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Microwave Spectra and Substitution Structure of Fluoroallene

Teruhiko Ogata,*† Kazuhito Fujii,† Mitsugu Yoshikawa,† and Fumihiko Hirota‡

Contribution from the Faculty of Liberal Arts and the Faculty of Education, Shizuoka University, Ohya, Shizuoka 422, Japan. *Received April 27, 1987*

Abstract: The microwave spectra of normal fluoroallene and all the singly substituted isotope species except for fluorine have been assigned leading to a substitution structure. The following structural parameters have been determined: $r(C_1{=}C_2) = 1.301 \pm 0.004$ Å; $r(C_2{=}C_3) = 1.309 \pm 0.003$ Å; $r(C_1{-}F) = 1.360 \pm 0.006$ Å; $r(C_1{-}H) = 1.083 \pm 0.002$ Å; $r(C_3{-}H) = 1.086 \pm 0.002$ Å; $\angle C_1C_2C_3 = 178.2 \pm 0.6°$; $\angle C_2C_1F = 121.9 \pm 0.5°$; $\angle C_2C_1H = 124.3 \pm 0.3°$; $\angle C_2C_3H = 120.8 \pm 0.2°$. The cumulative double bond, $C_1{=}C_2{=}C_3$, is found to be bent by approximately 1.8° from the linear configuration on the other side of fluorine, and $C_1{=}C_2$ is found shorter than $C_2{=}C_3$ by approximately 0.008 Å. The ab initio calculation of the structure optimization was carried out with the GAUSSIAN 80 program. The structure, fully optimized with the STO-3G basis set, is in fair agreement with the observed structure. The structure of fluoroallene is compared with those of allene and fluorine-substituted allenes. The systematic changes in the structural parameter with the change in number of substituted fluorine atoms are found.

There has recently been considerable interest in the structure of the cumulative double bond particularly in its linearity. Brown et al.[1] found that the heavy-atom chain of atoms in $H_2C{=}C{=}C{=}O$ was bent at the middle carbon by approximately 30° from the linear configuration. On the other hand, Yamada et al.[2] found that the $N{=}C{=}S$ chain in isothiocyanic acid, $HN{=}C{=}S$ was not linear but at an angle of 173.8°. Similarly the $N{=}C{=}O$ angle in isocyanic acid, $HN{=}C{=}O$, was found to be 172.6° and 172° by Yamada[3] and Fusina and Mills,[4] respectively. The $N{=}C{=}O$ angle in chlorine isocyanate ($ClN{=}C{=}O$, 170° 52′)[5] and the azide chain in chlorine azide ($ClN{=}N{=}N$, 171° 56′)[6] were also shown to be bent.

There is a possibility of a bent $C{=}C{=}C$ bond in allene and substituted allenes, too. For all allenes, however, the linearity has been assumed for the $C{=}C{=}C$ bond, and as a result no bent bond has so far been reported. We therefore investigated the microwave spectra of fluoroallenes for normal and all singly substituted isotope species except for fluorine in order to determine the substitution structure. The microwave spectrum of normal fluoroallene has already been measured, and the rotational constants, dipole moments, and a crude structure have been reported.[7]

Experimental Section

Synthesis. The sample of fluoroallene was synthesized by the photochemical reaction of carbon suboxide with fluoroethene.[8] A mixture of C_3O_2 and $HFC{=}CH_2$ in a 1-L Pyrex vessel was irradiated by a 20-W low-pressure mercury tube (Ushio UL1-2DQ), inserted into a water-cooled silica tube in the center of the vessel. Unfiltered radiation was used. In all runs, this vessel was immersed in crushed ice to minimize thermal polymerization of carbon suboxide. The reaction was monitored by gas chromatography. In 20 min, however, the reaction became slower, because polymerized carbon suboxide adhered to the irradiation tube and interfered with further irradiation. The reactants were removed from the vessel to another container, the adhered substance was wiped off, and the irradiation was then continued. This procedure was repeated three times. The product was separated by gas chromatography and used for spectroscopy. The samples of monodeuteriated fluoroallenes were prepared by the same procedure but from 1- and 2-monodeuteriated fluoroethenes, which were synthesized by the method of Bak and Christensen.[9]

Microwave Spectroscopy. The microwave spectrometers used were of conventional Stark modulation type at Shizuoka University[10] and at the National Chemical Laboratory for Industry.[7] All measurements were made at the temperature of dry ice.

The microwave spectra of three ^{13}C species were studied in their natural abundances in the sample. The assignment was made as follows: The spectra of normal species for a-type, $J = 5 \leftarrow 4$ transitions were first recorded with attenuation of 40 dB and were compared with those of the ^{13}C species which were recorded under the same conditions but without attenuation of 40 dB. The lines exhibiting shapes and intensities very similar to those of the normal species were easily assigned, and the assignments were confirmed by the reproduction of other transitions. By using these transition frequencies, the *B* and *C* rotational constants were determined. The *A* rotational constants were calculated by the inertial relation $I_c - I_a - I_b = \Delta'$, where Δ' is the value for the main species. The assignments of the *b*-type transitions were more difficult, because the dipole component along the *b* axis is about one-half of the *a* component, and prediction of the transition frequency is less accurate. The microwave spectra of the deuteriated compounds were studied in a mixture of $DFC{=}C{=}CH_2$ and $HFC{=}C{=}CHD$ by a ratio of 2 to 5, respectively. Both spectra were easily assigned. Only one microwave spectrum corresponding to the $HFC{=}C{=}CHD$ species was found: the careful investigation could find no lines attributed to another species within few hundred megahertz. The results are listed in Table I (supplementary material) along with the frequency differences from those calculated with the rotational constants listed in Table II.

Molecular Structure. The fluoroallene molecule is described by the center-of-mass principal axis system of the main isotopic species. The numbering of the atoms is shown in Figure 1. Since only one microwave spectrum was observed for fluoroallene-*3-d*$_1$ ($HFC{=}C{=}CHD$), H_2 and H_3 atoms in Figure 1 are equivalent, that is, fluoroallene clearly has a plane of symmetry. Substitution coordinates were calculated by the method described by Costain[11] and Kraitchman.[12] The coordinate of the fluorine atom was calculated from the first moment condition, $\sum m_i x_i = 0$ $(x = a, b)$. The "substitution coordinates" obtained in this way are listed in Table III. The angle between the $C_2{=}C_3$ bond and the $H{-}C{-}H$ plane is calculated to be 179.7 ± 0.4°, that is, the $C{=}CH_2$ group is almost coplanar. The structural parameters of fluoroallene computed from these coordinates are listed in Table IV (see also Figure 1). The cumulative double bond, $C_1{=}C_2{=}C_3$, in fluoroallene is slightly bent by approximately 1.8 ± 0.6° from the linear configuration on the other side of fluorine.

Geometry-Optimized Structure. In order to examine the results, the ab initio calculation of the structure optimization was carried out with the GAUSSIAN 80 program.[13] The structure, fully optimized with the STO-3G basis set, is in fair agreement with the observed structure, and it shows C_s symmetry within the small error of 0.0005 Å and 0.10°. So the C_s symmetry was assumed in the calculation with the 6-31G* basis set. Further in the MP2 calculation, the parameters related to the hydrogen atoms were fixed at the values optimized in the SCF calculation.

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† Faculty of Liberal Arts.
‡ Faculty of Education.

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Table II. Rotational and Centrifugal Distortion Constants of Fluoroallene and Its Isotopic Species (MHz)[a]

parameter	normal species	$HF^{13}CCCH_2$	$HFC^{13}CCH_2$	$HFCC^{13}CH_2$	$DFCCCH_2$	HFCCCHD
A	46276.658 (10)	45115.79 (15)	46190.95 (13)	46112.65 (8)	37872.435 (60)	42643.134 (37)
B	4300.038 (2)	4289.736 (16)	4282.240 (20)	4164.976 (14)	4273.528 (10)	4056.830 (8)
C	4039.161 (2)	4020.909 (17)	4022.739 (21)	3918.523 (14)	3939.621 (11)	3843.406 (8)
Δ_J	0.00168 (10)	0.00153 (19)	0.00168 (22)	0.00163 (17)	0.00143 (23)	0.00149 (13)
Δ_{JK}	−0.0940 (4)	−0.0884 (2)	−0.0945 (3)	−0.0910 (2)	−0.0519 (6)	−0.0760 (3)
δ_J	0.000324 (1)	0.000371 (54)	0.000476 (94)	0.000329 (64)	0.000282 (35)	0.000193 (56)
Δ'[b]	−3.32998 (6)	−3.3253 (5)	−3.3280 (6)	−3.3281 (4)	−3.3212 (3)	−4.9337 (2)

[a] Numbers in parentheses are one standard deviation in units of the last significant figures. [b] $\Delta' = I_c - I_a - I_b$ in uÅ^2. The conversion factor is 505379.05 MHz·uÅ^2.

Table III. Substitution Coordinates of Fluoroallene (Å)[a]

atom	a	b	c
C_1	−0.5365 (10)	−0.5368 (10)	0.0
C_2	0.7044 (10)	−0.1472 (47)	0.0
C_3	1.9657 (2)	0.2044 (25)	0.0
H_1	−0.8513 (4)	−1.5725 (2)	0.0
H_2	2.5022 (1)	0.3509 (9)	0.9325 (3)
H_3	2.5022 (1)	0.3509 (9)	−0.9325 (3)
F	−1.5680 (15)[b]	0.3491 (53)[b]	0.0

[a] Numbers in parentheses are errors due to uncertainties in the moment of inertia only and apply to the last significant figures. [b] Calculated from the first moment condition.

Table IV. Structural Parameters for Fluoroallene[a]

$r(C_1{=}C_2) = 1.301 \pm 0.004$	$\angle C_1C_2C_3 = 178.2 \pm 0.6$
$r(C_2{=}C_3) = 1.309 \pm 0.003$	$\angle C_2C_1F = 121.9 \pm 0.5$
$r(C_1{-}F) = 1.360 \pm 0.006$	$\angle C_2C_1H_1 = 124.3 \pm 0.3$
$r(C_1{-}H_1) = 1.083 \pm 0.002$	$\angle C_2C_3H_{2,3} = 120.8 \pm 0.2$
$r(C_3{-}H_{2,3}) = 1.086 \pm 0.002$	

[a] Distances in Å and angles in deg. Limits of error are calculated from errors for the coordinate of atoms in Table III.

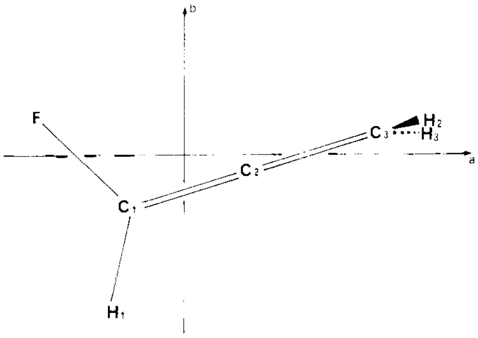

Figure 1. Structure and numbering of the atoms in fluoroallene: *a* and *b* are principal axes; the *c* axis is perpendicular to the paper which is a symmetry plane of the molecule; H_2 and H_3 are the identical out-of-plane hydrogen atoms.

The results are shown in Table V. The reliability of the MP2 calculation was estimated to be 1.4° for bond angles and 0.023 Å for bond lengths between nonhydrogen atoms.[14] It is noted that the $\angle C_1C_2C_3$ is bent by 1.8°, which is larger than the above value. One of the reasons for this bending may be the repulsion between the negative charge on the F atom (−0.37e) and the negative of the C_3 atom (−0.45e).

Discussion

To confirm the very small deviation from linearity of the C=C=C chain in fluoroallene, a dynamical contribution to the structural parameters arising from the zero-point motion of the low-frequency vibrational mode should be estimated. As shown in Table II, the pseudo-inertial defects, $\Delta' = I_c - I_a - I_b$, for the ^{13}C species are higher than that for the normal species by 0.0019 to 0.0047 uÅ^2 due to the isotopic effect on a zero-point vibration of the primarily in-plane bending mode. This effect makes the substitution coordinate of the *c* axis small imaginary for atoms in the symmetry plane of the molecule. In order to estimate the influence of this zero-point vibration on the structural parameters, the r_s coordinates of the three-carbon atoms are calculated by using only two moments of inertia among three with the relation for a rigid-planar molecule, $\Delta I_c = \Delta I_a + \Delta I_b$. The obtained *b* coordinates for carbon atoms, whose magnitudes are small and most poorly determined, and the angle $C_1C_2C_3$ are shown in Table VI. The deviations for the $C_1C_2C_3$ angle from 178.2 ± 0.6° which we accept as the most reliable value are between +0.2° and −0.4°. Since these deviations are much smaller than the bent angle of 1.8 ± 0.6°, the C=C=C chain in fluoroallene should be bent form the linear configuration.

Table V. The Calculation Structure of Fluoroallene[a]

	SCF/STO-3G	SCF/6-31G*	MP2/6-31G*
$r(C_1{=}C_2)$	1.2939	1.2922	1.3088
$r(C_2{=}C_3)$	1.2871	1.2947	1.3121
$r(C_1{-}F)$	1.3630	1.3341	1.3611
$r(C_1{-}H)$	1.0920	1.0713	(1.0713)[b]
$r(C_3{-}H)$	1.0849	1.0762	(1.0762)
$\angle C_1C_2C_3$	179.09	178.26	178.12
$\angle C_2C_1F$	123.66	122.59	(122.59)
$\angle C_2C_1H$	122.14	124.56	124.85
$\angle C_2C_3H$	122.16	121.37	(121.37)

[a] Distances are in Å and angles in deg. [b] Numbers in parentheses are assumed values.

Table VI. r_s Coordinates (Å) of Carbon Atoms and the Angle (deg) for $C_1{=}C_2{=}C_3$ Calculated by Using Various Sets of Moments of Inertia

moments of inertia	I_a, I_b	I_b, I_c	I_c, I_a	I_a, I_b, I_c
$b(C_1)$	−0.5345	−0.5389	−0.5345	−0.5368
$b(C_2)$	−0.1437	−0.1507	−0.1437	−0.1472
$b(C_3)$	0.2020	0.2069	0.2020	0.2044
$\angle C_1C_2C_3$	177.8 (6)	178.4 (6)	177.9 (6)	178.2 (6)[a]

[a] The values of Table IV which we accept as the most reliable structure.

The bent angle, 1.8 ± 0.6°, for the C=C=C in fluoroallene is smaller than the corresponding angles reported for other molecules, 30°[1] in $H_2C{=}C{=}C{=}O$, 6.2°[2] in HN=C=S, 7.4°[3] (or 8°[4]) in HN=C=O, 9° 08′[5] in ClN=C=O, and 8° 0.4′[6] in ClN_3. The C=C distances, $r(C_1{=}C_2)$ = 1.301 ± 0.004 Å and $r(C_2{=}C_3)$ = 1.309 ± 0.003 Å in fluoroallene, indicate the shortening of about 0.008 Å caused by the fluorine substitution. However, the distance $r(C_2{=}C_3)$ = 1.309 ± 0.003 Å, to which no fluorine attaches, indicates no significant difference from the corresponding distance 1.308 ± 0.003 Å in allene[15] or $r(C_2{=}C_3)$ = 1.306 ± 0.002 Å in 1,1-difluoroallene.[16] The C_1-H and C_3-H distances, 1.083 ± 0.002 and 1.086 ± 0.002 Å, respectively, also show the shortening by the fluorine substitution. The C_2C_1F angle of 121.9° is smaller than that in 1,1-difluoroallene, 124.9°.[16]

Summary

Substitution structure for fluoroallene is reported, where the fluorine coordinates are calculated from the first moment con-

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dition. The cumulative double bond, C=C=C, in fluoroallene is found to be slightly bent by 1.8 ± 0.6° from the linear configuration on the other side of fluorine. Another feature of the structure is that the $C_1=C_2$ bond, 1.301 ± 0.004 Å, is shorter than the $C_2=C_3$ bond, 1.309 ± 0.003 Å, by approximately 0.008 Å. The ab initio calculation of the structure optimization was carried out with the GAUSSIAN 80 program. The structure, fully optimized with the STO-3G basis set, is in fair agreement with the observed structure. The structural parameters in allene and fluorine-substituted allenes are found to change systematically with the number of substituted fluorine atoms.

Acknowledgment. The authors thank Drs. C. Matsumura, H. Takeo, and M. Sugie at the National Chemical Laboratory for Industry for the use of microwave spectrometer and helpful discussions. They express their thanks to Prof. Kozo Kuchitsu and Dr. A. P. Cox for critical reading of the manuscript and useful comments. They also thank the Computer Center, Institute for Molecular Science, Okazaki National Research Institute for the use of the HITAC-680H and S810/10 computer.

Registry No. $FCH=C=CH_2$, 51584-22-6; $F^{13}CH=C=CH_2$, 110971-94-3; $FCH={}^{13}C=CH_2$, 110971-95-4; $FCH=C={}^{13}CH_2$, 110971-96-5; $FCD=C=CH_2$, 110971-97-6; $FCH=C=CHD$, 110971-98-7; carbon suboxide, 504-64-3; fluoroethene, 75-02-5.

Supplementary Material Available: Table I, transition frequencies of fluoroallene and its isotopic species (1 page). Ordering information is given on any current masthead page.

Electronic Structure of Cyclopropenone and Its Relationship to Methylenecyclopropene. Evaluation of Criteria for Aromaticity

Stuart W. Staley,*[1a,b] Timothy D. Norden,[1b] William H. Taylor,[1c] and Marlin D. Harmony*[1c]

Contribution from the Departments of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, University of Nebraska-Lincoln, Lincoln, Nebraska 68588, and University of Kansas, Lawrence, Kansas 66045.

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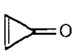
Abstract: The heavy-atom microwave (r_s) structure of cyclopropenone has been redetermined to be $r(C_1O) = 1.212$ Å, $r(C_1C_2) = 1.423$ Å, and $r(C_2C_3) = 1.349$ Å. These values agree closely with ab initio geometry-optimized bond lengths calculated at the MP2/6-31G* level. Cyclopropenone has approximately twice the π-delocalization energy of methylenecyclopropene and can be considered to be moderately "aromatic". In addition, this molecule is significantly stabilized by in-plane lone-pair donation from oxygen to the unoccupied $4b_1$ orbital of the ring. It is concluded that structure, electron distribution, and thermodynamic stability respond to a similar degree to π delocalization relative to appropriate model compounds.

Cyclopropenone (**1**) has received considerable attention during the last three decades owing primarily to its possible description as an "aromatic" compound.[2] The latter is exemplified by dipolar resonance forms **1a–c** (equivalent to **1d**) and is expected to result in a high polarity and increased stability relative to related compounds, such as cyclopropanone (**2**). (Structures and their numbering are given in Figure 1.) This has indeed been shown to be the case,[2] but a consensus has by no means been reached concerning the electronic character of **1**.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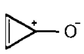
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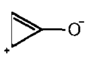
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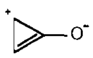
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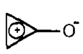
1d

Thermodynamic results (both thermochemical[3] and ab initio molecular orbital calculations[3a,4]) have led to the conclusion that there is substantial ground-state "aromatic" stabilization in this molecule. The results of an early thermochemical study[5] that pointed to the opposite conclusion for 2,3-diphenylcyclopropenone have been invalidated by subsequent studies.[3] Hase et al.[4b] employed the technique of conjugative interruption to suggest that significant stabilization arises from π-electron delocalization, in support of previous conclusions based on simple π-electron calculations.[6]

The available evidence concerning molecular structure and electron distribution is more ambiguous. The key study is the microwave study of Benson et al. in which the C=C length ($r(C_2C_3)$) was found to be 1.302 Å,[7] essentially identical with the 1.296-Å value found for cyclopropene.[8] This, along with an analysis of the magnetic susceptibility anisotropy of **1**, led these authors to conclude that resonance forms **1b** and **1c** are relatively unimportant and that the large molecular dipole (4.39 D) and quadrupole moments are largely a reflection of the importance of the C=O bond polarity alone, as exemplified by **1a**. This view appeared to be supported by a partial geometry optimization of **1** at the HF/STO-3G level[9] and by an analysis of the bond lengths in **1** and related compounds.[10]

Although Ammon concluded that the crystallographic molecular structure of 2,3-diphenylcyclopropenone monohydrate suggests

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