Acta Chemica Scandinavica A 34 (1980) 541–545

The Complete Substitution Structure of *trans*-1-Chloro-1,3-butadiene Determined with Microwave Spectroscopy

PER CEDERBALK and FRED KARLSSON

Department of Physical Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden

Microwave transitions of the two natural isotopic species of *trans*-1-chloro-1,3-butadiene, $CH^{35}ClCHCHCH_2$ and $CH^{37}ClCHCHCH_2$, together with all monosubstituted species with deuterium or ^{13}C isotopes have been measured and assigned in the spectral region 18 000 – 26 500 MHz. The complete substitution structure has been determined. Two of the structural parameters obtained were: $r(C=C)_{chlorovinyl} = 1.313(10)$ Å and $r(C=C)_{vinyl} = 1.340(7)$ Å. Evidence was found for a weak non-bonded interaction between the chlorine atom and the hydrogen atom three bonds away. The nuclear quadrupole coupling constants χ_{xx} and χ_{yy} for the parent molecule were found to have the same values as those previously obtained for *cis*-1-chloro-1,3-butadiene. Force field calculations were used to predict the values of the centrifugal distortion constants Δ_J and Δ_{JK} for all isotopic species.

The complete substitution structure of *cis*-1-chloro-1,3-butadiene has recently been obtained.[1] A significant difference between the two carbon-carbon double bond distances was found. Support of the hypothesis of a weak non-bonded interaction between the chlorine atom and the hydrogen atom four bonds away[2] was also obtained. Such finer structural details are only available from a microwave spectroscopical determination of structures. To learn if some of the structural features of *cis*-1-chloro-1,3-butadiene were the same in the *trans*-molecule, we undertook a microwave spectroscopical investigation of all the isotopic species of *trans*-1-chloro-1,3-butadiene.

EXPERIMENTAL

The synthesis and separation of the isotopic species of *trans*-1-chloro-1,3-butadiene will be described elsewhere.[1] The microwave spectra were recorded on a Hewlett-Packard 8460A microwave spectrometer with Stark modulation at 33.33 kHz. The spectra were recorded in the K-band region (18 000 – 26 500 MHz). A few of the lines from the parent molecule were measured between 28 000 and 32 000 MHz. The microwave cell was cooled down to about −20 °C. The transitions were recorded at pressures ranging from 20 to 40 mTorr. A sweep rate of 0.05 MHz/s was used. The uncertainty in the measured frequencies was estimated to be 0.05 MHz.

MICROWAVE SPECTRA

trans-1-Chloro-1,3-butadiene was expected to be an almost symmetric prolate rotor molecule ($\kappa = -0.995$). It was expected and confirmed from spectra that only μ_a-transitions would be observable, partly because of the much smaller magnitude of the μ_b dipole moment component.

The measurement and assignment of the transitions from the isotopically monosubstituted species were complicated by the frequently occurring overlap from other isotopic species or vibrational states. This difficulty was partly overcome by close comparisons between spectra from samples with and without substituted species, recorded at the same pressure and temperature. The measured frequencies were used to determine the rotational constants A, B and C and the centrifugal distortion constants Δ_J and Δ_{JK} by the least-squares method: see Table 1. It was not possible to determine accurately the centrifugal distortion constants Δ_K, δ_J and δ_K, due to the fact that only a-type R-branch transitions were found. This had the further consequence that the rotational constant A could not be well-determined. To get the best fit of the molecular constants

0302-4377/80/070541-05$02.50
© 1980 Acta Chemica Scandinavica

Table 1. Rotational constants and centrifugal distortion constants of *trans*-1-chloro-1,3-butadiene in the ground state.

Species	n[a]	*A*/MHz	*B*/MHz	*C*/MHz	Δ_J/kHz			Δ_{JK}/kHz		
					Fitted	Calc.[b]	Calc.[c]	Fitted	Calc.[b]	Calc.[c]
$CH^{35}ClCHCHCH_2$	20	30388(38)	1453.572(1)	1387.426(1)	0.081(6)		0.1005	−6.15(24)		−5.577
$CH^{37}ClCHCHCH_2$	12	30503(37)	1419.811(2)	1356.494(2)	0.065(11)	0.077	0.0965	−7.26(27)	−6.08	−5.512
$^{13}CH^{35}ClCHCHCH_2$	5	29884(84)	1452.702(4)	1385.528(7)		0.081	0.0999		−6.08	−5.516
$CH^{35}Cl^{13}CHCHCH_2$	7	30718(74)	1451.967(3)	1385.780(4)	0.085(20)	0.081	0.1003	−6.86(36)	−6.08	−5.516
$CH^{35}ClCH^{13}CHCH_2$	7	29964(102)	1437.775(7)	1372.491(10)	0.158(60)	0.079	0.0977	−4.76(69)	−5.905	−5.337
$CH^{35}ClCHCH^{13}CH_2$	12	30296(142)	1414.931(8)	1351.777(7)	0.093(44)	0.0765	0.0956	−5.93(109)	−6.16	−5.588
$CD^{35}ClCHCHCH_2$	13	26379(35)	1452.469(3)	1376.631(3)	0.084(20)	0.079	0.0983	−5.01(52)	−4.965	−4.397
$CH^{35}ClCDCHCH_2$	14	27687(51)	1452.681(4)	1380.290(4)	0.101(24)	0.081	0.1000	−4.75(61)	−4.93	−4.365
$CH^{35}ClCHCDCH_2$	10	27053(22)	1436.597(2)	1364.102(2)	0.063(11)	0.077	0.0960	−5.20(29)	−4.585	−4.017
$CH^{35}ClCHCHCDH$[d]	13	30447(105)	1387.901(5)	1327.439(5)	0.089(31)	0.0695	0.0886	−5.87(73)	−5.73	−5.160
$CH^{35}ClCHCHCHD$[e]	13	27339(70)	1415.706(5)	1345.752(6)	0.088(31)	0.080	0.0995	−6.89(82)	−5.45	−4.884

[a] Number of transitions in final fit. [b] Obtained from the corresponding parent value together with a force field calculation (see text). [c] Obtained from a force field calculation. [d] Deuterium in position H(8) in Fig. 1. [e] Deuterium in position H(9) in Fig. 1.

for the isotope-substituted species we found that it was of great help to compare the fitted values of Δ_J and Δ_{JK} with the expected calculated values, obtained with a method to be described in the next section. In fact, it turned out to be necessary to use these calculated values for $^{13}CH^{35}ClCHCHCH_2$ as constants in the fit for this species.

We used the calculated Δ_J- and Δ_{JK}-values as fixed parameters also in the fits for the other isotopic species, to see if the values of the rotational constants were significantly changed due to the dependence on Δ_J and Δ_{JK}. The result was that at least *B* and *C* were changed very little; in most cases the values fell within the error limits of the originally obtained values. Therefore the values of *B* and *C* were deemed to be quite reliable. It was essential to have at least two rotational constants accurately determined for each isotopic species in order to be able to calculate the structure of the molecule.

FORCE FIELD CALCULATIONS

Force field calculations for each of the isotopic species were carried out in order to get predicted values for Δ_J and Δ_{JK}. This special method has been described earlier.[1] It consists in using the differences in the values of centrifugal distortion constants (and inertial defects), due to isotopic substitution, together with the best determined corresponding constants which are obtained from the spectrum of the parent molecule. It is assumed that these differences obtained from the force field calculations are more reliable than the absolute values. This is confirmed by a comparison of the values of Δ_{JK} in the last three columns of Table 1. For the Δ_J-values, however, the absolute values serve quite as well for predictive purposes.

The force constants were taken from a normal coordinate analysis of the vibrational spectrum of the molecule.[3]

The measured value of the inertial defect of the normal-isotopic species, $CH^{35}ClCHCHCH_2$, was $-0.055(21)$ uÅ^2, whereas the value obtained from the force field calculation (assuming a planar structure) was -0.021 uÅ^2. Therefore it is concluded that the molecular structure should be planar.

STRUCTURE

The cartesian coordinates of the atoms were calculated in the principal axis system of the

normal-isotopic molecule from the change in the principal moments of inertia I_b and I_c upon isotopic substitution.[4,5] The result is shown in Table 2, column I. The *b*-coordinates of the carbon atoms C(3) and C(4) (0.3828 and −0.3395 Å, respectively) are close to the critical distance 0.3 Å. For the atoms C(2), H(8) and Cl the *b*-coordinates (−0.2208, 0.1008 and −0.1427 Å, respectively) are well below this critical distance, so for these atoms the uncertainty in the *b*-coordinates should be

Table 2. Nuclear coordinates (Å) for *trans*-1-chloro-1,3-butadiene.

Atom[a]	I[b]		II[c]	
	a	*b*	*a*	*b*
C(1)	−0.4579	0.5416	−0.4618	0.5387
C(2)	0.6224	−0.2208	0.6367	−0.1803
C(3)	1.9619	0.3828	1.9638	0.3755
C(4)	3.0932	−0.3395	3.0941	−0.3440
H(5)	−0.5131	1.6148	−0.5164	1.6160
H(6)	0.4618	−1.2960	0.4686	−1.2964
H(7)	2.0255	1.4688	2.0279	1.4684
H(8)	4.0663	0.1008	4.0669	0.1236
H(9)	3.0481	−1.4306	3.0499	−1.4299
Cl	−2.0575	−0.1427	−2.0579	−0.1477

[a] The atoms are numbered as in Fig. 1. [b] Coordinates calculated with Kraitchman's equations. [c] Coordinates calculated with a least-squares method.

Table 3. The molecular structure of *trans*-1-chloro-1,3-butadiene compared with the structures of *cis*-1-chloro-1,3-butadiene, 1,3-butadiene and vinyl chloride.

Method:	*trans*-1-Chloro-1,3-butadiene MW[a]	*cis*-1-Chloro-1,3-butadiene MW	1,3-Butadiene[c] ED[b]	Vinyl chloride[c] MW
Bond distances (Å)				
C(1)=C(2)	1.313(10)	1.327(6)	1.345(2)	1.332(5)
C(2)−C(3)	1.439(6)	1.449(13)	1.465(3)	
C(3)=C(4)	1.340(7)	1.343(2)	1.345(2)	
C(1)−H(5)	1.079(8)	1.100(11)		1.079(10)
C(2)−H(6)	1.129(10)	1.099(11)		1.090(10)[e]
				1.078(10)[f]
C(3)−H(7)	1.095(7)	1.132(16)		
C(4)−H(8)	1.079(9)	1.087(13)		
C(4)−H(9)	1.087(5)	1.071(13)	1.108(4)[d]	
C(1)−Cl	1.737(4)	1.731(8)		1.726(5)
Bond angles (deg)				
C(1)=C(2)−C(3)	124.1(11)	126.5(3)	123.3(3)	
C(2)−C(3)=C(4)	124.8(10)	123.0(7)	123.3(3)	
C(2)=C(1)−H(5)	126.1(4)	125.5(4)		123.8(10)
C(1)=C(2)−H(6)	114.6(5)	117.9(4)		121.0(10)[e]
				119.5(10)[f]
C(4)=C(3)−H(7)	119.1(6)	122.3(5)	123.0(32)	
C(3)=C(4)−H(8)	121.8(5)	121.0(5)	122.4(22)	
C(3)=C(4)−H(9)	120.1(6)	121.7(5)	120.0(24)	
C(2)=C(1)−Cl	123.5(7)	123.7(3)		122.3(5)

[a] Microwave spectroscopy. [b] Electron diffraction. [c] Ref. 7 and references therein. [d] Weighted mean value of all C−H distances. [e] H in *cis*-position to Cl. [f] H in *trans*-position to Cl.

especially large.

Therefore it was an advantage to calculate the structure with a least-squares method according to Nösberger *et al.*,[6] where the absolute values of the rotational constants for the parent species could be used together with the differences due to substitution. With this method a better performance for small values of nuclear coordinates has been experienced. The method was found to work well in the case of *cis*-1-chloro-1,3-butadiene. For *trans*-1-chloro-1,3-butadiene it was not possible to use the rotational constants A due to their low accuracy, so the constants B and C were used together with the assumption of planarity with all $\Delta = 0$, which is reasonable for an almost symmetric prolate rotor (Δ is the inertial defect defined as $I_c - I_a - I_b$).

Unfortunately this iterative structure-determining method gives a result that to some extent is dependent on the initial structure model. Nösberger *et al.* recommend that r_s-values should be employed whenever possible. But some structural parameters obtained from the solution of Kraitchman's equations were uncertain, and the results were not altogether satisfactory when these values were used in the initial structure. However, when the reliable coordinates calculated with the Kraitchman method were used together with assumed values of the uncertain parameters as starting values, a good fit and an acceptable structure were obtained. The results are shown in column II of Table 2 and in Table 3 as well as in Fig. 1.

The error limits for the structural parameters given by the least-squares computer program are too small, since they do not include the effect of vibration. To obtain the listed error limits for *trans*-1-chloro-1,3-butadiene in Table 3 the effect of small coordinate values on the accuracy of the structure was taken into account.

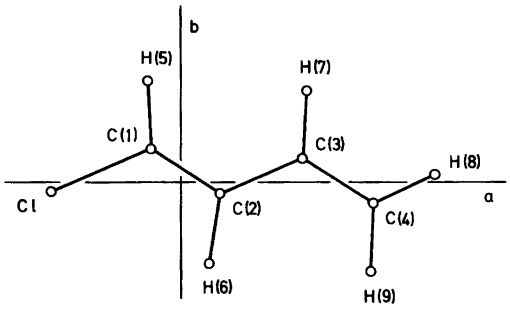

Fig. 1. Molecular structure of *trans*-1-chloro-1,3-butadiene with principal axes of inertia. Obtained values of the structural parameters are given in Table 3.

A significant difference between the two carbon-carbon double bond lengths is evident, and this was also found for *cis*-1-chloro-1,3-butadiene: see Table 3. The C(2)–H(6) distance is unusually long, and the angle C(1)=C(2)–H(6) is smaller than usual. These two results support the hypothesis of a weak non-bonded interaction between the chlorine atom and the hydrogen atom three bonds away. This result is very similar to what was found for the *cis*-molecule. For that molecule a non-bonded interaction between the chlorine atom and the hydrogen atom four bonds away seemed probable. That assumption was also supported by an NMR-investigation of some halogenated 1,3-butadienes.[8] A downfield shift of 0.49 ppm for the hydrogen atom close to chlorine four bonds away in chloroprene was observed. For the hydrogen atom close to the chlorine atom three bonds away, a downfield shift of 0.13 ppm was obtained in chloroprene. Although smaller, this downfield shift nevertheless supports the non-bonded interaction concluded to be present in *trans*-1-chloro-1,3-butadiene. It is not surprising that one finds such an interaction in both isomers, because the chlorine-hydrogen distance is about the same in the two molecules.

Apart from the interaction described above, one cannot rule out the possibility of a corresponding interaction between the chlorine atom and the hydrogen atom two bonds away. In both *cis*- and *trans*-1-chloro-1,3-butadiene the angle H(5)–C(1)=C(2) is found to be unusually large. The bond distance C(1)–H(5) is, however, not significantly lengthened.

In 1-chloroethene (vinyl chloride) only a suggestion of this kind of interaction can be observed. The reason why no larger effects are observed is not quite clear, but it is apparent that C(2) and also the chlorine atom and one of the hydrogens have small b-coordinates: about 0.3, 0.1 and 0.1 Å, respectively.[9]

In *cis*-1-chloro-1,3-butadiene steric repulsion by the chlorine atom caused a difference in the two carbon-chain angles of 3.5 degrees. In the *trans*-molecule no such effect should be present, so it is not surprising that the angles C(1)=C(2)–C(3) and C(2)–C(3)=C(4) are found to be of the same size.

QUADRUPOLE COUPLING

The interaction between the quadrupole moment of the chlorine nucleus and the rotation of the

molecule produces a splitting of the rotational transitions. Theoretically there should appear four lines for each transition, but in practice no transition was observed as a quartet. Instead, some transitions appeared as doublets and the rest as unresolved lines. Totally only 8 splitting parameters were observed for the parent species. This was insufficient for a good determination of the quadrupole coupling constants. Instead another approach was chosen.

The quadrupole coupling constants χ_{xx} and χ_{yy} for the ^{35}Cl nucleus in *cis*-1-chloro-1,3-butadiene (parent species) had been rather accurately determined by Karlsson *et al.*[1] This was possible because of the different character of the spectrum, where some of the *b*-type transitions were observed as quartets. The values obtained for χ_{xx} and χ_{yy} by the least-squares method were 37.6(8) and 30.5(8) MHz, respectively.

Those values were assumed to be relevant also for the *trans*-1-chloro-1,3-butadiene molecule. The quadrupole coupling constants χ_{aa} and χ_{bb} for this molecule were obtained by a transformation from the principal axis system of the quadrupole coupling tensor. The assumption was made that the tensor axis *z* coincides with the C–Cl bond, and that the *y* axis is perpendicular to the molecular plane. The angle between the C–Cl bond and the *a* axis, necessary in this transformation, was calculated from the obtained coordinates of the Cl and C(1) atoms (coordinates of column II, Table 2, were used). The following values for the quadrupole coupling constants were obtained: $\chi_{aa} = -51.603$ and $\chi_{bb} = 21.103$ MHz. With these values the quadrupole splittings of the transitions were computed. The calculated doublet splittings were compared with the experimentally found values: see Table 4. The agreement is quite satisfactory, and therefore the values of the constants χ_{xx} and χ_{yy}, reported for *cis*-1-chloro-1,3-butadiene, should also be valid for the parent species of *trans*-1-chloro-1,3-butadiene.

Table 4. Observed and calculated[a] quadrupole splittings (MHz) for some of the transitions of the normal species of *trans*-1-chloro-1,3-butadiene.

Transition	Obs.[b]	Calc.
$7_{07} \leftarrow 6_{06}$	0.45	0.421
$7_{26} \leftarrow 6_{25}$	0.88	0.923
$7_{25} \leftarrow 6_{24}$	0.93	0.914
$8_{08} \leftarrow 7_{07}$	0.30	0.317
$8_{27} \leftarrow 7_{26}$	0.62	0.616
$8_{26} \leftarrow 7_{25}$	0.56	0.605
$9_{28} \leftarrow 8_{27}$	0.33	0.432
$9_{27} \leftarrow 8_{26}$	0.38	0.420

[a] See text. [b] The uncertainty was estimated to be 0.07 MHz.

Acknowledgement. We are very grateful to Dr. Stig Ljunggren at the Royal Institute of Technology, Stockholm, for pleasant cooperation.

REFERENCES

1. Karlsson, F. and Smith, Z. *J. Mol. Spectrosc. 81* (1980) 327.
2. Viehe, H. G. *Chem. Ber. 97* (1964) 598.
3. Borg, A., Smith, Z., Gundersen, G. and Klæboe, P. *Spectrochim. Acta Part A 36* (1980) 119.
4. Kraitchman, J. *Am. J. Phys. 21* (1953) 17.
5. Costain, C. C. *J. Chem. Phys. 29* (1958) 864.
6. Nösberger, P., Bauder, A. and Günthard, H. H. *Chem. Phys. 1* (1973) 418.
7. Hirota, E. and Kuchitsu, K. In Hellwege, K.-H. and Hellwege, A. M., Eds., *Structure Data of Free Polyatomic Molecules*, Springer, Berlin, Heidelberg, New York 1976: Landolt-Börnstein. New Series, Group II, Vol. 7.
8. Bothner-By, A. A. and Harris, R. K. *J. Am. Chem. Soc. 87* (1965) 3445.
9. Kivelson, D., Wilson, E. B., Jr. and Lide, D. R., Jr. *J. Chem. Phys. 32* (1960) 205.

Received March 21, 1980.