

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

FRED KARLSSON, MATS GRANBERG and RAGNAR VESTIN

Department of Physical Chemistry, Arrhenius Laboratory, University of Stockholm, S-104 05 Stockholm, Sweden

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: $\text{CH}_2\text{CCHCH}_2^{35}\text{Cl}$ and $\text{CH}_2\text{CCHCH}_2^{37}\text{Cl}$ together with the two deuterated species: $\text{CDHCCHCH}_2^{35}\text{Cl}$ and $\text{CDHCCHCH}_2^{37}\text{Cl}$.

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 diffraction² and spectroscopical methods including microwave,³ infrared⁴ and proton magnetic resonance^{5–7} spectroscopy. The microwave spectroscopical investigation by Hirota³ 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.

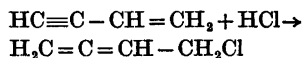
Rondeau and Harrah⁷ developed a simple equation for calculating the population of the *cis* rotamer in 3-halopropene from the coupling constant between the halomethyl protons and

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



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

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

J	K_{-1}	K_{+1}	J	K_{-1}	K_{+1}	$\text{CH}_3\text{CCHCH}_2^{35}\text{Cl}$	$\text{CH}_3\text{CCHCH}_2^{37}\text{Cl}$	$\text{CHDCCHCH}_2^{35}\text{Cl}^a$	$\text{CDHCCHCH}_2^{35}\text{Cl}^b$
9	1	9	8	1	8	28249.42	27639.30	27059.20	27255.91
9	0	9	8	0	8	28454.62	27839.69	27242.47	27488.35
9	2	8	8	2	7	28471.55	27855.96	27256.50	27510.13
9	3	7	8	3	6	28480.99	27865.08	27264.70	27520.82
9	2	7	8	2	6	28486.74	27870.43	27268.51	27531.50
9	4	6	8	4	5	28487.27	27871.35	27270.56	27526.30
9	5	5	8	5	4	28496.08	27879.90	27278.69	27534.11
9	6	4	8	6	3	28506.86	27890.81	27288.97	27544.02
9	1	8	8	1	7	28684.89	28064.02	27445.90	27754.95
10	1	10	9	1	9	31386.76	30708.99	30064.51	30282.48
10	0	10	9	0	9	31611.54	30928.45	30265.61	30536.23
10	2	9	9	2	8	31633.75	30949.75	30283.90	30565.26
10	3	8	9	3	7	31645.33	30961.03	30293.82	30578.77
10	4	7	9	4	6	31652.13	30967.84	30300.25	30584.45
10	2	8	9	2	7	31654.50	30969.58	30300.42	30594.50
10	5	6	9	5	5	31661.71	30977.16	30309.19	30593.04
10	6	5	9	6	4	31673.87	30989.23	30320.41	
10	1	9	9	1	8	31870.20	31180.39	30493.94	30836.53
11	1	11	10	1	10	34523.55	33778.05	33069.35	33308.35
11	0	11	10	0	10	34767.03	34015.93	33287.60	33582.30
11	2	10	10	2	9	34795.52	34043.15	33310.87	33619.88
11	3	9	10	3	8	34809.61	34056.82	33322.90	33636.52
11	4	8	10	4	7	34816.75	34063.90	33329.71	33642.42
11	2	9	10	2	8	34823.03	34069.56	33332.79	33658.90
11	5	7	10	5	6	34827.16	34074.31	33339.52	33651.84
11	6	6	10	6	5	34840.49	34087.29	33351.76	33663.67
11	7	5	10	7	4	34856.25	34102.98		
11	1	10	10	1	9	35054.90	34296.28	33541.40	33917.39

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

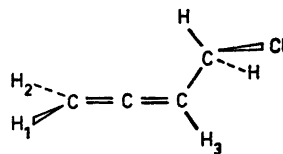


Fig. 1. The model structure of *skew*-4-chloro-1,2-butadiene.

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

	<i>A</i>	<i>B</i>	<i>C</i>
$\text{CH}_2\text{CCHCH}_2\text{ }^{35}\text{Cl}$			
Ground state	15484. \pm 12	1606.07 \pm 0.01	1557.55 \pm 0.01
$v_1 = 1$	15606. \pm 17	1612.84 \pm 0.02	1560.80 \pm 0.02
$v_1 = 2$	15722. \pm 18	1619.59 \pm 0.02	1564.01 \pm 0.02
$v_2 = 1$	15668. \pm 18	1601.19 \pm 0.02	1555.65 \pm 0.02
$\text{CH}_2\text{CCHCH}_2\text{ }^{37}\text{Cl}$			
Ground state	15396. \pm 13	1571.26 \pm 0.01	1523.94 \pm 0.01
$\text{CHDCCHCH}_2\text{ }^{35}\text{Cl}^a$			
Ground state	15296. \pm 16	1535.8 \pm 0.01	1492.75 \pm 0.01
$\text{CDHCCHCH}_2\text{ }^{35}\text{Cl}^b$			
Ground state	14470. \pm 12	1556.25 \pm 0.02	1500.67 \pm 0.02

^a Deuterium in the position H_2 of Fig. 1. ^b Deuterium in the position H_1 of Fig. 1.

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

	A_J	A_{JK}	δ_J
$\text{CH}_2\text{CCHCH}_2^{35}\text{Cl}$			
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
$\text{CH}_2\text{CCHCH}_2^{37}\text{Cl}$			
Ground state	0.91 ± 0.01	-55.54 ± 0.03	0.19 ± 0.02
$\text{CHDCCHCH}_2^{35}\text{Cl}^a$			
Ground state	0.84 ± 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 H_2 of Fig. 1. ^b Deuterium in the position H_1 of Fig. 1.

skeletal bending states, were measured for $v_2=1$ for the ^{35}Cl species. Relative intensities of the satellites indicate that the torsional frequency is about $60-70\text{ cm}^{-1}$ and the skeletal bending frequency is about $170-190\text{ cm}^{-1}$. Despite the low precision, these measurements are valuable for identification of the low-lying infrared transitions. This has been demonstrated by Hirota³ 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 A_J , A_{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 NMR-parameters, 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	$\angle\text{C}=\text{C}-\text{C}$
C=C	$\angle\text{C}=\text{C}-\text{H}_1$
C—H ₁	$\angle\text{C}=\text{C}-\text{H}_2$
C—H ₂	$\angle\text{C}-\text{C}-\text{H}_3$
C—H ₃	$\angle\text{C}-\text{C}-\text{H}$ (methylene)
C—H (methylene)	$\angle\text{HCH}$ (methylene)
C—Cl	$\angle\text{C}-\text{C}-\text{Cl}$
	Dihedral angle

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 (Å)			Estimated structure (Å)		
Coordinate	Cl	H ₁	H ₂	Cl	H ₁	H ₂
a	1.889	3.164	3.754	1.887	3.154	3.751
b	0.312	1.530	0.218	0.304	1.511	0.181
c	0.018	0.200	0.613	0.048	0.051	0.535
Distance	Cl-H ₁	Cl-H ₂	H ₁ -H ₂	Cl-H ₁	Cl-H ₂	H ₁ -H ₂
r _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 allene¹² 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 Hirota³ 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 reason-

able 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.

Acknowledgements. We thank all those who have contributed to this paper and especially Dr. Stig Ljunggren and Dr. Hasse Karlsson for pleasant cooperation and valuable discussions.

REFERENCES

- Carothers, W. H., Berchet, G. J. and Collins, A. M. *J. Am. Chem. Soc.* 54 (1932) 4066.
- Bowen, H. J. M., Gilchrist, A. and Sutton, L. E. *Trans. Faraday Soc.* 51 (1955) 1341.
- Hirota, E. *J. Mol. Spectrosc.* 35 (1970) 9.
- Radcliffe, K. and Wood, J. L. *Trans. Faraday Soc.* 62 (1966) 2038.
- Bothner-By, A. A. and Günther H. *Discuss. Faraday Soc.* 34 (1962) 127.
- Bothner-By, A. A., Castellano, S. S., Ebersole, S. J. and Günther, H. *J. Am. Chem. Soc.* 88 (1966) 2466.
- Rondeau, R. E. and Harrah, L. A. *J. Mol. Spectrosc.* 21 (1966) 332.
- Ferguson, R. C. *J. Phys. Chem.* 68 (1964) 1594.
- Viehe, H. G. *Chem. Ber.* 97 (1964) 598.
- Viehe, H. G. and Franchimont, E. *Chem. Ber.* 97 (1964) 602.
- Harris, W. C., Coe, D. A., Parpart, M. K. and Pyron, R. S. *Private communication.*
- Almenningen, A., Bastiansen, O. and Tretteberg, M. *Acta Chem. Scand.* 13 (1959) 1699.
- Kraitchman, J. *Am. J. Phys.* 21 (1953) 17.
- Costain, C. C. *J. Chem. Phys.* 29 (1958) 864.
- Laurie, V. W. and Herschbach, D. R. *J. Chem. Phys.* 37 (1962) 1687.

Received January 12, 1977.