Microwave Spectrum, Structural Parameters and Quadrupole Coupling of *trans*-1-Chlorobuten-3-yne

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The microwave spectra of three isotopic species of *trans*-1-chloro-buten-3-yne: $CH^{35}ClCHCCH$, $CH^{37}ClCHCCH$, and $CH^{35}ClCHCCD$, have been measured in the region 26 500 — 40 000 MHz.

The rotational constants A, B, and C for the ground state as well as the centrifugal distortion constants, D_J and D_{JK}, were determined. From the hyperfine splittings of the rotational lines, the nuclear quadrupole coupling constants χ_{aa} were calculated for the $CH^{35}ClCHCCH$ and $CH^{37}ClCHCCH$ species, in the principal-axis systems of the molecules. The distance between the chlorine atom and the ethynyl hydrogen atom was determined by isotopic substitution. The molecule length was found to be 6.236 Å.

In order to supply complementary data for electron diffraction measurements the inertial moments corresponding to the average structure were calculated from an estimated force field.

The structure of butenyne has been determined by electron diffraction [1] and microwave spectroscopy [2] in combination. In order to confirm these results on parent molecules we have started to investigate *trans*-1-chloro-buten-3-yne and *cis*-1-chlorobuten-3-yne with microwave spectroscopy. These substances were discovered by Vestin *et al.*[3] They are unstable at room temperature but can be handled at − 70C°.

The original identification of these substances was based on mass spectro-scopical analysis, IR spectroscopy, and their relative retention in gas-liquid chromatography. Microwave spectroscopical analysis confirms the *trans* conformation of *trans*-1-chlorobuten-3-yne.

The *cis*-conformation has a very complicated and yet unassigned spectrum, which was expected from the assumed structure and calculated dipole moment components.

EXPERIMENTAL

Incomplete dehydrochlorination of 1,4-dichloro-2-butyne by alkali yields small amounts of *cis*- and *trans*-1-chlorobuten-3-yne. These substances can be isolated from the reaction mixture and purified with gas-liquid chromatography. The monodeuteriated

sample of *trans*-1-chlorobuten-3-yne was prepared by reacting the normal species with deuterium oxide D_2O and monodeuteriated ethanol C_2H_5OD.

The microwave spectra were recorded on a Hewlett-Packard model 8460 A R-band microwave spectrometer with a phase stabilized source oscillator. The recordings were made at room temperature and a pressure ranging from 10 to 50 mTorr. The frequency region was 26 500 − 40 000 MHz. The precision of the measured transitions was estimated to be 0.05 MHz.

MICROWAVE SPECTRUM

Most of the lines in the spectrum are grouped in bands at intervals of approximately 2 970 MHz. Each band begins abruptly on the low frequency side and continues for 200 − 300 MHz with decreasing intensity. The very characteristic appearance of a bandhead is shown in Fig. 1.
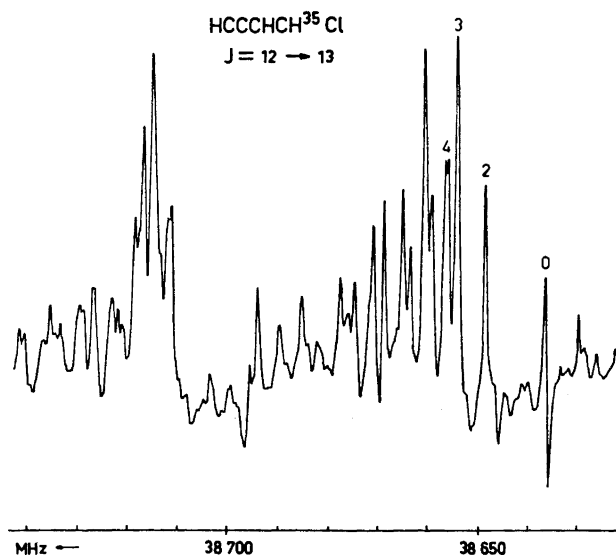

HCCCHCH^{35}Cl

J = 12 → 13

MHz ←   38 700   38 650

Fig. 1. Band of the $J = 12 \to 13$ transitions of normal *trans*-1-chlorobuten-3-yne near 38 700 MHz. Sweep rate 0.5 MHz/sec.

trans-1-Chlorobuten-3-yne is expected to be an almost prolate symmetric rotor; see Fig. 2. Consequently the regions of dense absorption are logically assigned to $\Delta J = +1$, $\Delta K_{-1} = 0$ transitions which are active through the μ_a dipole moment. CNDO calculation gives the theoretical dipole moment $\mu_a = -1.82$, $\mu_b = -0.64$, and $\mu_c = 0$ debye.

The line abundance of the bands and the repeated structure within the bands indicates the existence of low lying excited vibrational modes, presumably states in which the skeletal bending mode is excited.

The lines from the ground state are easily assigned in high resolution spectra. Outside each group, lines were found which could be identified as $K_{-1} = 0$ and $K_{-1} = 1$ transitions on the basis of their characteristic second-

Table 1. Observed rotational transitions and nuclear quadrupole hyperfine splitting in MHz for three isotopic species of *trans*-1-chlorobuten-3-yne.

		Transition				$CH^{35}ClCHCCH$		$CH^{37}ClCHCCH$		$CH^{35}ClCHCCD$	
J	K_{-1}	K_{+1}	$\leftarrow J$	K_{-1}	K_{+1}	ν_{obs}	$\Delta\nu Q_{obs}$	ν_{obs}	$\Delta\nu Q_{obs}$	ν_{obs}	$\Delta\nu Q_{obs}$
9	0	9	8	0	8	26753.22					
9	1	8	8	1	7	26964.30					
10	1	10	9	1	9	29498.47		28837.00		28047.45	
10	0	10	9	0	9	29724.68		29053.30		28255.42	
10	2	9	9	2	8	29730.68		29058.84			
10	3	8	9	3	7	29733.93	0.86	29061.19	0.61		
10	1	9	9	1	8	29960.01		29277.89		28471.31	
11	1	11	10	1	10	32447.90		31720.30		30851.77	
11	0	11	10	0	10	32695.75		31957.29		31079.70	
11	2	10	10	2	9	32703.44		31964.46		31086.62	
11	3	9	10	3	8	32707.40	0.66	31968.13	0.51		
11	4	8	10	4	7	32709.45	1.19	31970.13	0.93		
11	2	9	10	2	8	32710.92					
11	5	7	10	5	6	32712.43	1.85	31973.07	1.45		
11	6	6	10	6	5	32716.30	2.63				
11	7	5	10	7	4	32720.92	3.70				
11	8	4	10	8	3	32726.28	4.78				
11	1	10	10	1	9	32955.53		32205.32		31318.10	
12	1	12	11	1	11	35397.19		34603.50		33656.09	
12	0	12	11	0	11	35666.40		34860.95		33903.70	
12	2	11	11	2	10	35676.08		34869.90		33912.40	
12	3	10	11	3	9	35680.88	0.51	34874.38	0.36	33916.85	
12	4	9	11	4	8	35683.00	0.87	34876.48	0.71	33919.17	0.92
12	2	10	11	2	9	35685.80		34878.94		33920.70	
12	5	8	11	5	7	35686.28	1.33			33922.67	1.28
12	6	7	11	6	6	35690.41	1.94				
12	7	6	11	7	5	35695.45	2.72				
12	1	11	11	1	10	35951.00		35132.57		34164.75	
13	1	13	12	1	12	38346.37		37486.59		36460.28	
13	0	13	12	0	12	38636.59		37764.21		36727.34	
13	2	12	12	2	11	38648.67		37775.33		36738.00	
13	3	11	12	3	10	38654.37	0.35	37780.60		36743.32	
13	4	10	12	4	9	38656.55	0.69	37782.84	0.55	36745.76	0.72
13	5	9	12	5	8	38660.06	1.11	37786.22	0.84		
13	2	11	12	2	10	38661.00		37786.64			
13	6	8	12	6	7	38664.50	1.52	37790.60	1.21		
13	7	7	12	7	6	38669.93	2.09	37795.86	1.70		
13	8	6	12	8	5	38676.22	2.84	37802.01	1.90		
13	9	5	12	9	4	38683.55	3.48				
13	10	4	12	10	3	38691.67	4.26				
13	1	12	12	1	11	38946.31		38059.72		37011.37	
14	1	14	13	1	13					39264.32	
14	0	14	13	0	13					39550.58	
14	2	13	13	2	12					39563.57	
14	3	12	13	3	11					39569.82	
14	4	11	13	4	10					39572.38	0.58
14	5	10	13	5	9					39576.38	0.89
14	2	12	13	2	11					39576.82	
14	6	9	13	6	8					39581.46	1.24
14	7	8	13	7	7					39587.55	1.68
14	1	13	13	1	12					39857.73	

order (but unresolved) Stark effects. Within the band the transitions $K_{-1} \geq 2$ were detected by their relative intensities and quadrupole hyperfine splittings which increase with K_{-1}; see Table 1.

The rotational constants were fitted to the observed spectrum by the least squares method. It was necessary to include centrifugal distortion terms D_J and D_{JK}. The D_{JK} term makes an important contribution and reverses the normal ordering of the K_{-1} values; see Table 2. The vibrational bands

Table 2. Observed rotational constants in MHz for the three isotopic species or *trans*-1-chlorobuten-3-yne.

	CH^{35}ClCHCCH	CH^{37}ClCHCCH	CH^{35}ClCHCCD
A	48604 $\pm$ 41	48500 $\pm$ 62	47730 $\pm$ 49
B	1509.612 $\pm$ 0.002	1474.986 $\pm$ 0.002	1434.222 $\pm$ 0.002
C	1463.459 $\pm$ 0.002	1430.895 $\pm$ 0.002	1391.832 $\pm$ 0.002
D_J	0.000110 $\pm$ 0.000003	0.000109 $\pm$ 0.000004	0.000087 $\pm$ 0.000003
D_{JK}	$-$ 0.01619 $\pm$ 0.00002	$-$ 0.01572 $\pm$ 0.00002	$-$ 0.01706 $\pm$ 0.00002

have a very complicated structure in high resolution spectra. All attempts to assign them have been unsuccessful so far.

The CH^{37}ClCHCCH species could be studied at its natural concentration and CH^{35}ClCHCCD was synthesized.

QUADRUPOLE COUPLING

In good agreement with theory[4] the observable nuclear quadrupole splitting is due to transisions with $\Delta F = +1$. The splitting increases with K_{-1}. Thus, for low values of K_{-1}, the four quadrupole components merge into one single peak. As K_{-1} increases the peak splits into two, and finally into four, observable peaks.

The nuclear quadrupole energy of a nearly prolate symmetric rotor having one quadrupole nucleus can be written as,[4]

$$E_Q = \frac{\chi_{aa}}{J(J+1)} Y(J,I,F)[3K_{-1}^2 - J(J+1) - 3b_p^2(C_2 + 2C_3b_p)$$
$$+ \eta(C_1 + 2C_2b_p + 3C_3b_p^2 + 4C_4b_p^3)]$$

where $Y(J,I,F)$ is Casimir's function: b_p is Wang's asymmetry parameter. If χ_{gg} is the component of the quadrupole coupling tensor along the g-principal inertial axis, η is defined by η $\chi_{aa} = \chi_{bb} - \chi_{cc}$. The constants C_1, C_2, C_3, and C_4 could be found in tables.[5]

For *trans*-1-chlorobuten-3-yne the asymmetry parameter b_p is very small: $b_p = -0.0005$. Further, the nuclear quadrupole splitting is only observable for rotational transitions with $K_{-1} \geq 2$ where $C_1 = 0$. Thus the energy expres-

sion above reduces to that of a symmetric rotor, and since only the splitting into doublets is completly resolved, the measurable nuclear hyperfine splitting for $\Delta F = +1$ transitions can be calculated from the formula

$$\Delta \nu_Q = -3K_{-1}{}^2 \chi_{aa}/2J(J+1)(J+2)$$

Consequently the quadrupole effect is mainly determined by only one quadrupole coupling constant, χ_{aa} in this case. For ^{35}Cl in $CH^{35}ClCHCCH$ this value was determined to be $\chi_{aa} = -63.6 \pm 0.4$ MHz and for ^{35}Cl in $CH^{37}ClCHCCH$ $\chi_{aa} = -51.0 \pm 0.4$ MHz.

MOLECULAR STRUCTURE

The position of the ethynyl hydrogen atom and the chlorine atom in the main axes system of $CH^{35}ClCHCCH$ was calculated by the method of Costain [6] from the differences in the moments of inertia caused by isotopic substitution of these atoms with deuterium and 37-chlorine. The uncertainty in the b-coordinates is expected to be rather great since the atoms concerned are lying very near to the a-axis; see Fig. 2. Another ambiguity is introduced by
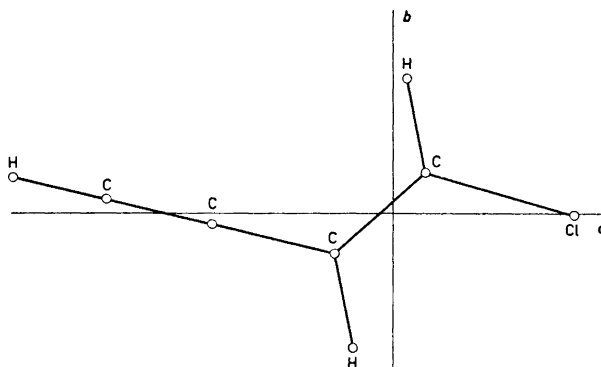

Fig. 2. Assumed structure of normal *trans*-1-chlorobuten-3-yne with principal axes of inertia.

the uncertainty in the I_a-inertial moment emanating from the fact that we are only observing a-type transitions which have a weak dependence on the A-rotational constant. The b-coordinates however have only a minor effect on the distance between the ethynyl hydrogen atom and the chlorine atom. This length is therefore expected to be accurate and the value is 6.236 Å.

Evidently these substitutions are not sufficient to give the complete r_s-structure. The main purpose of this work was therefore to give complementary data for an electron diffraction investigation (in progress) of the molecular structure. The inertial moments however are related to the r_0-structure. This is a different vibrational average structure than that observed in electron diffraction.[6] However both of these methods are comparable in the r_z-structure

which can be calculated if the harmonic part of the fundamental vibrations are known. In order to see if the r_z-structural parameters differ significantly from the corresponding r_0-parameters we have calculated the corrections due to harmonic vibrations from a normal coordinate analysis of the molecular vibrations; see Table 3. The force field necessary for this analysis was estimated. The theory for these calculations is given by Herschbach and Laurie [8] and Oka.[9] The computational method used was mainly taken from Oka and Morino.[10]

Actually the moments of inertia also have to be corrected for the centrifugal distortion. Since the molecule is a planar rotor it would seem reasonable to get the centrifugal distortion correction out of a 7 parameter fitting of rotational constants A, B, C, τ_{aaaa}, τ_{bbbb}, τ_{abab}, and τ_{aabb} to the observed spectra. This was not possible, however, mainly because the near degeneracy to a symmetric rotor spectrum.[11] So we have calculated these centrifugal distortion corrections from the estimated force field.[4] They are actually too small to be significant; see Table 3. The main uncertainty in cal-

Table 3. Vibration-rotation correction for the moments of inertia in the ground vibrational state (in amu Å²). Conversion factor 505 376 amu Å² MHz.

| | CH³⁵ClCHCCH | | CH³⁷ClCHCCH | | CH³⁵ClCHCCD | |
	I_b	I_c	I_b	I_c	I_b	I_c
r_0-Parameters	334.771	345.328	342.630	353.187	352.368	363.100
Vibration correction	0.104	0.003	0.106	0.004	0.098	− 0.005
Centrifugal distortion correction	0.00049	− 0.00079	0.00050	− 0.00079	0.00051	− 0.00081
r_z-Parameters	334.875	345.330	342.736	353.191	352.467	353.094

culations of the kind mentioned above is the lack of information about the interatomic force field of the molecule. Therefore the calculated r_z-parameters must be treated carefully. The r_z-length of the molecule derived from these is 6.238 Å. The difference from the r_s-length is not significant but for comparison with electron diffraction data we need the absolute values of the inertial moments rather than the differences caused by substitution. For I_b the change from r_0 to r_z structure affects the first decimal place; see Table 3. Consequently it cannot be neglected. For I_c on the other hand, the change is minor and presumedly I_c can be used without correction.

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