0.03	20,370.11	−0.02
$1_{10}-2_{20}$	21,616.62	0.02	21,974.40	0.02	21,928.58	0.02	22,265.18	0.03	21,782.48	−0.01	20,628.51	0.00
$1_{11}-2_{21}$	21,989.44	0.05	22,407.87	0.01	22,364.51	0.02	22,779.30	−0.00	22,131.05	0.01	21,598.60	0.03
$2_{11}-3_{21}$	31,472.71	−0.02	31,837.55	−0.00	31,687.42	−0.01	31,750.17	−0.00	31,880.78	0.00		
$2_{02}-3_{12}$	31,551.71	−0.01	31,911.14	−0.02	31,681.37	−0.01	31,508.59	−0.01				
$2_{12}-3_{22}$	32,161.32	−0.02	32,643.09	−0.02	32,518.51	−0.02	32,788.42	−0.01	32,495.40	−0.03		
$2_{20}-3_{30}$	32,770.94	−0.02	33,375.04	−0.05	33,355.66	−0.02	34,068.26	−0.01	32,927.67	−0.01		
$2_{21}-3_{31}$	33,080.80	−0.02	33,728.35	−0.01	33,682.37	−0.00	34,385.38	−0.00	33,263.38	−0.01		
$1_{10}-2_{21}$									21,015.91	0.03		
$1_{11}-2_{20}$	22,582.62	0.02	23,071.67	0.02			23,267.44	0.02			22,167.08	−0.02
$1_{01}-2_{12}$												
$2_{12}-3_{03}$			25,379.15	0.00	25,572.49	−0.00	25,133.99	0.00	25,664.58	−0.01	24,925.08	0.05
$2_{02}-3_{13}$	26,039.08	0.01			25,883.52	0.00					25,187.13	−0.05
$2_{21}-3_{30}$												

[a] All values in MHz. [b] Obtained using the rotational constants in Table II.

tively. For the sample containing the mixture of ^{13}C enriched species of benzvalene, the 2_{11}-3_{12} transition was used. The total ^{13}C enrichment was 90%. Since we were only interested in following the distribution of the ^{13}C label through the reaction sequence, the percent of each ^{13}C isomer was determined relative to the total ^{13}C enrichment. Again, two determinations were performed and the average of the two was taken. The relative amounts of $1\text{-}^{13}C$, $2\text{-}^{13}C$, and $3\text{-}^{13}C$ isomers in the reaction mixture were 63 ± 1, 23 ± 1, and 13 ± 1%, respectively. These distributions are in good agreement with the previously reported values.[4b]

Since the tricyclohexane spectrum was weaker than the benzvalene spectrum and more dense, more transitions were used to determine the relative amounts of the various isomers. In the determination of the percentages of the deuterated isomers five transitions were used, (1_{10}-2_{20}, 2_{20}-3_{30}, 2_{12}-3_{22}, 2_{21}-3_{31}, and 2_{11}-3_{21}). Two types of errors were calculated. The first is the experimental uncertainty in the measurement of the intensity of the microwave lines due to random noise associated with the detection system. These errors were propagated through the calculations. They were found to range from 2 to 4% and were larger than the second error (error of the mean) which was calculated directly from the variations of the final percentages of the five transitions used. The error of the mean is reported in parentheses following the experimental uncertainties. The amounts of the deuterated species are listed in Table IX.

Three transitions were used in the determination of the relative amounts of ^{13}C isomers (1_{11}-2_{21}, 2_{21}-3_{31}, and 2_{02}-3_{12}). As with benzvalene, the results were determined as the percent of each ^{13}C isomer with respect to the total ^{13}C present. Both types of errors were calculated for this mixture also. The results are reported in Table IX.

Results

Observed Spectrum and Assignment. Initial predictions indicated that both b- and c-type transitions might be possible but because of the uncertainty of the molecular structure and electron distribution in the molecule the relative magnitudes of μ_b and μ_c were not known. The spectrum turned out to be fairly sparse which indicated that the largest dipole moment must be along the c principal axis. The initial assignment was obtained by observing the Stark effect of the low-J, R-branch, c-type transitions and comparing the observed frequencies with predicted values. Once the assignment was made, the b-type transitions were also easily found. The transitions which were used to determine the rotational constants for the normal species are listed in Table I. As is usually found for molecules of this type, the transitions are quite narrow, typically having a full width at half-height of about 0.2 MHz. The large amount of strain in the molecule makes it quite rigid so the transitions fit nicely to rigid rotor theory. The computer program used to fit the transitions was the NBS Spectral Analysis Program, Version III.

Assignment of the isotopic species was facilitated by the fact that the assumed structure gave predicted values of rotational constants which were fortuitously close to the true ones. Thus the spectral predictions were only several hundred megahertz off for the low-J transitions. The transitions used to determine the best set of rotational constants

Table II. Rotational Constants and Moments of Inertia[a] for Tricyclohexane Isotopes

	Normal species	$1\text{-}^{13}C$	$2\text{-}^{13}C$	$3\text{-}^{13}C$	$4\text{-}^{13}C$	
A	5954.071 ± 0.003[b]	5867.626 ± 0.003	5901.561 ± 0.002	5920.845 ± 0.002	5876.278 ± 0.010	
B	5256.393 ± 0.003	5210.559 ± 0.004	5216.169 ± 0.003	5167.746 ± 0.003	5240.566 ± 0.009	
C	4174.399 ± 0.003	4160.403 ± 0.002	4131.711 ± 0.001	4110.496 ± 0.002	4146.176 ± 0.007	
κ[c]	0.2159478	0.2302660	0.2254805	0.1680069	0.2649982	
I_a	84.8791	86.1296	85.6343	85.3554	86.0027	
I_b	96.1450	96.9907	96.8864	97.7943	96.4354	
I_c	121.0656	121.4728	122.3164	122.9477	122.8897	
	$1\text{-}^{2}H$	$2\text{-}^{2}H$	3-*endo*-^{2}H	3-*exo*-^{2}H	$4\text{-}^{2}H$	3-*endo*-, 5-*endo*-^{2}H
A	5634.473 ± 0.004	5763.411 ± 0.003	5762.491 ± 0.002	5924.913 ± 0.002	5649.614 ± 0.004	5553.196 ± 0.011
B	5085.973 ± 0.004	5117.623 ± 0.003	5077.017 ± 0.002	5004.566 ± 0.002	5182.197 ± 0.005	4938.978 ± 0.014
C	4119.973 ± 0.005	4020.351 ± 0.004	4069.970 ± 0.002	4002.300 ± 0.002	4067.030 ± 0.005	3968.920 ± 0.007
κ	0.2756682	0.2590066	0.1899957	0.0426086	0.4092981	0.2242857
I_a	89.6936	87.6870	87.7010	85.2968	89.4532	91.0063
I_b	99.3666	98.7521	99.5419	100.9830	97.5216	102.3240
I_c	122.6649	125.7044	124.1719	126.2714	124.2617	127.3334

[a] The rotational constants have units of megahertz. The moments of inertia are in atomic mass units square angströms and are obtained by using the factor 505,376 amu Å^2 MHz. [b] Standard deviation. [c] κ is Ray's asymmetric parameter and is defined to be $(2B - A - C)/(A - C)$.

Table III. Experimental Values for the Moment of Inertia Relationship (Eq 1)

Substituted atom	$\Delta I_b + \Delta I_c - \Delta I_a$, amu Å^2
$1\text{-}^{13}C$	0.002
$4\text{-}^{13}C$	−0.009
$7\text{-}^{2}H$	0.006
$11\text{-}^{2}H$	−0.001

for the ^2H species and the ^{13}C species are also presented in Table I. The rotational constants, moments of inertia, and κ values for all the species studied are tabulated in Table II. These were obtained from a least-squares fit of the transitions in Table I using the aforementioned computer program. As shown in Table II the rotational constants of all the species are well determined.

Structure. If the molecule is to have a plane of symmetry containing atoms 7, 1, 4, and 11, then the isotopic substitutions of these atoms should require the following relationship to be obeyed.

$$\Delta I_i + \Delta I_j - \Delta I_k = 0 \qquad (1)$$

In this equation i and j define the plane of the substitution and ΔI_m is the difference in the moments of inertia of the ^{12}C molecule and the isotopically substituted molecule in question. The experimentally determined values of the left side of the equation for the isotopes in the plane are presented in Table III. The values are all sufficiently close to zero to confirm the presence of a plane of symmetry.

Since all of the unique atomic positions in the molecule have been isotopically substituted it is possible to obtain a complete r_s structure by the method of Costain[21] with the use of Kraitchman's equations.[22] This method has the virtue that vibration-rotation effects are at least partially canceled since only differences in moments of inertia of the two species are involved. The atomic coordinates for all the atoms in tricyclohexane are presented in Table IV. The a coordinates of atoms 1, 4, 7, and 11 were initially calculated and found to be very close to zero as one would expect since these atoms lie in the b–c symmetry plane. These a coordinates were then all set to zero for all subsequent calculations so that the symmetry condition is obeyed. There is only one small coordinate whose sign may be in question and that is the c coordinate of hydrogen atom 10 (and 13 by symmetry). When a positive sign is chosen, however, an absurd value for the C–H bond length results, hence the sign must be negative.

There are 23 independent structural parameters in tricyclohexane that are needed to completely specify the molecular geometry. In Table V some of the structural parameters are presented. Two types of structures were calculated. In column *I*, r_s parameters were calculated from the Kraitchman coordinates of Table IV. The errors listed in this column are the experimenal standard deviations propagated through from the uncertainties in the experimental rotational constants of Table II. These errors are entirely experimental and do not take into account any uncertainty which might arise from vibration-rotation effects. They offer some estimate of the experimental precision of the data but underestimate considerably the true uncertainty of the parameters which is usually on the order of several thousandths of an ångström in the bond lengths and several tenths of a degree in the angles. A set of parameters was also calculated using a fitting program developed by Schwendeman of Michigan State University. For this set of parameters, the r_s atomic coordinates were chosen to initially define the location of all the atoms then the two independent first moment equations ($\Sigma_i m_i b_i = 0$ and $\Sigma_i m_i c_i = 0$) and the product equation ($\Sigma_i m_i b_i c_i = 0$) of the normal species along with the moments of inertia of all the other isotopic species except the dideuterio species were fit in a least-squares fashion to obtain a new set of atomic coordinates. The atomic coordinates so obtained were then used in the calculation of a second set of parameters. This was done to get a better estimate of the actual uncertainty associated with each r_s parameter due to vibration-rotation effects. In column II the difference between the r_s and r_0 values is presented ($r_0 - r_s$). The numbers in column III are Costain uncertainties.[23] In all cases except for the C_2-C_6 bond length the Costain uncertainties agree pretty well with the differences found by the r_0 calculation. The best value of uncertainty for each parameter should be the largest of column II or III.

Mechanistic Aspects. Since no 3-endo-deuterated tricyclohexane was observed in the reaction mixture when synthesized from the mixture of monodeuterio benzvalene isomers, it was concluded that deuterium could be placed in this position only by deuterating with $LiAlD_4$ in the final reaction. It was not clear initially, however, whether all the deuterium would end up in the 3-endo and 5-endo positions or whether some might go to the 3-exo and 5-exo locations. There were three possible isomers that one might obtain: the endo-endo, the endo-exo, or the exo-exo. To ascertain which product or products resulted, the reaction was carried out and the microwave spectrum of the resulting tricyclohexane product mixture was scanned. There appeared to be

Table IV. Atomic Coordinates for Tricyclohexane[a]

Atom	a	b	c
1	0	−0.62916 ± 0.00006	−0.93063 ± 0.00004
2	0.76624 ± 0.00004[b]	−0.81842 ± 0.00004	0.3597 ± 0.0001
3	1.21982 ± 0.00003	0.63590 ± 0.00006	0.3603 ± 0.0001
4	0	0.9091 ± 0.0001	−0.5546 ± 0.0001
5	−1.21982 ± 0.00003	0.63590 ± 0.00006	0.3603 ± 0.0001
6	−0.76624 ± 0.00004	−0.81842 ± 0.00004	0.3597 ± 0.0001
7	0	−1.18265 ± 0.00004	−1.85633 ± 0.00003
8	1.31700 ± 0.00003	−1.69387 ± 0.00004	0.67429 ± 0.00008
9	1.25435 ± 0.00002	1.17862 ± 0.00003	1.31499 ± 0.00003
10	2.16126 ± 0.00002	0.75067 ± 0.00007	−0.1700 ± 0.0003
11	0	1.74330 ± 0.00004	−1.25047 ± 0.00005
12	−1.25435 ± 0.00002	1.17862 ± 0.00003	1.31499 ± 0.00003
13	−2.16126 ± 0.00002	0.75067 ± 0.00007	−0.1700 ± 0.0003
14	−1.31700 ± 0.00003	−1.69387 ± 0.00004	0.67429 ± 0.00008

[a] See Figure 1 for atom numbering; all values in angströms. [b] Experimental standard deviations.

Table V. Structural Parameters of Tricyclohexane

Parameter[a]	I[b]	II[c]	III[d]
C_1–C_2	1.5125 (0.0001)[e]	0.005	0.004
C_1–C_4	1.5835 (0.0002)	0.005	0.003
C_2–C_3	1.523 (0.001)	0.004	0.003
C_2–C_6	1.5325 (0.0008)	0.008	0.003
C_3–C_4	1.5491 (0.0001)	0.004	0.003
C_1–H_7	1.07855 (0.00008)	−0.002	0.002
C_2–H_8	1.08109 (0.00009)	−0.002	0.002
C_3–H_9	1.0987 (0.0001)	−0.001	0.004
C_3–H_{10}	1.0866 (0.0002)	0.003	0.005
C_4–H_{11}	1.0864 (0.0001)	−0.000	0.002
H_9–C_3–H_{10}	110.16 (0.02)	0.5	0.4
C_1–C_4–H_{11}	126.429 (0.009)	0.07	0.2
C_3–C_4–H_{11}	120.913 (0.006)	−0.003	0.1
C_4–C_1–H_7	134.613 (0.007)	−0.1	0.2
C_2–C_1–H_7	131.909 (0.005)	−0.09	0.2
C_1–C_2–H_8	127.422 (0.009)	−0.02	0.3
C_6–C_2–H_8	120.627 (0.006)	−0.1	0.2
C_3–C_2–H_8	128.408 (0.006)	0.2	0.2

[a] See Figure 1 for atom labeling. Bond lengths are in angströms and angles are in degrees. [b] From the Kraitchman coordinates of Table IV. [c] Values of $r_0 - r_s$. See text for discussion. [d] Costain uncertainties $\Delta q_i = 0.0015/q_i$ where q_i is an atomic coordinate. [e] Standard deviation; obtained by propagating the errors from the rotational constants.

Table VI. Comparison of Calculated and Experimental Rotational Constants and κ Values for the Normal Species and the Dideuterio Species Obtained from the $LiAlD_4$ Reduction of 5,6-Dibromobicyclo[2.1.1]hex-2-ene

	Exptl, MHz	Calcd from r_s parameters,[a] MHz	Obsd − Calcd, MHz
		Normal Species	
A	5954.071	5984	−30
B	5256.393	5281	−28
C	4174.399	4193	−19
κ	0.2159478	0.2148	
		Dideuterio	
		3-Endo-5-endo	
A	5553.196	5580	−27
B	4938.978	4960	−21
C	3968.920	3986	−17
κ	0.2242857	0.2227	
		3-Endo-5-exo	
A		5742	−189
B		4876	67
C		3921	48
κ		0.0492	
		3-Exo-5-exo	
A		5903	−350
B		4806	133
C		3857	112
κ		−0.0721	

[a] Calculated from the r_s atomic coordinates of Table IV.

Table VII. Stark Effect Measurements

		$\Delta\nu/E^2 \times 10^5$	
Transition	M	Obsd[a]	Calcd[b]
1_{01}–2_{11}	1	0.3948	0.3943
1_{11}–2_{21}	1	−0.3507	−0.3480
2_{02}–3_{12}	1	0.4351	0.4350
2_{12}–3_{22}	1	−0.4234	−0.4255

I[c] $\mu_b = 0.090 \pm 0.004$; $\mu_c = 0.2025 \pm 0.0003$; $\mu_T = 0.222 \pm 0.002$

II $\mu_b = 0.089 \pm 0.004$; $\mu_c = 0.2043 \pm 0.0004$; $\mu_T = 0.223 \pm 0.002$

III $\mu_b = 0.090 \pm 0.01$; $\mu_c = 0.203 \pm 0.01$; $\mu_T = 0.220 \pm 0.01$

[a] Stark cell calibrated using $\mu(OCS) = 0.71521$ D. The conversion factor used was $\mu E = 0.503452$ MHz/(D/(V/cm)). The units are MHz/(V/cm)^2. [b] Calculated using $\mu_b = 0.090$ D and $\mu_c = 0.2025$ D. [c] All dipole moment values are in units of Debye.

only one major constituent in the mixture. The spectrum was assigned and comparisons with initial spectral predictions indicated that the isomer was probably the 3-endo-5-endo compound. The spectral predictions were refined once the complete structure was known and these results are presented in Table VI. It is clear by comparison of the results in Table VI that the dideuterio species produced in the reaction is indeed the 3-endo-5-endo isomer.

In order to obtain the 3-endo-monodeuterio species, a 1:1 mixture of $LiAlH_4$ and $LiAlD_4$ was used to reduce 5,6-dibromobicyclo[2.1.1]hex-2-ene. This resulted in a tricyclohexane product mixture which contained some of the 3-endo-deuterio isomer. Since all the other monodeuterio species had been previously assigned, it was an easy matter to verify the presence or absence of any of them in this reaction mixture by simply looking for microwave absorptions from each species. Lines from all the other monodeuterio species were absent so none of the other monodeuterio species were present in this reaction mixture.

Dipole Moment. The four c-type transitions listed in Table VII were used to determine the dipole moment by observation and analysis of their second-order Stark effect.[24] The data were treated by two statistical methods. The first method was the one normally used where a least-squares fit of the frequency shift vs. voltage squared is obtained for each transition in a preliminary data reduction. This results in four slopes of $\Delta\nu/V^2$ which were subsequently used along with the rotational constants of the normal species and the previously determined cell constant to determine the nonzero dipole moment components (μ_b and μ_c) in a least-squares fashion by the standard second-order perturbation theory.

Table VIII. Comparison of Average Bond Lengths[a] of Three- and Four-Membered Rings in Various Cyclic and Polycyclic Compounds

Compd	Δ	□	Ref
Cyclopropane	1.510		28
Cyclobutane		1.548	29
Bicyclo[1.1.0]butane	1.498		1
Bicyclo[1.1.1]pentane		1.545	30
Bicyclo[2.1.0]pentane	1.517	1.539	3
Bicyclo[2.2.0]hexane		1.56	31
Bicyclo[2.1.1]hexane		1.544	32
Tricyclo[3.1.0.0^{2,6}]hex-3-ene	1.503		4b
Tricyclo[2.2.0.0^{2,6}]hexane	1.520	1.542	This work
Cyclopropyl chloride	1.514		33
Cyclobutyl chloride		1.538	34
1-Chlorobicyclo[1.1.1]pentane		1.545	2
4-Chlorotricyclo[2.2.1.0^{2,6}]heptane	1.527		5
Average	1.513	1.545	

[a] All bond lengths are in angströms.

In the second method that was used each measurement of frequency shift vs. voltage squared was treated as a separate piece of data and only one least-squares fit was performed. This second method has the advantage that the inherent uncertainties of the least-squares $\Delta\nu/V^2$ values are not ignored. One drawback is that the least-squares $\Delta\nu/E^2$ values ($\Delta\nu/E^2 = \Delta\nu/V^2 \times$ cell spacing^2) are not easily reported and they are the numbers which allow one to calculate the actual frequency shift for a given electric field for each transition. One should also be careful that the second method is not masking any deviation from second-order theory for any particular transition. If the first method is used initially any irregular behavior of a particular transition will immediately show up and it can be discarded. Then the second method can be used with confidence. All the data in Table VII except the bottom two rows of values for the dipole moment components (headed II and III) are concerned with the data work-up by the first method. Row II gives the least-squares values of the dipole moment components as determined by the second method along with the corresponding standard deviations of the values. The values in the last row (III) are averages of the two methods and the errors are taken to be 0.01 D for all values.

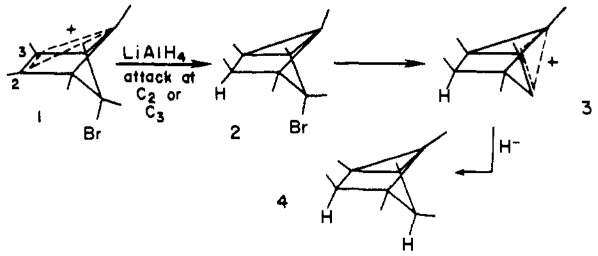
Discussion

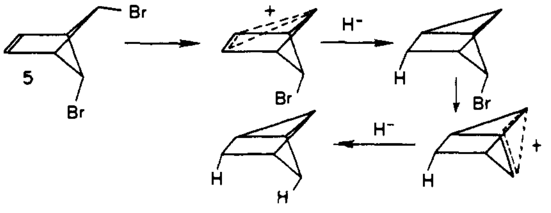
Structure. There are several structural parameters that are worthy of comment. First, the C_1-C_4 bridgehead bond is quite long for a carbon-carbon single bond. The unusual length of this bond is in order, however, with the corresponding bond length found in bicyclo[2.2.0]hexane (1.577 Å).[25] Second, the four-membered ring defined by atoms C_1-C_2-C_3-C_4 is nonplanar. The angle of intersection of the two planes defined by atoms C_1-C_2-C_4 and C_2-C_3-C_4 is 30.3°. This is only slightly smaller than the dihedral angle of 35° found for cyclobutane itself.[26]

The CH bond lengths of the methine hydrogens, H_7, H_8, H_{14}, and H_{11}, are notably shorter than those usually found for aliphatic CH bonds (CH bond lengths in propane are 1.096 and 1.091 Å).[27] In view of the previous data, however, this is to be expected. Methine CH bond lengths for bicyclo[1.1.0]butane (1.071 Å) and tricyclo[3.1.0.0^{2,6}]hex-3-ene (1.078 and 1.082 Å)[4b] were also very short. In general, this shortening of CH bonds correlates with increased acidity and in a simple chemical bonding scheme implies an increased s character in the carbon bonding orbital. The orientation of the methine hydrogen atoms also bears mentioning. In the previous work with bicyclobutane and benzvalene these atoms tended toward equal angles with all CC bonds adjoining the methine carbon.[1,4b] In the work presented here, the HCC angles show a wider variation from equality but the largest deviation is still only about 8°. Thus for a first approximation in attempting to predict structures of similar molecules the equal angle assumption should be quite valid.

In previous work it was demonstrated that the average bond length of a given sized ring remained fairly constant in strained polycyclic hydrocarbons even though the individual bond lengths in the ring were varying over a large range.[3,4b] Table VIII summarizes the data involving average bond lengths for a number of cyclic and polycyclic compounds. The average bond length of all the cyclopropyl ring systems is 1.513 Å which is within 0.003 Å of the bond length of cyclopropane itself. For the four-membered ring systems the average ring bond is 1.545 Å which again is only 0.003 Å different from the CC bond length found in cyclobutane. The fact that the average bond length remains constant within a given sized ring can be a useful tool for estimating structural parameters for similar type molecules.

Mechanism. Recently Hogeveen and Kwant[35-37] have studied 1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hexenyl cations and proposed a mechanism for their reaction with nucleophiles. Among the ions studied was the endo-5-bromo analog (**1**) which was generated by the reaction of bromine with hexamethyl (Dewar benzene) in methylene chloride at −90° with $LiAlH_4$. This ion underwent attack at C-2 or C-3 to give **2** which dissociated into a bromide ion and **3**. $LiAlH_4$ then attacked a second time yielding the tricyclic hydrocarbon **4**. Their conclusions are based on the observation of ion **1** at −70° by ^1H NMR and ^{13}C NMR spectroscopy and identification of hydrocarbon **4** by ^1H NMR spectroscopy. It has been suggested that the reaction of 5,6-dibromobicyclo[2.1.1]hex-2-ene (**5**) with $LiAlH_4$ proceeds via the same type of intermediates.[36] There is certainly some reason to expect this but the hexamethyl cation (**1**) is derived from hexamethyl (Dewar benzene) and the corresponding hexamethyl-5,6-dibromobicyclo[2.1.1]hex-2-ene has never been isolated in this reaction sequence. Furthermore, when the parent compound (Dewar benzene) is treated with bromine one does not get **5** as expected, but instead





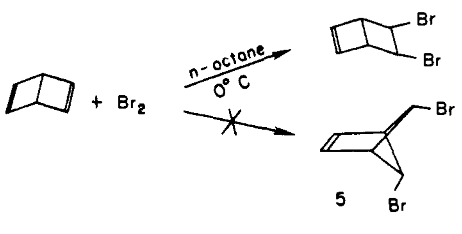


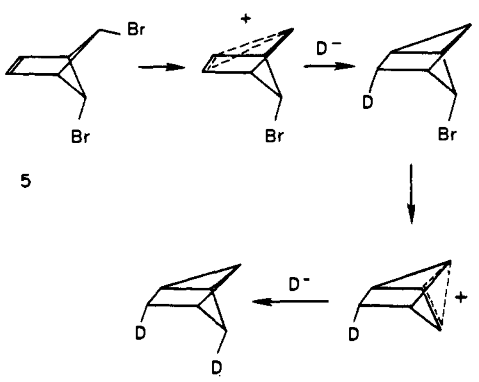
Table IX. Comparison of Experimental and Theoretically Predicted Percentages of Labeled Tricyclohexanes in the Product Mixture

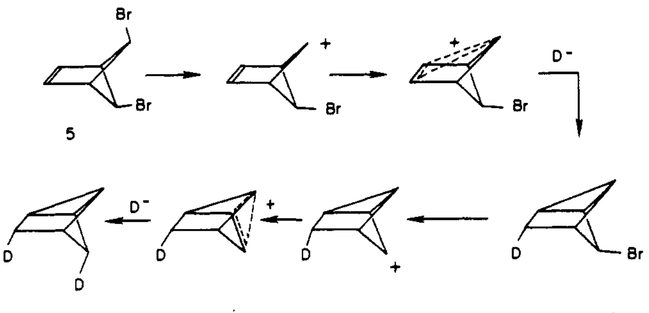
^{2}H	1-^{2}H	2-^{2}H	3-*endo*-^{2}H	3-*exo*-^{2}H	4-^{2}H
Endo Br removed first	10	35	0	41	14
Exo Br removed first	35	23	0	29	14
Exptl	46 ± 2 (1.3)[a]	17 ± 3 (0.4)	None detected[b]	26 ± 3 (0.5)	12 ± 3 (1.1)
^{13}C	1-^{13}C	2-^{13}C	3-^{13}C	4-^{13}C	
Endo Br removed first	10	35	40	14	
Exo Br removed first	32	24	29	14	
Exptl	48 ± 3 (2.4)[a]	17 ± 4 (1.2)	26 ± 4 (3.1)	9 ± 4 (1.3)	

[a] See text for a discussion of errors. [b] The minimum detectable amount is less than 1%. This conclusion is based on the results of an experiment where microwave lines from the 4-^{13}C and 1-^{13}C species were seen in natural abundance in a sample of the ^{12}C species. (The natural abundance of ^{13}C is 1.1%.)

2,3-dibromobicyclo[2.2.0]hex-5-ene is obtained.[38] This simply stresses the fact that there are definitive differences between the behavior of the parent compound and its hexamethyl derivative. Because of the differences pointed out above, it seemed desirable to carry out an independent determination of the reaction pathway involved in the reduction of **5** with $LiAlH_4$ to form tricyclohexane.

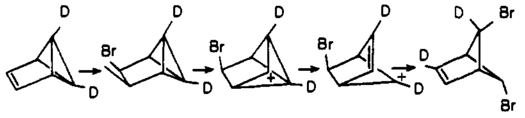
The isotopic labeling experiments performed during the course of the microwave work provide definitive information about this reaction pathway. Two complementary isotopic labeling experiments were performed. The first involved the reduction of **5** with $LiAlD_4$. This led to 3-endo-5-endo-dideuteriotricyclohexane as the only product. This is consistent with the mechanism proposed for the hexamethyl system. However, the results of this experiment were not conclusive since the reaction sequence could also be rationalized if the endo bromine was the first to be removed,

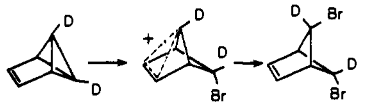




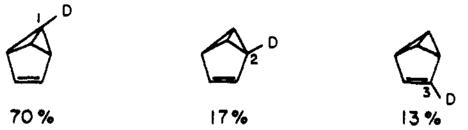
The isotopic labeling experiments which employed ^{2}H and ^{13}C enriched benzvalene as starting material provided much more decisive information about the reaction sequence. The results of the ^{2}H and ^{13}C syntheses are similar. For simplity, only the ^{2}H synthesis will be discussed in detail with the understanding that the discussion could be applied to the ^{13}C synthesis in an analogous manner.

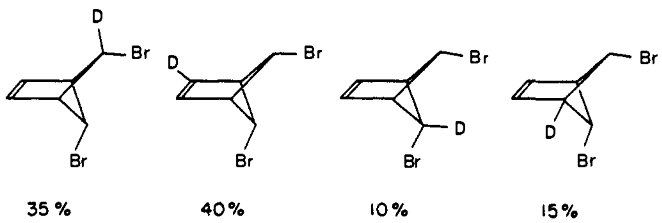
The mechanism of the addition of bromine to benzvalene has been worked out by Roth and Katz.[9,39] They started with dideuteriobenzvalene labeled in the 1 and 6 positions. This was reacted with bromine in carbon tetrachloride and the resulting mixture of the dideuterio isomers of **5** was analyzed by NMR techniques. From this they concluded that the reaction was proceeding via two competing pathways. The first involved initial attack of the bromine at the double bond in benzvalene followed by a Wagner-Meerwein rearrangement to give a deuterated isomer of **5**. This reaction pathway accounted for 87% of the product. In the second pathway, the bromine attacked the 1-6 bridgehead bond directly yielding a second deuterated isomer of **5**. This pathway yielded 13% of the product mixture.





A mixture of monodeuterated benzvalenes was prepared and the proportions of the 1-^{2}H, 2-^{2}H, and 3-^{2}H species were determined by microwave relative intensity measurements. Each deuterated benzvalene isomer was taken through the accepted mechanism outlined above for benzvalene reacting with bromine with the appropriate allocations being made for the competing points of attack on the benzvalene molecule. This led to the theoretical relative percentages of the deuterated isomers of **5** indicated below:[40]





Next this mixture was treated in the standard way with $LiAlH_4$ and the percentages of the various monodeuterated species of tricyclohexane were determined by relative microwave intensities. These values are compared with those predicted theoretically for each of the two mechanisms (endo bromine removed first or exo bromine removed first). In obtaining the theoretical values, each of the starting monodeuterated dibromo compounds was followed through the appropriate mechanism and its contribution to the various monodeuterated products was added in. Table IX shows the results. It is clear that the experimental results are consistent with the exo bromine being the first to be removed. Thus the reaction is proceeding via the *endo*-5-bromobicyclo[2.1.1]hexenyl cation in analogy to the hexamethyl derivative case.

Acknowledgment. Support of this research by the National Science Foundation (GP-37066X) is gratefully acknowledged. The support of Professor E. B. Wilson and the use of his laboratory is greatly appreciated. Thanks are due to Professor T. J. Katz for a sample of tricyclohexane. The many helpful suggestions offered by Dr. C. W. Gillies during the course of this work are kindly acknowledged. Many helpful discussions with R. Balanson were greatly appreciated. The author would also like to express thanks to Professor R. H. Schwendeman for the fitting program.

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Solvation Numbers of Strong Electrolytes in Methanol Determined from Temperature Effects on Proton Shift[1a]

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Abstract: Experimental techniques, involving spinning side bands, are developed and used for determining the chemical shifts, relative to gaseous methane, of the hydroxyl and methyl protons of pure methanol and of methanol in the presence of strong electrolytes. The strong temperature dependence of the chemical shift of the hydroxyl proton is similar to that of water and is consistent with the model developed earlier for aqueous solutions. In this model the single resonance line is interpreted to be a time average of the proton in its solvated and unsolvated environments. From these studies the total "effective" solvation numbers of NaI, $LiNO_3$, $CaCl_2$, $LiClO_4$, LiBr, LiI, LiCl, and KI are determined. The fact that the solvation numbers are quite similar to the hydration numbers provides evidence that the ions bind water and methanol primarily through the oxygen atom. The methyl proton shift varies with the concentration of electrolyte but does not vary with temperature. It is shown that these observations are compatible with the proposed model.

Malinowski and coworkers[2-4] have determined the extent of hydration by studying the temperature dependence of the proton chemical shift of water in strong electrolyte solutions. Other investigators[5-8] have also used this technique for aqueous studies. The present investigation is an exploration of the feasibility of using this method for the study of the extent of solvation of strong electrolytes by nonaqueous solvents. Methanol was chosen as the solvent for this study for several reasons. It exhibits extensive hydrogen bonding and therefore the shift of the hydroxyl proton should be temperature dependent. It is a liquid over a temperature range which is adequate for the shift measurements. A number of strong electrolytes are sufficiently soluble in this solvent. In comparison to aqueous studies, the methanol molecule possesses a methyl group which can be used as an additional test of the theoretical equations.

Experimental Procedure

Reagent grade anhydrous salts and spectro grade methanol were used. The solutions were prepared in a dry atmosphere. Low-tem-