

# The Complete Molecular Structure of 2-Chloro-1,3-butadiene Determined with Microwave Spectroscopy

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Microwave transitions of six isotopic species of 2-chloro-1,3-butadiene, chloroprene, have been measured and assigned in the frequency region 18.0–26.5 GHz. Together with earlier measured and assigned transitions of four other isotopic species of the compound the present results have made it possible to calculate the complete structure of the molecule with a least-squares method. Two of the structural parameters calculated were:  $r(\text{C}=\text{C})_{\text{chlorovinyl}} = 1.349(5)$  and  $r(\text{C}=\text{C})_{\text{vinyl}} = 1.341(4)$  Å, which is strikingly different from what is found in the 1-chloro-1,3-butadienes. Another difference is that no non-bonded attraction between chlorine and hydrogen is found.

The quadrupole coupling constants  $\chi_{xx}$  and  $\chi_{yy}$  were calculated and then used to obtain the double bond character,  $\delta$ , of the C–Cl bond.  $\delta$  was found to have the value 0.018(6), which is somewhat smaller than the values obtained for *cis*-1-chloro-1,3-butadiene and *cis*-1-chlorobuten-3-yne.

Force field calculations were used to predict values for the inertial defect and all the centrifugal distortion constants of each monosubstituted species.

The complete molecular structures of *cis*-1-chloro-1,3-butadiene and *trans*-1-chloro-1,3-butadiene have recently been determined at our department with microwave spectroscopy.<sup>1,2</sup> For the 2-chloro-1,3-butadiene molecule some preliminary results, obtained from the microwave spectra of four isotopic species of the molecule, were reported recently.<sup>3</sup> The assignment of microwave transitions of the remaining monosubstituted species of the molecule turned out to be quite difficult then. Later on it was, however, possible to assign a few such transitions, which inspired hope of determining the complete structure of this interesting molecule.

## EXPERIMENTAL

The preparation of 2-chloro-1,3-butadiene and of two of the monodeuterated species has been described earlier.<sup>3</sup> The <sup>13</sup>C-monosubstituted species were synthesized as described in detail in a recent publication.<sup>4</sup>

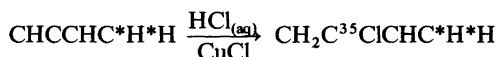
During the work with the microwave spectra it became apparent that the isotopic species  $\text{CH}_2\text{C}^{35}\text{ClC}^{\text{D}}\text{CH}_2$  was missing in one of the deuterated samples, and we think we know the reason for that. In the preparation butenyne with deuterium in any one hydrogen position is treated with potassium hydroxide in water, so that D in the acidic hydrogen position on the acetylene group is exchanged for H. However, this exchange will probably also happen to a molecule with D situated on the carbon next to the acetylene group:



(\* means a possible site for deuterium)

The fact that this hydrogen has some acidity has been noted before by one of us (F.K.).

The product is then treated with aqueous hydrochloric acid and a small amount of CuCl as catalyst to yield a sample containing two more monodeuterated species of 2-chloro-1,3-butadiene:



The microwave spectra were recorded in the K-band region (18.0–26.5 GHz). A Hewlett-Packard 8460A spectrometer with Stark modulation at 33.33 kHz was used. The microwave cell was normally kept at about –20 °C, and a total pressure between 20 and 40 mTorr was usually employed. The uncertainty in the measured frequencies was estimated to be 0.05 MHz.

## MICROWAVE SPECTRA AND ROTATIONAL CONSTANTS

2-Chloro-1,3-butadiene is a highly asymmetric rotor molecule ( $\kappa \sim 0$ ). Its microwave spectrum is dominated by strong  $Q$ -branch transitions of the  $b$ -type and these were first identified. Subsequently it was also possible to assign  $R$ -branch  $b$ -type transitions and weaker  $R$ -branch  $a$ -type transitions.<sup>3</sup>

The spectra of the <sup>13</sup>C-substituted species were quite complex, not only because of the complicated nature of the spectrum of 2-chloro-1,3-butadiene but also because of the frequently occurring overlap with lines of the more abundant normal species. The same difficulties were experienced during the assignment of the spectra of the deuterated species CH<sub>2</sub>C<sup>35</sup>ClCHCDH and CH<sub>2</sub>C<sup>35</sup>ClCHCHD; and so for each of these six species it was only possible to assign and measure accurately a few lines. Moreover, those lines all corresponded to  $Q$ -branch  $b$ -type transitions, which meant that it was not possible to fit the rotational constant  $C$  accurately to the measured frequencies. Consequently, for these species a somewhat different method had to be used in order to get accurate values of the rotational constants.

Reasonable estimates of the  $C$  rotational constants were first obtained from calculations of the changes in the parent value due to isotopic substitutions. Those estimated values were then used as fixed parameters in the least-squares fits for the six species. Trustworthy values of the centrifugal

distortion constants were obtained: see Tables 1 and 3. However, correct absolute values for the  $A$  and  $B$  rotational constants were of course not obtained, but the differences  $A-C$  and  $B-C$  were regarded as quite reliable. The reason for that is that  $Q$ -lines depend principally on  $A-C$  and  $\kappa$ . But  $\kappa = (2B - A - C)/(A - C) = [2(B - C) - (A - C)]/(A - C)$ , so  $Q$ -lines could therefore equally well be said to depend only on  $A - C$  and  $B - C$ .

Furthermore, with force field calculations it was possible to obtain good estimates of the inertial defect,  $\Delta$ , for each isotopic species: see Tables 2 and 3. Thus, for each of the six species excellent values for  $A - C$ ,  $B - C$  and  $\Delta$  were available, and these values were used to calculate the true absolute values of  $A$ ,  $B$  and  $C$  as will be described below.

The inertial defect,  $\Delta$ , is related to the principal moments of inertia in the following way:  $\Delta = I_c - I_a - I_b$ , or in terms of the rotational constants:  $\Delta = k/C - k/A - k/B$ , where  $k$  is the conversion factor (505374 MHz uÅ<sup>2</sup>). Since  $A - C$  and  $B - C$  are constants, we call them  $a$  and  $b$ , respectively, and write:  $\Delta = k/C - k/(a + C) - k/(b + C)$ , or  $k/C - k/(a + C) - k/(b + C) - \Delta = 0$ . This is an equation only in  $C$ , since  $a$ ,  $b$ ,  $\Delta$  and  $k$  all are known constants. However, the equation is difficult to solve analytically. Therefore it is solved with the Newton-Raphson iterative method with the estimated value of  $C$  as starting value of the iteration. The resulting values for the rotational constants together with calculated error limits are shown in Table 1, where also the results for the other four species are shown.

Table 1. Rotational constants and centrifugal distortion constants of 2-chloro-1,3-butadiene in the group vibrational state obtained from observed frequencies. Constants of the <sup>13</sup>C, D(8) and D(9) isotopic species were fitted with the  $C$  rotational constant held fixed, due to the assignment of only  $Q_b$ -lines. The rotational constants for these species were then calculated with a correction method as described in the text.

Species	$A$ /MHz	$B$ /MHz	$C$ /MHz	$\Delta_j$ /kHz	$\Delta_{JK}$ /kHz	$\Delta_K$ /kHz	$\delta_j$ /kHz	$\delta_K$ /kHz	$n^a$
CH <sub>2</sub> C <sup>35</sup> ClCHCH <sub>2</sub>	5438.865(4)	3743.080(4)	2216.321(4)	0.83(8)	-1.80(9)	3.3(1)	0.50(1)	0.96(6)	23
CH <sub>2</sub> C <sup>37</sup> ClCHCH <sub>2</sub>	5359.405(8)	3685.570(8)	2182.939(7)	0.54(16)	-2.72(55)	4.3(7)	0.44(5)	1.26(35)	18
<sup>13</sup> CH <sub>2</sub> C <sup>35</sup> ClCHCH <sub>2</sub>	5262.03(2)	3727.32(1)	2180.97(1)		-1.46(16)		0.49(3)	0.93(14)	8
CH <sub>2</sub> <sup>13</sup> C <sup>35</sup> ClCHCH <sub>2</sub>	5417.71(2)	3743.02(2)	2212.78(1)		-1.79(3)	2.8(2)	0.465(9)		6
CH <sub>2</sub> C <sup>35</sup> Cl <sup>13</sup> CHCH <sub>2</sub>	5426.30(1)	3692.52(1)	2196.45(1)			3.1(1)			4
CH <sub>2</sub> C <sup>35</sup> ClCH <sup>13</sup> CH <sub>2</sub>	5414.95(2)	3630.24(1)	2172.42(1)		-1.34(13)	2.5(4)		1.03(4)	6
CDHC <sup>35</sup> ClCHCH <sub>2</sub> <sup>b</sup>	5262.809(4)	3647.444(3)	2153.546(3)	0.82(6)	-0.77(22)	2.4(3)	0.42(2)	0.96(14)	21
CHDC <sup>35</sup> ClCHCH <sub>2</sub> <sup>c</sup>	5045.631(6)	3742.129(5)	2147.757(4)	0.68(10)	-1.75(5)		0.49(1)	0.94(4)	19
CH <sub>2</sub> C <sup>35</sup> ClCHCDH <sup>d</sup>	5417.81(1)	3489.54(1)	2121.69(1)		-1.27(6)	3.4(2)		1.12(4)	6
CH <sub>2</sub> C <sup>35</sup> ClCHCHD <sup>e</sup>	5295.70(3)	3676.95(2)	2169.45(2)					0.92(7)	4

<sup>a</sup> Number of transitions in fit. Observed frequencies available on request. <sup>b</sup> Deuterium in *cis*-position to chlorine. <sup>c</sup> Deuterium in *trans*-position to chlorine. <sup>d</sup> Deuterium in *trans*-position to chlorovinyl. <sup>e</sup> Deuterium in *cis*-position to chlorovinyl.

Table 2. Values of the centrifugal distortion constants and the inertial defect for different isotopic species of 2-chloro-1,3-butadiene from force field calculations.

Species	$\Delta_j/\text{kHz}$	$\Delta_{jk}/\text{kHz}$	$\Delta_k/\text{kHz}$	$\delta_j/\text{kHz}$	$\delta_k/\text{kHz}$	$\Delta/\text{u}\text{\AA}^2$
$\text{CH}_2\text{C}^{35}\text{ClCHCH}_2$	1.238	-2.123	3.870	0.5071	0.8711	0.081971
$\text{CH}_2\text{C}^{37}\text{ClCHCH}_2$	1.246	-2.323	3.959	0.5124	0.8094	0.084070
$^{13}\text{CH}_2\text{C}^{35}\text{ClCHCH}_2$	2.484	-5.734	3.461	0.1657	1.7548	0.084661
$\text{CH}_2\text{C}^{35}\text{Cl}^{13}\text{CHCH}_2$	1.235	-2.121	3.862	0.5066	0.8609	0.082214
$\text{CH}_2\text{C}^{35}\text{Cl}^{13}\text{CHCH}_2$	1.200	-2.113	3.874	0.4906	0.8457	0.081127
$\text{CH}_2\text{C}^{35}\text{ClCH}^{13}\text{CH}_2$	1.159	-1.846	3.656	0.4697	0.9173	0.083061
$\text{CDHC}^{35}\text{ClCHCH}_2^d$	2.418	-5.347	3.130	0.2731	1.4024	0.082509
$\text{CHDC}^{35}\text{ClCHCH}_2^b$	2.328	-5.370	3.241	0.0418	1.5193	0.083121
$\text{CH}_2\text{C}^{35}\text{ClCDCH}_2$	1.132	-2.097	3.662	0.4649	0.7398	0.069520
$\text{CH}_2\text{C}^{35}\text{ClCHCDH}^c$	1.022	-1.437	3.439	0.4086	0.9675	0.081373
$\text{CH}_2\text{C}^{35}\text{ClCHCHD}^d$	1.217	-1.941	3.443	0.4960	0.8679	0.068374

<sup>a</sup>Deuterium in *cis*-position to chlorine. <sup>b</sup>Deuterium in *trans*-position to chlorine. <sup>c</sup>Deuterium in *trans*-position to chlorovinyl. <sup>d</sup>Deuterium in *cis*-position to chlorovinyl.

Table 3. Estimated values of the centrifugal distortion constants and the inertial defect for different isotopic species of 2-chloro-1,3-butadiene. They are obtained from the observed parent values and from the force field calculations.<sup>a</sup>

Species	$\Delta_j/\text{kHz}$	$\Delta_{jk}/\text{kHz}$	$\Delta_k/\text{kHz}$	$\delta_j/\text{kHz}$	$\delta_k/\text{kHz}$	$\Delta/\text{u}\text{\AA}^2$
$\text{CH}_2\text{C}^{35}\text{ClCHCH}_2$	0.83 <sup>b</sup>	-1.80 <sup>b</sup>	3.3 <sup>b</sup>	0.50 <sup>b</sup>	0.96 <sup>b</sup>	0.08926 <sup>b,c</sup>
$\text{CH}_2\text{C}^{37}\text{ClCHCH}_2$	0.84	-2.00	3.4	0.51	0.90	0.09136
$^{13}\text{CH}_2\text{C}^{35}\text{ClCHCH}_2$	2.08	-5.41	2.9	0.16	1.84	0.09195
$\text{CH}_2\text{C}^{35}\text{Cl}^{13}\text{CHCH}_2$	0.83	-1.80	3.3	0.50	0.95	0.08950
$\text{CH}_2\text{C}^{35}\text{Cl}^{13}\text{CHCH}_2$	0.79	-1.79	3.3	0.48	0.93	0.08842
$\text{CH}_2\text{C}^{35}\text{ClCH}^{13}\text{CH}_2$	0.75	-1.52	3.1	0.46	1.01	0.09035
$\text{CDHC}^{35}\text{ClCHCH}_2^d$	2.01	-5.02	2.6	0.27	1.49	0.08980
$\text{CHDC}^{35}\text{ClCHCH}_2^e$	1.92	-5.05	2.7	0.03	1.61	0.09041
$\text{CH}_2\text{C}^{35}\text{ClCDCH}_2$	0.72	-1.77	3.1	0.46	0.83	0.07681
$\text{CH}_2\text{C}^{35}\text{ClCHCDH}^f$	0.61	-1.11	2.9	0.40	1.06	0.08866
$\text{CH}_2\text{C}^{35}\text{ClCHCHD}^g$	0.81	-1.62	2.9	0.49	0.96	0.07566

<sup>a</sup>See Table 2. <sup>b</sup>Observed value. <sup>c</sup>Conversion factor 505374 (MHz) ( $\text{u}\text{\AA}^2$ ). <sup>d</sup>Deuterium in *cis*-position to chlorine. <sup>e</sup>Deuterium in *trans*-position to chlorine. <sup>f</sup>Deuterium in *trans*-position to chlorovinyl. <sup>g</sup>Deuterium in *cis*-position to chlorovinyl.

## MOLECULAR STRUCTURE

The force field calculations not only yielded the value of the inertial defect but also values of all the centrifugal distortion constants for each isotopically substituted species: see Tables 2 and 3. This was of great help when the best fit of constants to the measured transition frequencies was to be chosen for those species. The method has been used earlier at our department and has been found to work satisfactory.<sup>1,2</sup> It is particularly useful when only a few transition frequencies are known.

From the measured value of the inertial defect of the normal species it was concluded that the molecule has a planar structure: see Table 3. The cartesian coordinates of the atoms in the molecule were first calculated from the change in the principal moments of inertia  $I_a$  and  $I_b$  due to isotopic substitution.<sup>5,6</sup> The result is shown in Table 4, column I. The coordinates of the H(7) atom are of course missing, since the corresponding deuterated species, D(7), was not observed, as explained in the experi-

Table 4. Nuclear coordinates (Å) for the atoms of 2-chloro-1,3-butadiene calculated with the Kraitchman-Costain method (I) and a least-squares method (II). The conversion factor used was 505374 (MHz) (uÅ<sup>2</sup>).

Atom	I		II	
	a	b	a	b
C(1)	-0.7299	1.7862	-0.7310	1.7867
C(2)	-0.0465	0.6048	-0.0804	0.6055
C(3)	1.3616	0.4758	1.3609	0.4785
C(4)	2.0467	-0.6745	2.0471	-0.6735
H(5)	-1.8154	1.8404	-1.8152	1.8403
H(6)	-0.1690	2.6990	-0.1744	2.6992
H(7)			1.9003	1.4156
H(8)	3.1266	-0.6690	3.1265	-0.6688
H(9)	1.5149	-1.6342	1.5136	-1.6326
Cl	-1.0216	-0.8607	-1.0222	-0.8593

Table 5. The molecular structure of 2-chloro-1,3-butadiene compared with the structures of the 1-chloro-1,3-butadienes, 1,3-butadiene and vinyl chloride.

Method:	2-Chloro-1,3-butadiene MW <sup>a</sup>	<i>trans</i> -1-Chloro-1,3-butadiene <sup>a</sup> MW	<i>cis</i> -1-Chloro-1,3-butadiene <sup>b</sup> MW	1,3-Butadiene <sup>c</sup> ED <sup>e</sup>	Vinyl chloride <sup>c</sup> MW
<b>Bond lengths (Å)</b>					
C(1)=C(2)	1.349(5)	1.313(10)	1.327(6)	1.345(2)	1.332(5)
C(2)-C(3)	1.447(9)	1.439(6)	1.449(13)	1.465(3)	
C(3)=C(4)	1.341(4)	1.340(7)	1.343(2)	1.345(2)	
C(1)-H(5)	1.085(4)		1.100(11)		1.090(10)
C(1)-H(6)	1.069(5)	1.079(8)			1.078(10)
C(3)-H(7)	1.08(2)	1.095(7)	1.132(16)		
C(4)-H(8)	1.079(2)	1.079(9)	1.087(13)		
C(4)-H(9)	1.097(4)	1.087(5)	1.071(13)	1.108(4) <sup>f</sup>	
C-Cl	1.741(9)	1.737(4)	1.731(8)		1.726(5)
<b>Bond angles (deg.)</b>					
C(1)=C(2)-C(3)	123.9(6)	124.1(11)	126.5(3)	123.3(3)	
C(2)-C(3)=C(4)	125.8(3)	124.8(10)	123.0(7)	123.3(3)	
C(2)=C(1)-H(5)	121.7(5)		125.5(4)		121.0(10)
C(2)=C(1)-H(6)	119.8(5)	126.1(4)			119.5(10)
C(4)=C(3)-H(7)	119.3(7)	119.1(6)	122.3(5)	123.0(32)	
C(3)=C(4)-H(8)	120.5(4)	121.8(5)	121.0(5)	122.4(22)	
C(3)=C(4)-H(9)	120.1(2)	120.1(6)	121.7(5)	120.0(24)	
C=C-Cl	118.4(7)	123.5(7)	123.7(3)		122.3(5)

<sup>a</sup>Ref. 2. <sup>b</sup>Ref. 1. <sup>c</sup>Ref. 8 and references therein. <sup>d</sup>Microwave spectroscopy. <sup>e</sup>Electron diffraction. <sup>f</sup>Weighted mean value of all C-H distances.

mental section. Moreover, for the atoms C(2) and H(6) the a-coordinates are below the critical distance 0.3 Å, so these values are of low accuracy.

In order to calculate an accurate complete molecular structure the method of Nösberger *et al.* had to be used.<sup>7</sup> With this iterative least-squares method

the absolute values of the rotational constants of the normal species could be used together with the differences due to isotopic substitution. This method has shown a better performance for small nuclear coordinates.<sup>7</sup> The calculations converged rapidly, and the result showed only a minor dependence on

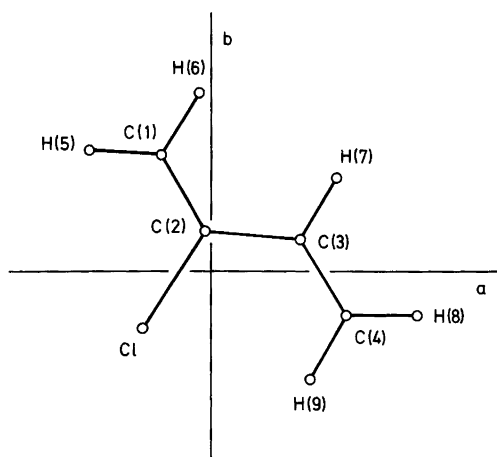


Fig. 1. Molecular structure of 2-chloro-1,3-butadiene with principal axes of inertia. Obtained values of the structural parameters are given in Table 5.

the starting structure of the iteration process. The result is shown in Table 4, column II, in Table 5 and in Fig. 1. The structure is of high accuracy apart from the C(3)–H(7) distance, but this is due to the fact that the rotational constants of the D(7)-species could not be incorporated in the fit.

Very good agreement between the coordinates calculated with the two methods was obtained for values greater than 0.3 Å. For coordinates smaller than 0.3 Å the values calculated with the least-squares method are probably more reliable.

For the 1-chloro-1,3-butadienes the C(1)=C(2) distance was found to be shorter than the C(3)=C(4) distance.<sup>1,2</sup> The result for 2-chloro-1,3-butadiene is markedly different in that respect.

A non-bonded attraction between chlorine and hydrogen was discovered in the two 1-chloro-1,3-butadienes. However, in 2-chloro-1,3-butadiene no such interaction is found. In fact, the only interaction between chlorine and hydrogen that can be observed has instead a steric repulsive character. The steric repulsion between chlorine and H(9) causes the angle C(2)–C(3)=C(4) to increase about 2 degrees from the normal value. A similar effect is present in the *cis*-1-chloro-1,3-butadiene molecule. The angle C(2)=C(1)–H(5) is also affected by such an interaction.

It is interesting to compare some of the structural details within the chlorovinyl group of 2-chloro-1,3-butadiene with those of vinyl chloride. They are found to be rather similar: see Table 5.

## QUADRUPOLE COUPLING CONSTANTS

The quadrupole coupling constants  $\chi_{aa}$  and  $\chi_{bb}$  for  $^{35}\text{Cl}$  in  $\text{CH}_2\text{C}^{35}\text{ClCHCH}_2$  have been determined earlier.<sup>3</sup> The values obtained were:  $\chi_{aa} = 5.2(2)$  and  $\chi_{bb} = -37.5(2)$  MHz.

Since the coordinates of C(2) and chlorine were now determined, it was possible to calculate the quadrupole coupling constants  $\chi_{xx}$ ,  $\chi_{yy}$  and  $\chi_{zz}$ . It was assumed that the *z* axis of the quadrupole coupling tensor coincides with the C–Cl bond and that the *y* axis is perpendicular to the molecular plane. The values obtained were:  $\chi_{xx} = 35.3(6)$ ,  $\chi_{yy} = 32.3(8)$  and  $\chi_{zz} = -67.6(6)$  MHz.

The double bond character,  $\delta$ , may be calculated as  $(\chi_{xx} - \chi_{yy})/164.6$ .<sup>9</sup> The resulting value for  $\delta$  was 0.018(6), which can be compared to  $\delta = 0.04(1)$  found for *cis*-1-chloro-1,3-butadiene,<sup>1</sup> and  $\delta = 0.05(1)$  obtained for *cis*-1-chlorobuten-3-yne.<sup>10</sup> It is not surprising that the double bond character in the carbon-chlorine bond is somewhat smaller in 2-chloro-1,3-butadiene, because for this molecule there exists only one possible contributing resonance form having a C=Cl bond, while for the other two molecules there are two such forms.

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