

One of the common justifications for obtaining information on homogeneous solutions of organometallic compounds is that this information perhaps can be extrapolated to catalysis in heterogeneous systems such as metal surfaces. One qualitative similarity between this work and surface phenomena involves the known ability of palladium metal to catalyze reactions involving olefins and the ability of nitrogen and phosphorus containing bases to poison catalytic surfaces. As previously suggested one possible reason for the above behavior is that the nitrogen and phosphorus donors are too strongly chemisorbed by the surface, eventually covering all the catalytic sites.^{40,41} Our relative displacement energies are consistent with this since pyridine and triphenylphosphine have much higher values than do the olefins. We had observed a similar result with polyolefins previously.¹ The

(40) D. O. Hayward and B. M. W. Trapnell, "Chemisorption," Butterworths, London, 1964, p 208.

(41) J. M. Thomas and W. J. Thomas, "Introduction to the Principles of Heterogeneous Catalysis," Academic Press, New York, N. Y., 1967, p 314.

relative displacement energies for palladium generally increase when electron donating substituents are present on the olefin. It has previously been observed⁴² that increasing π electron density in the olefin results in higher adsorption equilibrium constants on metallic palladium. The similarity of our data to surface phenomena is encouraging.

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Supplementary Material Available. All of the calorimetric data, concentrations of reagents and the results of the least-squares calculations, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-3800.

(42) A. P. G. Kieboom and H. Van Beckum, *J. Catal.*, **25**, 342 (1972).

Microwave Spectrum, Structure, Dipole Moment, and Coriolis Coupling of 1,1-Difluoroallene

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Abstract: The microwave spectra of five isotopic species of 1,1-difluoroallene, H_2CCCF_2 , $\text{H}_2^{13}\text{CCCF}_2$, $\text{H}_2\text{C}^{13}\text{CCF}_2$, HDCCCF_2 , and D_2CCCF_2 , have been recorded from 12.4 to 40.0 GHz. A-type transitions were observed and R-branch assignments have been made for the ground and two vibrationally excited states. The following structural parameters have been determined: $r(\text{C}_1=\text{C}_2) = 1.302 \pm 0.012 \text{ \AA}$; $r(\text{C}_2=\text{C}_3) = 1.306 \pm 0.002 \text{ \AA}$; $r(\text{C}_1-\text{F}) = 1.323 \pm 0.011 \text{ \AA}$; $r(\text{C}_3-\text{H}) = 1.086 \pm 0.003 \text{ \AA}$; $\angle \text{HC}_3\text{H} = 117.8 \pm 0.2^\circ$; $\angle \text{C}_2\text{C}_3\text{H} = 121.1 \pm 0.1^\circ$; $\angle \text{FC}_1\text{F} = 110.2 \pm 1.0^\circ$; $\angle \text{C}_2\text{C}_1\text{F} = 124.9 \pm 0.5^\circ$. The value of the dipole moment was obtained from Stark splittings to be $2.07 \pm 0.03 \text{ D}$. Coriolis coupling was observed between the two low-frequency $\text{C}=\text{C}=\text{C}$ bending modes. The dipole moment and structural values are compared with those of similar molecules.

An important objective of a theory of chemical shifts of diamagnetic molecules is the quantitative estimation of ^{13}C and ^1H nmr chemical shifts in organic molecules. This goal has often seemed remote due to problems associated with the gauge of the vector potential describing the magnetic field.¹ However, preliminary applications² of a recent gauge-invariant *ab initio* theory of magnetic shielding³ have given results for ^{13}C and ^1H chemical shifts which are in good agreement with experiment. To further document the performance of this method it is important to test it against experimental information for a variety of molecules. If sufficiently consistent success is obtained, this will allow some confidence to be acquired in its predictive power.

It is also important that the experimental systems chosen for the initial studies be inherently simple with

(1) For a recent review, see W. N. Lipscomb, *Advan. Magn. Resonance*, **2**, 137 (1966).

(2) R. Ditchfield, *Chem. Phys. Lett.*, **15**, 203 (1972).

(3) R. Ditchfield, *J. Chem. Phys.*, **56**, 5688 (1972).

respect to their structure and number of atoms and yet exhibit the major types of substituent effect on shielding at carbon nuclei (*e.g.*, inductive and mesomeric effects). A class of compounds which is particularly attractive from this point of view is the fluorocarbons. To this end we have recently determined the ^{13}C chemical shifts of the fluoroallenes, $\text{C}_3\text{F}_n\text{H}_{4-n}$.⁴ The measured ^{13}C shifts were compared to those predicted by SCF perturbation theory calculations employing a slightly extended Gaussian basis set of GIAO in an *ab initio* molecular orbital scheme.³ For these calculations, the geometry used was estimated from the standard geometrical model developed by Pople and Gordon.⁵ Although the level of agreement between the experimental data and the predicted results was good, it is essential to employ the best structural data possible in such calculations. With this goal in mind, we in-

(4) A. P. Zens, P. D. Ellis, and R. Ditchfield, *J. Amer. Chem. Soc.*, **96**, 1309 (1974).

(5) J. A. Pople and M. S. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

Table I. Rotational Frequencies (MHz) of 1,1-Difluoroallene and Its Carbon-13 and Deuterated Isotopic Species in the Ground Vibrational State

$J' \leftarrow J$	H_2CCCF_2		$\text{H}_2^{13}\text{CCCF}_2$		$\text{H}_2\text{C}^{13}\text{CCF}_2$		HDCCCF_2		D_2CCCF_2	
	ν_{obsd}	$\Delta\nu^a$	ν_{obsd}	$\Delta\nu^a$	ν_{obsd}	$\Delta\nu^a$	ν_{obsd}	$\Delta\nu^a$	ν_{obsd}	$\Delta\nu^a$
$2_{02} \leftarrow 1_{01}$	12,842.60	0.14								
$2_{11} \leftarrow 1_{10}$	13,793.55	0.10								
$3_{13} \leftarrow 2_{12}$	18,017.46	0.14								
$3_{03} \leftarrow 2_{02}$	19,079.85	0.06								
$3_{22} \leftarrow 2_{21}$	19,376.07	-0.12								
$3_{21} \leftarrow 2_{20}$	19,672.65	-0.06								
$3_{12} \leftarrow 2_{11}$	20,641.13	0.05					19,471.15	0.16		
$4_{14} \leftarrow 3_{13}$	23,944.61	0.12			23,810.50	0.05	22,811.82	0.10		
$4_{04} \leftarrow 3_{03}$	25,115.78	-0.12			24,975.23	0.20				
$4_{23} \leftarrow 3_{22}$	25,776.24	-0.24	24,943.20	-0.34	25,619.12	-0.15				
$4_{22} \leftarrow 3_{21}$	26,495.20	-0.10	25,570.42	0.09						
$4_{13} \leftarrow 3_{12}$	29,424.00	0.00					25,886.41	0.13		
$5_{15} \leftarrow 4_{14}$	29,815.41	0.13	28,938.41	0.13	29,650.41	0.01	28,422.63	0.12	27,192.42	0.13
$5_{05} \leftarrow 4_{04}$	30,934.99	0.22	30,049.98	0.10	30,769.01	0.13	29,501.71	-0.03	28,219.01	0.05
$5_{24} \leftarrow 4_{23}$			31,098.14	-0.20	31,932.91	-0.08	30,452.76	-0.34	28,985.45	-0.23
$5_{23} \leftarrow 4_{22}$	33,484.27	0.27			33,258.04	0.05	31,533.59	-0.02	29,854.84	-0.05
$5_{14} \leftarrow 4_{13}$	34,111.35	0.00	32,975.22	0.21					30,577.64	0.14
$6_{16} \leftarrow 5_{15}$	35,627.78	0.12	34,592.22	0.08	35,433.04	-0.01	33,984.96	-0.01	32,531.12	0.04
$6_{06} \leftarrow 5_{05}$	36,575.00	-0.52	35,561.06	-0.10	36,384.83	-0.14			33,474.66	-0.11
$6_{25} \leftarrow 5_{24}$	38,416.11	-0.51	37,199.79	0.23	38,186.99	-0.19				
$6_{24} \leftarrow 5_{23}$									36,127.62	0.01
$6_{15} \leftarrow 5_{14}$									36,534.57	0.03

^a $\Delta\nu = \nu_{\text{obsd}} - \nu_{\text{calcd}}$. ν_{calcd} is obtained from the rotational constants given in Table II.

Table II. Rotational Constants (MHz) and Moments of Inertia ($\mu \text{Å}^2$)^a of 1,1-Difluoroallene and Its Carbon-13 and Deuterated Isotopic Species in the Ground State

	H_2CCCF_2	$\text{H}_2^{13}\text{CCCF}_2$	$\text{H}_2\text{C}^{13}\text{CCF}_2$	HDCCCF_2	D_2CCCF_2
<i>A</i>	10,881.9 ± 2.8	10,879.3 ± 4.5	10,877.9 ± 2.7	10,695.1 ± 5.7	10,489.0 ± 2.4
<i>B</i>	3,667.34 ± 0.03	3,534.65 ± 0.06	3,642.16 ± 0.05	3,444.71 ± 0.05	3,251.49 ± 0.03
<i>C</i>	2,791.41 ± 0.03	2,713.90 ± 0.05	2,776.89 ± 0.04	2,671.91 ± 0.04	2,566.26 ± 0.03
κ	-0.78347	-0.79887	-0.78604	-0.80732	-0.82702
<i>I_a</i>	46.442	46.453	46.459	47.253	48.182
<i>I_b</i>	137.805	142.978	138.758	146.711	155.429
<i>I_c</i>	181.047	186.218	181.994	189.145	196.931
Δ_c^b	3.200	3.213	3.223	4.820	6.680

^a Conversion factor: 505,377 MHz $\mu \text{Å}^2$. $\Delta_c^b = I_a + I_b - I_c$

investigated the microwave spectrum of 1,1-difluoroallene and four of its isotopic species. The results of this study are reported herein.

Experimental Section

The sample of 1,1-difluoroallene-*d*₀ (H_2CCCF_2) was prepared by the following procedures. Dibromodifluoromethane (272 g), ethylene (8.4 g), and benzoyl peroxide (5 g) were placed in a bomb at 110° for 5 hr. The product, 1,3-dibromo-1,1-difluoropropane, was purified by distillation at 62° (86 mm) to give 42 g (59% conversion of ethylene) of propane. The propane was then decomposed (-2HBr) with molten potassium hydroxide at 140°. The product was swept into liquid nitrogen cooled traps on a standard high-vacuum line with helium as the carrier gas. The crude 1,1-difluoroallene was then distilled on a low-temperature fractionation column.⁶ The distillation yielded 3.2 g of 1,1-difluoroallene (24% conversion of propane). The purity of the 1,1-difluoroallene was checked by the infrared data reported by Blomquist and Longone.⁷ The 1,1-difluoroallene-*d*₁ sample was prepared in 50% isotopic purity by using ethylene-*d*₁ in the above synthesis of 1,1-difluoroallene-*d*₀. Ethylene-*d*₁ was prepared by dropping D_2O on to vinyl lithium in tetrahydrofuran. The gaseous product was swept into liquid nitrogen cooled traps on a high-vacuum line. The crude ethylene-*d*₁ was then distilled on a low-temperature fractionation column. The 1,1-difluoroallene-*d*₂ sample was synthesized by the use of ethylene-*d*₂ in the same synthetic route as given above for 1,1-difluoroallene-*d*₀. Ethylene-*d*₂ was obtained by the method

of Leitch and Morse.⁸ The isotopic purity of the 1,1-difluoroallene-*d*₂ obtained from this synthesis was determined from mass spectral data to be 93%. Both carbon-13 species were studied in their naturally occurring abundance.

The microwave spectra were investigated using a Hewlett-Packard Model 8460 A MRR spectrometer in the frequency region 12.4–40 GHz. The Stark cell was modulated with a square wave of 33.3 kHz in frequency. Frequency measurements were made with the cell being cooled with Dry Ice and the accuracy was better than 0.05 MHz.

Spectra

Because of the molecular symmetry, 1,1-difluoroallene is expected to have only one type of microwave transition. Based upon a preliminary structural estimate, 1,1-difluoroallene should have the principal *a* axis directed along the CCC bond with the *b* axis in the F_2C plane. The observed spectra were characteristic of an asymmetric rotor with a-type selection rules. Initial assignment was made from a careful Stark study and a rigid rotor model fit. Listed in Table I are the measured frequencies of the identified transitions along with the frequency difference from those calculated with the rotational constants listed in Table II. For the measured transitions, it is believed that the centrifugal distortion introduces little effect on the rotational constants; therefore, no correction for this effect has

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(7) A. T. Blomquist and D. L. Longone, *J. Amer. Chem. Soc.*, **79**, 4981 (1957).

(8) L. C. Leitch and A. T. Morse, *Can. J. Chem.*, **30**, 924 (1952).

Table III. Excited State Transitions (MHz) of 1,1-Difluoroallene and Its Deuterated Isotopic Species

	H_2CCCF_2				HDCCCF_2				D_2CCCF_2			
	$\nu(0,1)$		$\nu(1,0)$		$\nu(0,1)$		$\nu(1,0)$		$\nu(0,1)$		$\nu(1,0)$	
	ν_{obsd}	$\Delta\nu$	ν_{obsd}	$\Delta\nu$	ν_{obsd}	$\Delta\nu$	ν_{obsd}	$\Delta\nu$	ν_{obsd}	$\Delta\nu$	ν_{obsd}	$\Delta\nu$
$3_{03} \leftarrow 2_{02}$	19,126.54	0.12	19,134.99	-0.07								
$3_{12} \leftarrow 2_{11}$	20,717.95	-0.09	20,694.64	0.05	19,541.35	0.23	19,570.96	0.19				
$4_{14} \leftarrow 3_{13}$	23,993.73	0.10	24,012.32	0.09	22,857.92	-0.09	22,875.25	0.08				
$4_{04} \leftarrow 3_{03}$	25,164.47	0.02	25,193.05	-0.02								
$4_{23} \leftarrow 3_{22}$	25,853.96	-0.27	25,845.22	-0.34								
$4_{13} \leftarrow 3_{12}$	27,521.71	0.13	27,497.08	0.09	25,796.40	0.15	25,954.21	0.24				
$5_{05} \leftarrow 4_{04}$	30,979.98	-0.12	31,035.48	-0.08	29,546.25	0.07	29,595.95	0.05	28,263.99	0.07	28,305.53	0.04
$5_{15} \leftarrow 4_{14}$	29,872.22	0.17	29,901.23	0.07	28,673.31	0.11	28,503.12	0.11	27,244.39	0.15	27,266.01	0.14
$5_{14} \leftarrow 4_{13}$	34,224.38	-0.02	34,205.21	-0.02					30,675.77	0.12	30,657.47	0.13
$5_{24} \leftarrow 4_{23}$	32,219.53	-0.35	32,214.27	-0.43					29,065.74	-0.23	29,060.31	-0.26
$5_{23} \leftarrow 4_{22}$	33,632.39	-0.09	33,556.72	-0.06	31,666.78	-0.02	31,600.72	-0.06	29,975.68	-0.04	29,916.32	-0.03
$6_{16} \leftarrow 5_{15}$	35,690.35	0.07	35,732.09	0.04	34,044.61	0.00	34,082.96	0.03	32,589.32	0.05	32,620.75	0.07
$6_{06} \leftarrow 5_{05}$	36,616.00	-0.38	36,697.48	-0.34	34,980.91	-0.14	35,056.56	-0.15	33,515.87	-0.15	33,581.80	-0.13
$6_{24} \leftarrow 5_{23}$					38,359.75	-0.04	38,271.86	-0.03	36,280.78	-0.02	36,199.60	-0.02
$6_{15} \leftarrow 5_{14}$					38,584.38	-0.07	38,578.46	-0.10	36,643.07	0.05	36,633.78	0.07

Table IV. Rotational Constants (MHz) and Moments of Inertia ($\mu \text{Å}^2$) of H_2CCCF_2 , HDCCCF_2 , and D_2CCCF_2 in Excited Vibrational States

	H_2CCCF_2		HDCCCF_2		D_2CCCF_2	
	$\nu(0,1)$	$\nu(1,0)$	$\nu(0,1)$	$\nu(1,0)$	$\nu(0,1)$	$\nu(1,0)$
<i>A</i>	10,758.36 ± 0.84	11,017.02 ± 0.90	10,557.08 ± 0.58	10,845.42 ± 0.66	10,337.86 ± 0.79	10,654.86 ± 0.89
<i>B</i>	3,683.68 ± 0.02	3,676.42 ± 0.02	3,459.53 ± 0.01	3,453.13 ± 0.01	3,265.03 ± 0.013	3,259.27 ± 0.014
<i>C</i>	2,795.19 ± 0.02	2,799.40 ± 0.02	2,675.52 ± 0.01	2,679.41 ± 0.01	2,569.83 ± 0.013	2,573.09 ± 0.014
κ	-0.77685	-0.78655	-0.80105	-0.80941	-0.82101	-0.83019
<i>I_a</i>	46.9753	45.8724	47.8709	46.5982	48.8860	47.4316
<i>I_b</i>	137.194	137.464	146.083	146.353	154.785	155.058
<i>I_c</i>	180.802	180.531	188.889	188.615	196.658	196.409
Δ_c	3.366	2.806	5.064	4.336	7.013	6.081

^a Conversion factor: 505,377 MHz $\mu \text{Å}^2$.

been made. Spectra arising from the naturally abundant ^{13}C isotopic species, $\text{H}_2^{13}\text{CCCF}_2$ and $\text{H}_2\text{C}^{13}\text{CCF}_2$, were essentially identified from the intensity study at different temperatures.

In addition to the ground state lines, there are many other lines surrounding it. These lines are believed to be due to the rotational transitions of the molecules in the excited vibrational states. Measurements have been made on the two strongest satellites for H_2CCCF_2 , HDCCCF_2 , and D_2CCCF_2 . Given in Table III are the excited state transitions of these three isotopic species, and it was found that the frequencies fit the rigid rotor approximation. The effective rotational constants and the moments of inertia for these vibrationally excited states are listed in Table IV. It will be shown in a later section that these data are useful for obtaining the Coriolis coupling information.

The carbon atom bonded directly to the fluorine atoms is rather close to the center of mass of the molecule. The resulting small shifts from the carbon-12 lines make it difficult to identify the rotational transitions of $\text{H}_2\text{CC}^{13}\text{CF}_2$, since there is a good possibility that they will be overlapped by the rather intense, excited vibrational state lines.

Structure

The experimental moments of inertia of H_2CCCF_2 , $\text{H}_2^{13}\text{CCCF}_2$, $\text{H}_2\text{C}^{13}\text{CCF}_2$, and HDCCCF_2 should give sufficient information for determining the coordinates of H, C₃, and C₂ atoms by using the isotopic substitution method.⁹ The substituted coordinates in the

(9) J. Kraitchman, *Amer. J. Phys.*, 21, 17 (1953).

principal axis system of H_2CCCF_2 are, therefore, calculated and listed in Table V. After obtaining these

Table V. Coordinates of Atoms (Å) in the Principal Axis System of 1,1-Difluoroallene (H_2CCCF_2)

	<i>a</i>	<i>b</i>	<i>c</i>
H ₁	-2.8467	0.0	0.9262
H ₂	-2.8467	0.0	-0.9262
C ₂	-0.9795	0.0	0.0
C ₃	-2.2853	0.0	0.0
C ₁	0.3224	0.0	0.0
F ₁	1.0803	1.0846	0.0
F ₂	1.0803	-1.0846	0.0

coordinates, the next procedure was to determine the coordinates of C₁, F₁, and F₂ atoms by use of the center of mass condition as well as the moments of inertia relations. Molecular symmetry makes only three independent coordinates required for locating the positions of these three atoms. Consequently, the available information is greater than the number of unknowns. The mean coordinates obtained are listed in Table V, and the corresponding structure is given in Table VI. It is difficult to determine all the possible errors. From the uncertainty in the experimental moments of inertia,

Table VI. Structural Parameters for 1,1-Difluoroallene

$r(\text{C}_2=\text{C}_3)$	1.306 Å	$\angle \text{HC}_3\text{H}$	117.8°
$r(\text{C}_1=\text{C}_2)$	1.302 Å	$\angle \text{C}_2\text{C}_3\text{H}$	121.1°
$r(\text{C}_3-\text{H})$	1.086 Å	$\angle \text{FC}_1\text{F}$	110.2°
$r(\text{C}_1-\text{F})$	1.323 Å	$\angle \text{C}_2\text{C}_1\text{F}$	124.9°

one would obtain the errors to be 0.002 and 0.003 Å and 0.2° for the C₂C₃ and C₃H distances and H₁C₃H₂ angle, respectively. From both the uncertainty in the observed moments of inertia and the consistency of the coordinates obtained from different combinations of data, the estimated errors for the C₁C₂ and C₁F distances and F₁CF₂ angle are found to be 0.012 and 0.011 Å and 1.0°, respectively.

Instead of obtaining the coordinates of the hydrogen atoms from the moments of inertia of H₂CCCF₂ together with those of HDCCCF₂, one may also determine the coordinates with the experimental results of the H₂CCCF₂ and D₂CCCF₂ molecules. This set of data has led to the values of $a_{\text{H}} = 2.8463$ and $C_{\text{H}} = 0.9301$ Å, which are essentially identical with those obtained in the earlier calculation. The resulting structural parameters are found to be: $r(\text{CH}) = 1.086$ Å, $\angle\text{HCH} = 117.8^\circ$, $r(\text{C}_2\text{C}_3) = 1.306$ Å, $r(\text{C}_1\text{C}_2) = 1.304$ Å, $r(\text{C}_1\text{F}) = 1.322$ Å, and $\angle\text{FCF} = 110.3^\circ$, which are in excellent agreement with the corresponding parameters given in Table VI obtained by the earlier method.

Dipole Moment

The electric dipole moment of 1,1-difluoroallene has been determined by measuring the following Stark components: $|M| = 0, 1$, and 2 of the $3_{03} \leftarrow 2_{02}$ transition, $|M| = 1$ and 2 of the $3_{12} \leftarrow 2_{11}$ transition, and $|M| = 1$ of the $3_{13} \leftarrow 2_{12}$ transition. Each measured component was observed to have the quadratic Stark effect. The electric field was calibrated by using the $2 \leftarrow 1$ transition of OCS at 24325.92 MHz with its dipole moment taken as 0.71521 D.¹⁰ The data were analyzed by the method of Golden and Wilson.¹¹ Because of the molecular symmetry each measured component gives a value of the dipole moment. Listed in Table VII is the result of this Stark study, and μ_a was found

Table VII. Stark Coefficients and Dipole Moment of 1,1-Difluoroallene in the Ground State

Transition	$ M $	$\Delta\nu/E^2 \times 10^{-5}$ MHz (V ² /cm ²) ⁻¹		μ_a
		Obsd	Calcd ^a	
$3_{03} \leftarrow 2_{02}$	0	-0.439	-0.430	2.09
	1	-0.121	-0.123	2.05
	2	-0.810	-0.798	2.08
$3_{12} \leftarrow 2_{11}$	1	-0.950	-0.931	2.09
	2	-3.214	-3.387	2.02
$3_{13} \leftarrow 2_{12}$	1	1.107	1.088	2.09
μ_a (aV) = 2.07 ± 0.03 D				
$\mu_b = 0$ (by symmetry)				
$\mu_c = 0$ (by symmetry)				

^a Calculated from the average value.

to have a value of 2.07 ± 0.03 D. The quoted uncertainty represents the standard deviation obtained from the different Stark measurements.

Coriolis Coupling

The H₂CCCF₂ and D₂CCCF₂ molecules have C_{2v} symmetry and in a recent vibrational study of 1,1-difluoroallene¹² we observed Raman lines in the gaseous state

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(11) S. Golden and E. B. Wilson, Jr., *J. Chem. Phys.*, **16**, 669 (1948).

(12) J. R. Durig, Y. S. Li, A. P. Zens, P. D. Ellis, and J. D. Witt, to be submitted for publication.

at 167 and 151 cm⁻¹ with shoulders at 151 and 145 cm⁻¹ for the samples of H₂CCCF₂ and D₂CCCF₂, respectively. These two lines may be assigned to the two CCC bending motions (ν_{11} and ν_{15}) which belong to symmetry species B₁ and B₂. However, there is ambiguity in the assignments of ν_{11} and ν_{15} as to which mode should have the higher frequency. B₁ × B₂ has the same symmetry as the rotational angular momenta p_z and the first condition for strong perturbation is satisfied.¹³ Furthermore, the two vibrational energy levels are sufficiently close to give some observable corrections to the rigid rotor energy levels. In the molecular system, z has the same direction as principal axis a . Consequently, ν_{11} will couple with ν_{15} when the rotation about the a axis is excited.

If only the coupling between ν_{11} and ν_{15} is considered, the change in the effective moment of inertia I_a from the ground state to the first excited state can be expressed by the approximate forms¹⁴

$$I_a(v_{11} = 1) - I_a(v = 0) \approx (8k/\nu_{11})[\nu_{15}^2/(\nu_{15}^2 - \nu_{11}^2)](\zeta_{11,15}^a)^2 \quad (1)$$

and

$$I_a(v_{15} = 1) - I_a(v = 0) \approx (8k/\nu_{15})[\nu_{11}^2/(\nu_{11}^2 - \nu_{15}^2)](\zeta_{11,15}^a)^2 \quad (2)$$

where $k = h/8\pi^2c$, ν is the vibrational frequency, and $\zeta_{11,15}^a$ is the Coriolis coupling constant. It can be seen from Tables II and VI that the (0,1) state has a larger value of I_a than $v(0,0)$; therefore, one expects it to have a lower energy state than the $v(1,0)$ state. The opposite is true for the $v(1,0)$ state since I_a in the $v(1,0)$ state is smaller than that in the $v(0,0)$ state. By using the vibration frequencies and the moments of inertia along with the above expressions, one estimates the squares of the Coriolis coupling constants to be 0.11, 0.16 and 0.11, 0.15 for the H₂CCCF₂ and D₂CCCF₂ molecules, respectively.

The HDCCCF₂ molecule has C_s molecular symmetry and its corresponding bending motions belong to A' and A'' modes, respectively. The product of these two species has the same symmetry as the rotation about either the a axis or b axis. With the vibrational frequencies of 167 and 151 cm⁻¹, one estimates by a similar process the value of $(\zeta_{11,15}^a)^2$ to be 0.13 and 0.18 for HDCCCF₂. From a comparison of the values of I_a 's at different states, it is also found that $v(0,1)$ is in a lower energy state than $v(1,0)$.

Discussion

The dipole moment of 1,1-difluoroallene (2.07 D) is rather large in comparison to the dipole moment (1.37 D) of 1,1-difluoroethylene.¹⁵ Such a variation of dipole moment with the number of carbons in the chain may be rationalized by the alternation effect as given by Pople and Gordon⁵ in their calculation of the dipole moments of a series of simple organic compounds.

The C=C bond distances of 1.306 and 1.302 Å obtained for 1,1-difluoroallene do not indicate any significant differences from the corresponding bond lengths

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in allene.^{16,17} The experimental uncertainties in the bond lengths also limit the significance of the difference in the two C=C bonds which might be caused by the fluorine substitution. The C-F bond distance (1.323 Å) is identical with that in H₂CCF₂.¹⁸ Although the listed value of the FC₁F angle (110.2°) is larger than that in H₂CCF₂ (109.1°),¹⁸ the experimental error again prevents any significance being placed on the difference. The structure of the methylene (CH₂) group in H₂CCF₂ is quite typical.¹⁷

In 1962, Bernstein¹⁹ showed a close relation between the averaged CH stretching frequency of a molecule and its CH bond length. In the absence of resonance, Duncan²⁰ has demonstrated the correlation between the separation of asymmetric and symmetric CH₂ stretching frequencies and the HCH angle in the =CH₂ group of a molecule. From the closeness of the CH₂ geometries of allene and 1,1-difluoroallene, one would, thus, expect little difference in their CH stretching frequencies.

It was concluded in the Coriolis coupling section that the $\nu(0,1)$ state has a lower energy than the $\nu(1,0)$ state. Both vibrational modes (B₁ and B₂) are antisymmetry with respect to the C₂ operation. For the same rotational transition, both satellites should have the same statistical weights. Our relative intensity measurement has indicated consistently for all three isotopic species that the $\nu(0,1)$ state has a lower energy

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than the $\nu(1,0)$ state. This result is in complete agreement with that obtained from the vibration and rotation interaction study.

The structural parameters employed in the chemical shift calculations for 1,1-difluoroallene were $r(C_1-C_2) = r(C_2-C_3) = 1.31$ Å, $r(C_1-F) = 1.33$ Å, and $r(C_3-H) = 1.08$ Å, and all angles were taken at 120.0°. The distances used for these calculations are comparable to those found in this study. However, there are significant differences between the angles employed in the calculations and those obtained in the microwave study. In particular, the $\angle FC_1F$ of $110.2 \pm 1.0^\circ$ is considerably smaller than 120° and it is expected that such a difference could lead to significant changes in the predicted shielding constants.

It should be of interest to compare the dipole moments and the structures for a series of fluorine-substituted allenes. Also, it appears that additional structure work on these molecules would be of interest in attempting to predict shielding constants. Therefore, further microwave work on some of these molecules is warranted and we hope to initiate such studies in the near future.

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Photochemistry of Bioactive Compounds. Photochemical Processes of Polychlorinated Biphenyls

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Abstract: Six symmetrical tetrachlorobiphenyls have been synthesized. Cyclohexane and methanol solutions of I-VI were irradiated at 300 nm and the products of the reaction identified. In both solvents dechlorination is the major reaction. Intersystem crossing quantum yields and quantum yields of reaction for I-VI have been determined in solution. The excited state responsible for photoreaction was found to be the triplet, and its lifetime was measured in cyclohexane and methanol. The rate constants for triplet decay and reaction were obtained using these data. The position of chloro substitution was found to have a marked effect on the photochemical properties of polychlorobiphenyls; an increase in ortho substituents decreased the lifetime and increased the reactivity of the excited state.

The photoreactions of polychlorobiphenyls (PCB) have acquired considerable environmental significance in recent years. In the absence of adequate metabolic pathways for PCB degradation in most organisms and the chemical stability of these compounds, ultraviolet radiation from sunlight remains as a possible route for their inactivation in the environment.

Few studies of PCB photochemistry have been re-

ported.^{4,5} All the work published thus far has been concerned with the nature of the photoproducts arising from reactions in various solvents (dechlorination and oxygenation).^{6,7} Neither the mechanism of the reaction nor the properties of the excited state(s) involved have

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