Microwave Spectrum and Dipole Moment of
cis-1-Fluoro-1,3-butadiene

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Microwave transitions of cis-1-fluoro-1,3-buta-diene have been identified and measured in the region 18.0−26.5 GHz. The rotational constants $A=17477.996(3)$, $B=2761.3884(6)$ and $C=2384.3652(6)$ MHz were obtained for the ground vibrational state. An assumed structure of the molecule, based on the structure of previously examined chlorobutadienes, reproduced reasonably well these values of the rotational constants. The dipole moment was found to have the value 1.346(1) D from a study of the Stark effect.

The present investigation completes a series of microwave spectroscopical investigations of 1,3-butadienes monosubstituted with chlorine or fluorine.

The complete structure of cis-1-chloro-1,3-butadiene was determined from an analysis of the microwave spectra of all the monoisotopic species of that molecule.[1] An analogous investigation was then made for trans-1-chloro-1,3-butadiene.[2] In order to calculate the complete structure of the molecule it was an advantage to use a least-squares method. Evidence of non-bonded interactions between chlorine and hydrogen was found for both isomers. A significant difference between the C=C distances was also established for each isomer.

The 2-chloro-1,3-butadiene molecule has also been investigated by means of microwave spectroscopy at our department.[3,4] The obtained values of the rotational constants of all but one monoisotopic species were used in order to calculate the complete structure of the molecule with the same least-squares method.[4] The two

C=C distances were found to be of about the same size and no marked effect could be observed on the structure due to non-bonded attraction. The double bond character of the C−Cl bond was determined for all three chlorinated 1,3-butadienes.

The first fluorinated 1,3-butadiene to be examined was 2-fluoro-1,3-butadiene.[5] The molecule was shown to have a planar trans structure. The dipole moment was found to have the value 1.417(10) D and to make an angle of 10−15° with the C−F bond.

trans-1-Fluoro-1,3-butadiene has also been studied in the microwave region.[6] The derived values of the rotational constants indicated a planar structure for this molecule. The obtained value of the dipole moment was 1.380(17) D. The cis-1-fluoro-1,3-butadiene molecule has now been investigated with microwave spectroscopy in order to determine the value of its dipole moment and to obtain some information on its molecular structure.

EXPERIMENTAL

cis-1-Fluoro-1,3-butadiene was obtained together with the trans-isomer and was separated from it by gas-liquid chromatography.[6]

The spectra were recorded at the Royal Institute of Technology, Stockholm, with a Hewlett Packard 8460A microwave spectrometer equipped with Stark effect modulation at 33.33 kHz. The spectral region investigated was 18.0−26.5 GHz. During the recordings the microwave absorption cell was cooled down to about −10 °C and the total pressure therein was normally kept in the region 2.5 to 5 Pa.

MICROWAVE SPECTRUM

cis-1-Fluoro-1,3-butadiene was assumed to have the structure depicted in Fig. 1 with values of the structural parameters given in Table 1. With a few exceptions these values were taken from the structure of *cis*-1-chloro-1,3-butadiene.[1] This assumed fluorobutadiene structure was then used in order to calculate provisional values for the three rotational constants, see Table 2, first row. It was then assumed that the dipole moment of the molecule equalled the carbon—fluorine bond moment 1.51 D and that it was oriented along that bond. That resulted in the following provisional values for the components of the molecular dipole moment: $\mu_a=0.6591$, $\mu_b=1.3585$ and $\mu_c=0.0$ D.

The six provisional molecular constants mentioned above were then used in a calculation of the rotational spectrum. The strongest lines in the calculated spectrum corresponded to *Q*-branch *b*-type transitions and they are relatively difficult to identify. Transitions of the *b*-type dominate the spectrum for this molecule, since the dipole moment has its largest component along the *b* principal axis. For the *trans*-1-fluoro-1,3-butadiene molecule, however, the dipole moment has its strongest component along the *a*-axis which caused that spectrum to be strongly dominated by *a*-type *R*-branch transitions, and they were readily identified.[6]

Table 1. Assumed values for the structural parameters of *cis*-1-fluoro-1,3-butadiene.

Bond length (Å)[a]		Bond angle (°)	
C(1)=C(2)	1.33	C(1)=C(2)—C(3)	126
C(2)—C(3)	1.46	C(2)—C(3)=C(4)	122
C(3)=C(4)	1.34	F—C(1)=C(2)	121
C(1)—F	1.35	H(5)—C(1)=C(2)	125
all C—H	1.10	C(1)=C(2)—H(6)	118
		H(7)—C(3)=C(4)	123
		C(3)=C(4)—H(8)	121
		C(3)=C(4)—H(9)	121

[a] 1 Å=100 pm.

By the aid of the calculation mentioned above *Q*-branch *b*-type transitions were identified in a medium resolution spectrum within 100 MHz of the predicted positions. However, since *Q*-branch *b*-type transitions determine only the differences $\alpha=A-C$ and $\beta=B-C$, these differences were fitted to the observed Q_b-transitions with the least-squares method. The result is given in Table 2, second row. The differences α and β were then used to calculate more realistic values of the rotational constants. In order to do this the relation $I_c=I_a+I_b$ for a strictly planar rotor was used. This relation can be written $1/C-1/A-1/B=0$ or $1/C-1/(\alpha+C)-1/(\beta+C)=0$. The last equation was solved with the Newton-Raphson
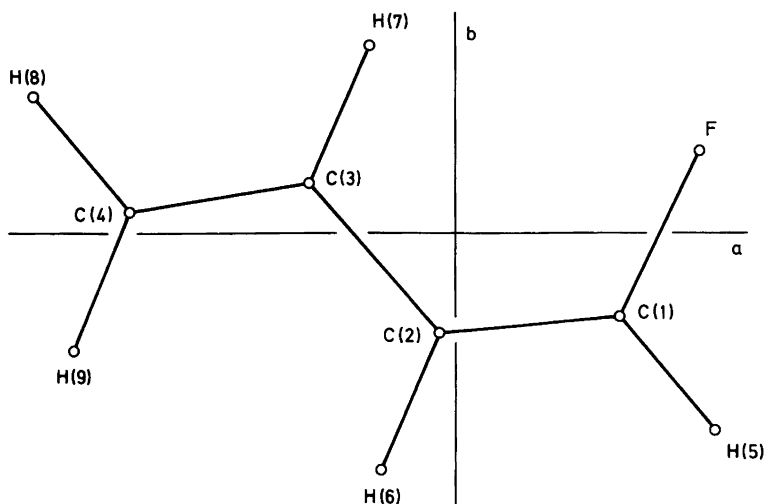

Fig. 1. The assumed structure of *cis*-1-fluoro-1,3-butadiene in the coordinate system of the principal axes of inertia. Values of the structural parameters are given in Table 1. The molecule was assumed to be planar.

iterative method; the result for *A, B* and *C* is given in Table 2, third row.

These values of the rotational constants were assumed to be accurate enough to be employed in a useful calculation of frequencies for other than *Q*-branch transitions; by the aid of this calculation a couple of *R*-branch *b*-type transitions with low *J* values were in fact successfully identified. They were then used in a least-squares fit together with the previously measured *Q*-branch transitions. All the rotational constants were in this way independently determined. With these constants more accurate values of frequencies were calculated and several *P*- and *R*-branch transitions with *J* up to 27 could be assigned. The differences between calculated and observed frequencies increased with *J*, since centrifugal distortion was not yet taken into account. For *J* up to about 10 the differences were only a few MHz but amounted to a maximum of 63.9 MHz for a *J*=27→26 transition. However, with these additional transitions the centrifugal distortion constants could be relatively well fitted. These constants were then included in further calculations of frequencies, with the result that transitions with *J* up to 40 could be assigned.

High resolution recordings (sweep rate 0.05 MHz/s) were then made of the assigned transitions; measured frequencies are given in Table 3. The first 30 lines were used in a least-squares fit that determined accurately the values of the rotational constants as well as the centrifugal distortion constants. These final values of the molecular constants are given in Table 2, fourth row. They were used in a calculation of frequencies which reproduced the observed values very

well, see Table 3. This is strong evidence of the correctness for the proposed assignment. Calculated line strengths were used in order to check the assignment for a few cases.

The inertial defect $I_c-I_a-I_b=0.02394(7)$ uÅ^2 was calculated from the obtained fitted values of the rotational constants (conversion factor 505 377 MHz uÅ^2).* This relatively low value is a strong indication that the molecule has a planar structure. However, a small fraction of the sample could be non-planar. For the *trans*-isomer of the molecule such conformers were sought but were not found. The spectroscopically determined values of the rotational constants are in reasonable agreement with the values obtained from the assumed structure of the molecule, see Table 2. That indicates that this is a rather good approximation to the true structure.

An attempt was then made to assign rotational transitions from vibrationally excited states. However, the spectrum did not have the obvious vibrational satellite structure which was observed for the *trans*-isomer. Several rather strong lines were tentatively assigned to *Q*-branch *b*-type transitions from three excited states. The same method as was used for the ground state was then employed in order to determine the values of the rotational constants. However, in addition to zero other values were also tried for $\Delta=I_c-I_a-I_b$, since Δ tends to deviate from zero for excited states. However, all such attempts to assign additional *P*- or *R*-branch transitions were

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* 1 uÅ^2=1.66043·10^{-47} kg m^2. The error given for a fitted parameter is one standard deviation throughout this article.

Table 2. The values of the rotational constants in the course of this investigation. The final values of the centrifugal distortion constants are also given. The numbers in parentheses refer to errors in the last digits.

Origin	*A*/MHz	*B*/MHz	*C*/MHz	
Assumed structure [a]	17666.85	2743.29	2374.57	
Q-line fit	17469.59(77)	2751.48(3)	2374.57	
Calculation [b]	17480.28	2762.17	2385.26	
Final fit	17477.996(3)	2761.3884(6)	2384.3652(6)	
Δ_J/kHz	Δ_{JK}/kHz	Δ_K/kHz	δ_J/kHz	δ_K/kHz
0.805(6)	−9.9(1)	94.9(4)	0.1688(7)	3.13(4)

[a] Conversion factor 505377 MHz uÅ^2. [b] See text.

Table 3. Observed rotational transition frequencies (MHz) in the microwave spectrum of *cis*-1-fluoro-1,3-butadiene. They all refer to the ground vibrational state. The differences from calculated frequencies are also given.[a]

Transition						Obs.[b]	Obs.−Calc.
J	K_{-1}	K_{+1}	$\leftarrow J$	K_{-1}	K_{+1}		
a-type							
5	1	5	4	1	4	24755.64	0.01
5	0	5	4	0	4	25586.16	0.02
b-type							
1	1	1	0	0	0	19862.28	−0.01
2	1	2	1	0	1	24631.05	−0.01
6	0	6	5	1	5	18348.07	0.00
6	1	5	6	0	6	19249.65	0.00
7	0	7	6	1	6	24286.88	−0.01
7	1	6	7	0	7	20862.01	0.00
8	1	7	8	0	8	22796.05	0.01
8	3	6	9	2	7	26466.19	−0.02
9	1	8	9	0	9	25078.32	0.00
9	3	7	10	2	8	20515.88	0.00
9	3	6	10	2	9	23960.44	0.01
10	3	7	11	2	10	19254.90	0.00
11	1	10	10	2	9	23476.39	−0.01
14	4	11	15	3	12	25064.67	0.02
15	4	12	16	3	13	19222.50	0.01
15	4	11	16	3	14	21443.96	0.00
16	2	14	15	3	13	20190.46	0.01
20	5	16	21	4	17	23534.41	0.02
20	5	15	21	4	18	24404.52	0.05
21	5	16	22	4	19	19040.88	0.04
22	3	19	21	4	18	20524.38	−0.04
25	3	23	24	4	20	19812.23	0.02
26	3	24	25	4	21	23202.56	0.01
26	6	21	27	5	22	21835.10	0.04
26	6	20	27	5	23	22289.80	0.03
27	3	25	26	4	22	26189.56	0.01
28	4	24	27	5	23	20144.08	−0.04
30	4	27	29	5	24	22459.99	−0.02
Not included in fit							
31	7	25	32	6	26	25619.04	0.01
31	7	24	32	6	27	25776.76	0.01
32	7	26	33	6	27	20023.02	0.01
32	7	25	33	6	28	20248.90	0.00
34	5	29	33	6	28	20314.33	−0.07
35	5	31	34	6	28	21689.83	0.03
37	8	30	38	7	31	23752.64	−0.10
37	8	29	38	7	32	23828.66	−0.11
38	8	31	39	7	32	18156.04	−0.13
38	8	30	39	7	33	18264.38	−0.12
40	6	35	39	7	32	19127.76	0.05
40	6	34	39	7	33	21181.12	0.00

[a] The constants of Table 2, fourth row, were used in the calculation. [b] Accuracy 0.05 MHz.

fruitless. The reason for this was probably that the values of the calculated rotational constants were too much dependent on the value of Δ.

DIPOLE MOMENT

From a study of the frequency shifts due to the Stark effect it was possible to obtain the values of the components μ_g ($g=a, b, c$) of the dipole moment vector for the molecule. The theoretical method in terms of which the Stark effect is treated is the perturbation method. *cis*-1-Fluoro-1,3-butadiene is an asymmetric rotor molecule and so most of its rotational transitions exhibit a pure second order Stark effect. From an expression for the second order Stark energy [eqn. (10.69) in Ref. 7] one can write the following formula for the total second order Stark energy for one specific sublevel specified by J_τ and M_J:

$$E^{(2)}_{J_\tau, M_J} = \sum_g (A_g + M_J^2 B_g)\mu_g^2 E^2 \quad (g=a, b, c)$$

This relation formed the basis for the calculations of the dipole moment components μ_g. The coefficients A_g and B_g depend on the rotational state J_τ and on the rotational constants as well as on the centrifugal distortion constants of the molecule.

Since the components μ_g were unknown initially, assumed values, $\mu_{g,a}$, had to be used instead of the real values, $\mu_{g,r}$. The electric field strength, E, was determined from measurements of the two Stark shifts of the $J=1\rightarrow2$ transition in carbonyl sulfide, OCS, using eqn. (10.16) in Ref. 7. The value used for the dipole moment of OCS was 0.71521 D. Values of necessary fundamental constants were the same as were used in all calculations dealing with the Stark effect.[8] However, one could equally well use an assumed value, E_a, for E and subsequently take the real value, E_r, into account as shown below. By doing the substitution $x_g=\mu_{g,r}^2 E_r^2/\mu_{g,a}^2 E_a^2$ the expression for $E^{(2)}_{J_\tau, M_J}$ is:

$$E^{(2)}_{J_\tau, M_J} = \sum_g (A_g + M_J^2 B_g)\mu_{g,a}^2 E_a^2 x_g =$$

$$\sum_g \alpha_{g,a} x_g + M_J^2 \sum_g \beta_{g,a} x_g$$

The substitutions $\alpha_{g,a}=A_g\mu_{g,a}^2 E_a^2$ and $\beta_{g,a}=B_g \mu_{g,a}^2 E_a^2$ have been used above. The components

$\mu_{g,a}$ had the same values as given in the previous section. A Stark effect computer program STARK (written by M. Ribeaud at the Swiss Federal Institute of Technology) was used for the calculations of the coefficients $\alpha_{g,a}$ and $\beta_{g,a}$ for each level J_τ, M_J. The coefficients $\Delta\alpha_{g,a}$ and $\Delta\beta_{g,a}$ were also calculated which was convenient, since the second order Stark shift can be written as:

$$\Delta\nu^{(2)} = \sum_g \Delta\alpha_{g,a} x_g + M_J^2 \sum_g \Delta\beta_{g,a} x_g$$

$$(\Delta M_J=0)$$

if $E^{(2)}_{J_\tau, M_J}$ is given in frequency units (here MHz). Upon insertions of calculated coefficients $\Delta\alpha_{g,a}$ and $\Delta\beta_{g,a}$ and measured values of $\Delta\nu$ into this expression it was possible to calculate the values of the parameters x_g. This was done by application of the least-squares method to the resulting system of equations.

The rotational transitions chosen were $5_{15}\leftarrow4_{14}$, $6_{06}\leftarrow5_{15}$ and $7_{07}\leftarrow6_{16}$, because the STARK-calculations showed that these transitions all exhibited a pure second order Stark effect with no near-degeneracies present at any of the electric field strengths that were going to be used. Compared to a previous investigation[6] this simplified the least-squares fit of the parameters x_g to the observed Stark shifts $\Delta\nu$.

The identification of all the Stark effect shifted lines used in the fit was accomplished by calculations of the approximate $\Delta\nu$-values by putting $x_a=x_b=1$ in the expression for $\Delta\nu^{(2)}$. The separations between consecutive Stark lines were in this way reasonably well reproduced. The $|M_J|$-values were then calculated from measured $\Delta\nu$-values [eqn. (10.78) Ref. 7]. This confirmed the initial assignments; the values differed from integers by less than 0.13.

The Stark shifts used in the determination of the parameters x_g were observed at 3146.1 V/cm, see Table 4, column 1. The least-squares fit converged very quickly and gave the result: $x_a=0.800(6)$ and $x_b=0.7607(7)$. The value of the standard deviation for the fit was 0.056. The parameter x_c was not determined, since all the coefficients $\Delta\alpha_{c,a}=\Delta\beta_{c,a}=0$. The components of the dipole moment vector were then calculated using the expression for x_g. From this relation error limits were also calculated. In order to do that the error in E_r first had to be derived. This

Table 4. Observed and calculated[a] Stark shifts, Δv (MHz), at different electric field strengths, E (V/cm). The uncertainties in Δv_{obs} are 0.07 MHz except where noted (see text).

Transition		$E=3146.1$		$E=2188$		$E=1206$	
		Δv_{obs}	Δv_{calc}	Δv_{obs}	Δv_{calc}	Δv_{obs}	Δv_{calc}
$5_{15} \leftarrow 4_{14}$	$|M_J|=0$	5.56	5.48	2.64[b]	2.65	not	0.80
	1	6.15	6.10	2.89[b]	2.95	re-	0.90
	2	7.98	7.96	3.87[b]	3.85	solv-	1.17
	3	11.12	11.07	5.36	5.35	ed	1.63
$6_{06} \leftarrow 5_{15}$	0	29.24[b]	29.30	14.23[b]	14.17	4.32[b]	4.31
	1	27.47[b]	27.37	13.23	13.24	4.02[b]	4.02
	2	21.52	21.57	10.39	10.43	3.14	3.17
	3	11.89	11.91	5.75	5.76	1.74	1.75
	4	−1.68	−1.62	−0.85[b]	−0.78		−0.24
$7_{07} \leftarrow 6_{16}$	0	23.00	23.04	11.09[b]	11.15	3.36[b]	3.39
	1	21.82	21.77	10.59[b]	10.53	3.24[b]	3.20
	2	17.90	17.95	8.75	8.68	2.65	2.64
	3	11.57	11.59	5.60	5.61	1.71	1.70
	4	2.68	2.68	1.29	1.30	0.42[b]	0.39
	5	−8.77	−8.78	−4.26	−4.25	−1.28	−1.29

[a] In order to calculate the shifts the obtained absolute values of the components of $\bar\mu$ were used. [b] Uncertainty 0.11 MHz.

was done using the formula relating Δv to E for the OCS molecule using estimates of the errors in the observed frequencies. The result for the errors in E_r was: 0.5, 3 and 1 V/cm relating to the values 3146.1, 2188 and 1206 V/cm, respectively. The result of all the calculations for the μ_g-components was: $|\mu_a|=0.600(2)$ D and $|\mu_b|=1.2052(6)$ D which resulted in the value 1.346(1) D for the dipole moment of *cis*-1-fluoro-1,3-butadiene.

The resulting values for μ_g were then used in the program STARK in order to calculate the Stark shifts at 3146.1 V/cm, see Table 4, column 2. The agreement with observed values was quite satisfactory, particularly when one considered the errors in Δv_{calc} due to uncertainties in E (which caused an error of about 0.01 MHz) and in μ_g (which caused an error of approximately another 0.02 MHz). Furthermore, the error in Δv_{calc} due to errors in A_g and B_g caused by uncertainties in the rotational constants and the centrifugal distortion constants should be realised. The uncertainties in Δv_{obs} were derived from estimates of the errors in the measured frequencies: Stark effect lines were estimated to have uncertainties of ±0.05 MHz, except for a

few lines that were difficult to measure due to low intensity and/or partial overlap. These frequencies were estimated to have an error of ±0.10 MHz. The unperturbed lines were estimated to have the error ±0.05 MHz.

Using the resulting values for μ_g Stark shifts were also calculated at the other two electric field strengths. Again, agreement with observed values was satisfactory, see Table 4. These last two calculations made it clear that the derived values for μ_g were not dependent upon the field strength.

The relative error in the dipole moment of *trans*-1-fluoro-1,3-butadiene was 0.017/1.380 which was larger than the value for *cis*-1-fluoro-1,3-butadiene which is 0.001/1.346. A major reason for the larger relative error could be the larger uncertainty in the rotational constant A for that molecule. This caused a larger error in the values of the calculated coefficients for the equations that were used in the least-squares fitting process.

The fact that the dipole moment is smaller in *cis*- than in *trans*-1-fluoro-1,3-butadiene could very well to a large extent be caused by different molecular structures. In the *cis*-isomer the dis-

tance between the oppositely charged centra is probably smaller than that of the *trans*-isomer. However, it is also possible that the charge distributions are different in the two molecules. Attempts will be made to calculate the dipole moments of the two isomers with an *ab initio* quantum chemical method.

The dipole moment vector of *cis*-1-fluoro-1,3-butadiene makes an angle of 63.5(1)° with the *a*-axis of the molecule. That is quite close to the direction of the C−F bond; from the assumed structure the value of that angle is 64.1°. Consequently, the dipole moment vector makes an angle of 0.6° with the C−F bond. In *trans*-1-fluoro-1,3-butadiene the dipole moment makes an angle of 1.9° with the C−F bond, and in 2-fluoro-1,3-butadiene the value of that angle is 10−15°.[5] Although the direction of the C−F bond was obtained from an assumed molecular structure in all these cases, it seems probable that the direction of the C−F bond largely determines the direction of the molecular dipole moment vector for mono-fluorinated 1,3-butadienes.

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