Microwave Spectrum, Conformation and Structural Parameters of 4-Chloro-1,2-butadiene

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The microwave spectrum of 4-chloro-1,2-butadiene has been measured in the region 27 000 - 35 000 MHz. All observed transitions originated from the molecule in the *skew* conformation.

The positions of the chlorine atom and the two terminal allenyl hydrogen atoms were determined by observing the two natural isotopic species: CH₂CCHCH₂³⁵Cl and CH₂CCHCH₂³⁷Cl together with the two deuterated species: CHDCCHCH₂²⁵Cl and CDHCCHCH₂²⁵Cl.

Vibrational satellites were observed and measured for the excited torsional state and a low-lying skeletal bending state.

The substance 4-chloro-1,2-butadiene was first described by Carothers *et al.*¹ as an important intermediate in the synthesis of chloroprene by addition of aqueous hydrogen chloride to vinylacetylene.

It is interesting to compare 4-chloro-1,2-butadiene with 3-chloropropene whose conformational properties have been closely examined by electron diffraction 2 and spectroscopical methods including microwave,3 infrared 4 and proton magnetic resonance 5-7 spectroscopy. The microwave spectroscopical investigation by Hirota 3 showed clearly the existence of two rotameric forms of 3-chloropropene: cis and skew. The effect of steric repulsion between the chlorine atom and the vinyl group was demonstrated and vibrational satellites due to torsional states of the cis and skew form were identified.

Rondeau and Harrah developed a simple equation for calculating the population of the cis rotamer in 3-halopropene from the coupling constant between the halomethyl protons and

the nearest vinyl proton measured with NMR. From this they determined a relative abundance of 0.16 for the *cis* form of 3-chloropropene, in good agreement with infrared measurements. We used this equation and inserted the derived value for the coupling constant between the chloromethyl protons and the nearest allenyl proton, as measured by Ferguson.⁸ According to these calculations there should be no *cis* form in 4-chloro-1,2-butadiene provided that *cis* and *skew* are the only possible rotamers.

If this is true, it would be interesting to ask why the *cis* form should be more abundant in 3-chloropropene than in 4-chloro-1,2-butadiene. The steric repulsion from an allenyl group is probably stronger than that from a vinyl group. Another possible explanation would be to assume a stabilizing nonbonded interaction between the chlorine atom and the nearest vinyl hydrogen atom for 3-chloropropene in the *cis* form which is not possible in 4-chloro-1,2-butadiene. This kind of interaction has been discussed by Viehe ^{9,10} for 1-halo-1,3-butadienes and 1,4-dihalo-1,3-butadienes.

EXPERIMENTAL

4-Chloro-1,2-butadiene was prepared by shaking vinylacetylene with conc. hydrochloric acid in a pressure bottle for 6 h:1

$$HC \equiv C - CH = CH_2 + HCl \rightarrow$$

 $H_2C = C = CH - CH_2Cl$

The sample was isolated by distillation in vacuo and finally gas-liquid chromatography at a temperature of 100 °C. The column was

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Table 1. Rotational transitions in MHz for four isotopic species of 4-chloro-1,2-butadiene.

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	11	1	10	10	-	6	35054.90	34296.28	33541.40	33917.39

 a Deuterium in the position $\rm H_2$ of Fig. 1. b Deuterium in the position $\rm H_1$ of Fig. 1.

packed with diethylhexylsebacate (15 %) absorbed on Chromosorb. Metallic columns, especially copper, should not be used since the 4-chloro-1,2-butadiene then rearranges to 2-chloro-1,3-butadiene (chloroprene). We used glass columns: length 1.5 m and internal diameter 8 mm.

The deuterated sample of 4-chloro-1,2-butadiene was prepared simply by using deuterated hydrochloric acid in the above reaction. The hydrochlorination of vinylacetylene is believed to be a 1,4-addition, and this was effectively proved by the microwave measurements on the deuterated sample which showed that deuterium only added to the end carbon of the acetylenic group in vinylacetylene.

The microwave spectra were recorded on a Hewlett-Packard model 8460 A R-band spectrometer with a phase stabilized source oscillator. The recordings were made at room temperature and at pressures ranging from 10 to 50 mTorr. The precision of the measured transitions was estimated to be 0.05 MHz.

MICROWAVE SPECTRUM

Most of the lines in the spectrum are gathered in bands at intervals of approximately 3160 MHz. These bands cover almost the whole spectral region. The line abundance and the repeated structure within the bands are mainly due to the low-lying torsional vibration mode.

The observed transitions were all R-branch a-type transitions with $\Delta J = +1$ and $\Delta K_{-1} = 0$, caused by the *skew* rotamer of 4-chloro-1,2-butadiene behaving as an almost prolate symmetric rotor: see Table 1.

$$c = c = c$$

$$H_3$$

Fig. 1. The model structure of skew-4-chloro-1,2-butadiene.

The effect of nuclear quadrupole coupling is observable as a splitting into doublets for transitions with $K_{-1} \! > \! 4$ and the separation increases with K_{-1} . However, the splitting of these doublets is mainly determined by the nuclear quadrupole coupling constant $\chi_{\rm aa}$ and since transitions with $K_{-1} \! > \! 8$ are obscured by the very dense vibrational bands, it is not possible to calculate $\chi_{\rm aa}$ accurately. The values $\chi_{\rm aa} = -30$ MHz for ³⁵Cl and $\chi_{\rm aa} = -24$ MHz for ³⁷Cl are sufficient to account for the observed splittings within the error of measurement.

The lines from the deuterated species were identified and measured with high resolution: see Table 1. The synthesis yields a product with one deuterium atom in the end position of the allenyl group. Due to the skew conformation, this gives two isotopic species in equal amounts with deuterium in the position H_1 or H_2 : see Fig. 1.

The vibrational satellites due to the excited torsional states were measured for $v_1=1$ and $v_1=2$ for the ³⁵Cl species. Another series of vibrational satellites, probably related to

Table 2. Rotational constants in MHz for four isotopic species of 4-chloro-1,2-butadiene.

	A	В	C
CIT COLLOTT 25CI			
CH ₂ CCHCH ₂ ³⁵ Cl Ground state	15484. + 12	1606 07 1 0 01	1557.55 + 0.01
		1606.07 ± 0.01	1560.80 ± 0.01 1560.80 ± 0.02
$v_1 = 1$	$15606. \pm 17$	1612.84 ± 0.02	
$v_1 = 2$	$15722. \pm 18$	1619.59 ± 0.02	1564.01 ± 0.02
$v_2 = 1$ CH ₂ CCHCH ₂ ³⁷ Cl	$15668.\pm18$	1601.19 ± 0.02	1555.65 ± 0.02
Ground state	$15396.\pm13$	1571.26 ± 0.01	1523.94 ± 0.01
CHDCCHCH ₂ ³⁵ Cl ^a			
Ground state	$15296. \pm 16$	1535.8 ± 0.01	1492.75 ± 0.01
CDHCCHCH ₂ ³⁵ Cl ^b			_
Ground state	$14470. \pm 12$	1556.25 ± 0.02	1500.67 ± 0.02

^a Deuterium in the position H₂ of Fig. 1. ^b Deuterium in the position H₁ of Fig. 1.

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Table 3. Centrifugal distortion constants in kHz for four isotopic species of 4-chloro-1,2-butadiene.

	$\Delta_{ m J}$	$\it \Delta_{ m JK}$	$\delta_{ m J}$
CH ₂ CCHCH ₂ ³⁵ Cl			
Ground state	0.94 ± 0.01	-56.38 ± 0.03	0.19 + 0.02
$v_1 = 1$	1.04 ± 0.02	-58.40 ± 0.05	0.23 + 0.04
$v_1 = 2$	1.04 ± 0.03	-60.62 ± 0.07	0.22 + 0.05
$v_2 = 1$	0.95 ± 0.02	-58.87 ± 0.04	0.17 ± 0.04
CH ₂ CCHCH ₂ ³⁷ Cl		_	
Ground state	0.91 ± 0.01	-55.54 ± 0.03	0.19 ± 0.02
CHDCCHCH ₂ ³⁵ Cl ^a			
Ground state	$\boldsymbol{0.84 \pm 0.02}$	-52.24 ± 0.04	0.14 ± 0.03
$\text{CDHCCHCH}_2^{35}\text{Cl}\ ^b$			
Ground state	0.89 ± 0.02	-51.71 ± 0.06	0.17 ± 0.04

^a Deuterium in the position H₂ of Fig. 1. ^b Deuterium in the position H₁ of Fig. 1.

skeletal bending states, were measured for $v_2=1$ for the ³⁵Cl species. Relative intensities of the satellites indicate that the torsional frequency is about 60-70 cm⁻¹ and the skeletal bending frequency is about 170-190 cm⁻¹. Despite the low precision, these measurements are valuable for identification of the low-lying infrared transitions. This has been demonstrated by Hirota ³ who was able to reassign the torsional frequency of *skew-3*-chloropropene originally reported by Radcliff and Wood.⁴

The rotational constants A, B and C, and the three centrifugal distortion parameters Δ_J , Δ_{JK} and δ_J were fitted to the observed spectra by the least-squares method: see Tables 2 and 3.

MOLECULAR STRUCTURE

All observed transitions are caused by the skew conformer and no lines have been found

that indicate the existence of another possible conformation of 4-chloro-1,2-butadiene. cis-4-Chloro-1,2-butadiene, if it exists, is expected to have a rather complicated spectrum mainly composed of Q-branch transitions active through the μ_b dipole moment. This, together with the fact that skew-4-chloro-1,2-butadiene has a very rich spectrum covering almost the whole spectral region, makes it hard to find expected contributions from the cis-form. In our experience it is not unlikely that even a relative abundance of 10 % might pass unnoticed under these circumstances. Thus the microwave measurements and, in fact, also the above-mentioned calculations using NMRparameters, do not completely rule out the possibility of other conformers. We think that the best method to prove the absence of other rotamers would be a spectroscopical investigation in the infrared region and this has recently been done by W. C. Harris et al.11 Their results

Table 4. Estimated molecular structure of 4-chloro-1,2-butadiene.

Bond length (Å)		Angle (°)	
$C-C$ $C=C$ $C-H_1$ $C-H_2$ $C-H_3$ $C-H \text{ (methylene)}$ $C-Cl$	1.486 1.312 1.082 1.082 1.080 1.095 1.809		121.6 120.8 120.8 120.0 107.0 111.0 109.6 120.0

Table 5. The absolute values of the coordinates for the chlorine atom and two allenyl hydrogen atoms calculated with Kraitchman's equations and the distance between these atoms compared with the coordinates and the distances from the estimated molecular structure above. Conversion factor 505 374 (MHz) (au Å2).

	Microwave	spectroscopy	7 (Å)	Estimated	structure (Å	.)
Coordinate	Cl	H_1	${ m H_2}$	Cl	$\mathbf{H_1}$	H_2
a b c	1.889 0.312 0.018	3.164 1.530 0.200	3.754 0.218 0.613	1.887 0.304 0.048	3.154 1.511 0.051	3.751 0.181 0.535
Distance	$Cl-H_1$	$Cl - H_2$	$\mathbf{H_1} - \mathbf{H_2}$	$Cl-H_1$	$Cl - H_2$	H_1-H_2
$r_{ m s}$	5.202	5.703	1.891	5.184	5.689	1.858

support our conclusion that a single skew form of 4-chloro-1,2-butadiene is predominant at ambient temperature.

In order to obtain a good model structure for skew-4-chloro-1,2-butadiene we used the distances and angles reported for allene 12 and 3-chloropropene:3 see Table 4. This structure did not fit the measured moments of inertia until we allowed the dihedral angle to change from 122.3°, reported by Hirota 3 for 3-chloropropene, to 120.0°. Since all structural parameters contribute to the moments of inertia, this value is of course very sensitive to the values of other parameters. However, after this partial fitting the model was found to be in good agreement even with the Cartesian coordinates of the chlorine atom and the two hydrogen atoms H₁ and H₂: see Table 5. These coordinates were calculated in the principal axis system of the CH2CCHCH235Cl molecule from the change in the moments of inertia on isotopic substitution.13,14

The accuracy of these values as well as the distance parameters obtained from these coordinates are limited due to several reasons. First we must observe that coordinates less than about 0.25 Å derived by this method are always uncertain due to the small change on isotopic substitution. Further, since the observed lines are all a-type R-branch transitions, it is not possible to determine the value of the moment I_a as accurately as the moments I_b and I_c. Finally vibrational effects always lower the precision especially for the coordinates of the hydrogen atoms. 15 However, it is reasonable to expect the error of the hydrogen-chlorine distances to be about +0.01 Å and the error of the hydrogen-hydrogen distances to be about +0.05 Å.

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