Journal of Molecular Structure, 223 (1990) 217-230
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

MICROWAVE SPECTRUM, STRUCTURE AND DIPOLE MOMENT OF DIFLUOROPROPADIENONE*

H.S. TAM and MARLIN D. HARMONY
Department of Chemistry, University of Kansas, Lawrence, KS 66045 (U.S.A.)
JOHN C. BRAHMS and WILLIAM P. DAILEY
Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323 (U.S.A.)

(Received 17 July 1989)

ABSTRACT

The microwave spectra of the normal and two monosubstituted isotopomers of difluoropropadienone were observed and assigned in the 26.5–40.0 GHz frequency region. For the normal species, the rotational constants were determined to be $A = 11\,558.126 \pm 0.004$, $B = 2023.911 \pm 0.001$ and $C = 1720.649 \pm 0.001$ MHz. Comparably precise results were obtained for the carbonyl ^{13}C and ^{18}O species. Stark effect measurements led to a total electric dipole moment of $\mu_T = 0.671 \pm 0.012$ D with components of $\mu_a = 0.418 \pm 0.013$ D and $\mu_b = 0.525 \pm 0.003$ D. In contrast with the parent propadienone molecule, the difluoro species shows no evidence of large amplitude tunneling motions. However, the data show clearly that the molecule is strongly distorted from C_{2v} symmetry with a cumulenone chain that is bent similarly to that in propadienone.

INTRODUCTION

Brahms and Dailey [1] recently reported the synthesis of difluoropropadienone (see Fig. 1) and described some of its chemical and physical properties. In addition to experimental studies of its mass, IR and UV spectra, the molecule was investigated theoretically by ab initio molecular orbital calculations

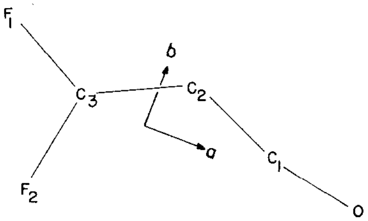


Fig. 1. Difluoropropadienone structure.

Dedicated to Professor E. Bright Wilson, Jr.

0022-2860/90/$03.50

at the HF/3-21G and HF/6-31G* levels. Full structure optimization in the former case predicted a C_{2v} structure with a linear cumulenone chain, whereas the larger basis set predicted a strongly bent structure of C_s symmetry as shown in Fig. 1. Although the IR spectrum as predicted by the 6-31G* basis set was in good agreement with the observed gas-phase spectrum, the experimental results did not definitively establish the molecular geometry.

The properties of difluoropropadienone are especially interesting in comparison with those of the parent propadienone molecule, which has been extensively studied spectroscopically by Brown and co-workers [2–4] and theoretically by Radom and co-workers [5–7]. The experimental microwave results show that propadienone is a strongly bent (C_s) cumulenone that undergoes a large-amplitude in-plane tunneling motion through a barrier of 359 cm^{-1} at the C_{2v} configuration [2]. Surprisingly, the ab initio results for propadienone at the Hartree–Fock level with large basis sets (6-31G**) predict the incorrect C_{2v} geometry [6]; only with the addition of configuration interaction terms do the computations predict the correct (bent) geometry [7,8] with a barrier at the linear cumulenone conformation.

In the case of difluoropropadienone, the prediction [1] of a distorted geometry at the 6-31G* Hartree–Fock level (with a substantial barrier of 650 cm^{-1} which increases to 1050 cm^{-1} at the MP3/6-31G* level [9]) suggests that the molecular geometry is most likely as shown in Fig. 1. The present microwave study was initiated to obtain experimental evidence for the geometry.

EXPERIMENTAL METHODS

Spectroscopy

Difluoropropadienone was prepared as reported earlier [1] by pyrolysis of 3,3-difluoroacrylic anhydride vapor in a pyrex tube at temperatures in the range 460–480 °C. The pyrolysis was performed in apparatus attached directly to one end of a standard 6 ft microwave wave-guide sample cell. In our initial work the pyrolysis products were pumped continuously through the cell at a low rate after trapping major by-products (primarily difluoroacrylic acid) and undecomposed precursor in a dry-ice trap. After identification of some key spectral features it was found that the sample could be effectively studied for periods of up to about 2 h under static conditions by shutting off the gas flow with valves at the entrance and exit ports to the sample cell. With the cell operated at dry-ice temperatures, difluoropropadienone was found to have a half-life of approximately 30 min at initial pressures of 25–50 mtorr. Spectra of the 1-^{13}C and ^{18}O isotopic species were obtained by identical procedures using samples of the precursor that were synthesized with isotopic enrichment in the carbonyl moiety.

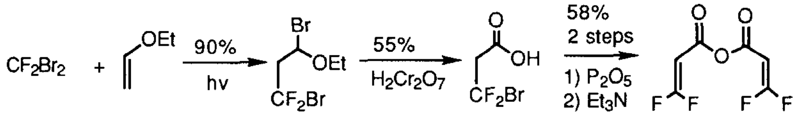
Microwave spectra were obtained in the 26.5–40.0 GHz region using an HP-

8460A microwave spectrometer. Radiofrequency–microwave double-resonance (RFMDR) measurements were performed with the instrumentation and procedures described earlier [10,11], except that the original RF source was replaced by a PTS 160 frequency synthesizer. Frequency measurements of rotational transitions are generally accurate to better than ±0.05 MHz, except in cases where lines are blended or overlapped with other transitions. The observed spectra were very dense due to the presence of unidentified pyrolysis or decomposition products. However, difluoropropadienone lines were generally easily identified by the characteristic time dependence of their intensities.

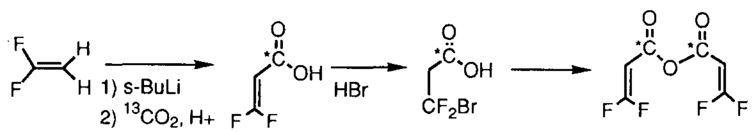
Finally, dipole moment measurements were accomplished by measuring the shifts of the *M* components of rotational transitions as a function of applied d.c. electric field. The Stark cell was calibrated by measurements of the second-order Stark effect of OCS, whose dipole moment is accurately known [12].

Preparation of 3,3-difluoroacrylic anhydride and ^{13}C- and ^{18}O-labeled derivatives

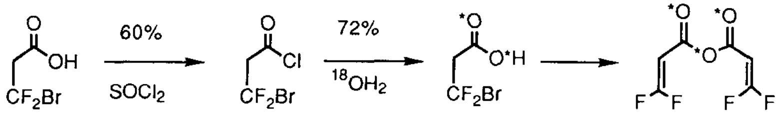
3,3-Difluoroacrylic anhydride was prepared in gram quantities by the following route, starting with the photochemical addition of dibromodifluoromethane to ethylvinyl ether [13].



The preparation of 1-^{13}C-3,3-difluoroacrylic anhydride required a slightly different route using the literature procedure for preparing 3,3-difluoroacrylic acid [14]. This was converted to the bromodifluoropropionic acid and an analogous sequence was used for formation of the acrylic anhydride.



The ^{18}O anhydride was prepared from the reaction of a 2.6 mol excess of ^{18}O water with 3-bromo-3,3-difluoropropionyl chloride. This compound was transformed into the acrylic anhydride in the same fashion as for the unlabeled compound. About 40% isotopic incorporation was achieved in the final product.



Preparation of 3,3-difluoroacrylic anhydride, (1-^{13}C)-3,3-difluoroacrylic anhydride and (^{18}O)-3,3-difluoroacrylic anhydride.

General

All reactions were carried out under a dry nitrogen atmosphere unless otherwise specified. All glassware was flame dried under high vacuum before use. Tetrahydrofuran and diethyl ether were freshly distilled from sodium benzophenone ketyl. Dichloromethane was distilled from calcium hydride. Triethylamine was distilled from calcium hydride and stored over freshly activated molecular sieves under dry nitrogen prior to use. ^{19}F chemical shifts are reported as parts per million upfield from $CFCl_3$ internal standard.

3-Bromo-3,3-difluoropropionic acid

Chromic acid (2.6 M) was prepared by combining CrO_3 (212 g, 2.12 mol) with water (165 ml). Concentrated H_2SO_4 (187.6 ml) was added in small portions while the mixture was cooled in an ice–water bath. The resulting slurry was carefully diluted to 816 ml with water. The freshly prepared chromic acid was placed together with 730 ml of water into a 3000 ml three-neck round-bottom flask equipped with large stirring bar and thermometer. The solution was cooled to $-5\,^\circ$C in an ice–salt bath. Ethyl-1,2-dibromo-2,2-difluoroethyl ether [13] (150 g, 530 mmol) was added dropwise over 1.5 h to the vigorously stirred mixture. The mixture was warmed to 10 °C over the course of 3 h. The reaction mixture contained considerable unreacted chromic acid which was quenched by adding small amounts of solid $NaHSO_3$ until the reaction mixture was dark blue. The reaction mixture was divided into two portions, each of which was extracted three times with 350 ml of diethyl ether. The combined ether solution was extracted with a saturated $NaHCO_3$ solution until the extract was basic, after which the bicarbonate phase was acidified to pH 1 and further extracted with 3×300 ml of diethyl ether. The resulting ether solution was washed with saturated NaCl, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by vacuum distillation to give 56.1 g (55%) of colorless oil (b.p. 53 °C at 0.7 torr). IR (thin film): 3200–2900 broad (COOH), 1730 (carbonyl), 1200 cm^{-1} (C–F). ^{1}H NMR: δ 12.5 ppm (s, 1H), 3.53 ppm (t, 12.8 Hz, 2H). ^{19}F NMR: 45.0 ppm (t, 12.8 Hz, 2F). HRMS (m/z): M+H 188.9335 ($C_3H_3F_2O_2{}^{79}Br$).

3-Bromo-3,3-difluoropropionic anhydride

A mixture of phosphorus pentoxide (4.21 g, 29.6 mmol) and 3-bromo-3,3-difluoropropionic acid (4.59 g, 24.3 mmol) was heated to 70 °C for 3 h. The product was purified by distillation under reduced pressure to yield 3.9 g (89%) of colorless oil (b.p. 80 °C at 0.5 torr). IR (thin film): 1830 (carbonyl), 1200–1050 cm^{-1} (C–F). ^{1}H NMR: δ 3.74 ppm (t, 12.1 Hz, 2H). ^{19}F NMR: 45.3 (t, $J=12.6$, 2F).

3,3-Difluoroacrylic anhydride

A solution of 3-bromo-3,3-difluoropropionic anhydride (773 mg, 2.15 mmol) in 5 ml of dichloromethane was cooled to 0 °C. Triethylamine (480 μl, 3.4 mmol) was added via syringe to the vigorously stirred solution over the course of 2 min. After stirring for 1 min at 0 °C the mixture was purified by dynamic vacuum transfer through a series of two traps, one at −20 °C and one at −196 °C. The product was collected as a white crystalline solid in the −20 °C trap and was further purified by a second fractionation to give 210 mg (65%) of pure product (m.p. 42–42.5 °C). IR (vapor phase): 1760, 1720 cm^{-1}, ^1H NMR: δ 5.05 (d,d J=1.5, 20.2, 2H). ^{19}F NMR: δ 58.2 (d,d J=20.7, 32.7, 1F), 63.3 (d,d J=1.9, 32.6, 1F). Elemental analysis: calculated for $C_6H_2F_4O_3$: 36.36% C, 1.01% H; found: 36.29% C, 1.11% H. MS (m/z): 199 M+H, 91 $C_3HF_2O^+$.

(1-^{13}C)-3-Bromo-3,3-difluoropropionic acid

(1-^{13}C)-3,3-Difluoroacrylic acid was prepared as described for the unlabeled compound [14] starting with 7.8 g of 1,1-difluoroethylene and 3.96 g of $^{13}CO_2$ (ISOTEC, 99% ^{13}C). The product from this reaction was dissolved in diethyl ether (30 ml) and was transferred to a 50 ml two-neck round-bottom flask equipped with magnetic stirrer, drying tube and gas dispersion tube. The solution was cooled in an ice–water bath and anhydrous HBr was bubbled through the solution until no more starting material was detected by gas–liquid chromatography (GLC). The reaction mixture was extracted with saturated sodium bicarbonate (3×50 ml). The bicarbonate extract was acidified to pH 1 and extracted with diethyl ether (3×50 ml). The ether extract was dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by vacuum distillation to give 5.01 g (49%) of colorless oil (b.p. 80 °C at 0.5 torr). Mass spectral analysis indicated 99% incorporation of ^{13}C.

(1-^{13}C)-3,3-Difluoroacrylic anhydride

This compound was prepared from the isotopically labeled 3-bromo-3,3-difluoropropionic acid by the same method as used for the unlabeled compound yielding more than 99% ^{13}C incorporation as determined by mass spectroscopy.

3-Bromo-3,3-difluoropropionyl chloride

A solution of 3-bromo-3,3-difluoropropionic acid (2.41 g, 12.75 mmol) and thionyl chloride (6.45 g, 47.8 mmol) was refluxed for 3 h and the product was purified by distillation at atmospheric pressure to yield 1.58 g (60%) of a colorless oil (b.p. 117 °C). IR (vapor phase): 1830, 1130 cm^{-1}. ^1H NMR: δ 3.68 (t, J=12.1, 2H). ^{19}F NMR: δ 46.9 (t, J=12.1, 2F). HRMS (m/z): 206.900 M+H ($C_3H_3F_2{}^{79}Br^{35}ClO$.

(^{18}O)-3-Bromo-3,3-difluoropropionic acid

Water (97% ^{18}O, 550 μl, 27.5 mmol) was added via syringe to an ice-cooled, stirred solution of 3-bromo-3,3-difluoropropionyl chloride (2.26 g, 10.89 mmol) in 5 ml of tetrahydrofuran. The mixture was allowed to warm to room temperature and was stirred for 18 h. The solvent was removed under reduced pressure and the product was purified by vacuum distillation to give 1.51 g (72%) of colorless oil (b.p. 80 °C at 0.5 torr).

(^{18}O)-3,3-Difluoroacrylic anhydride

This compound was prepared from the isotopically labeled 3-bromo-3,3-difluoropropionic acid by the same method as used for the unlabeled compound. Isotopic enrichment determined from mass spectroscopy: 3 ^{18}O (9%); 1 ^{16}O, 2 ^{18}O (29%); 2 ^{16}O, 1 ^{18}O (34%); 3^{16}O, 0 ^{18}O (26%). MS (*m/z*, 70 eV): 91 ($C_3HF_2{}^{16}O$) (100%), 93 ($C_3HF_2{}^{18}O$) (65%).

OBSERVED SPECTRUM AND ANALYSIS

For the expected bent C_s structure or the alternative, but less likely, C_{2v} conformation it was expected that the difluoropropadienone spectrum would show a prominent and characteristic *a*-type *R*-branch spectrum of a near-prolate asymmetric rotor. The initial assignments were obtained by observing the

TABLE 1

Microwave spectrum of normal isotopomer of difluoropropadienone[a]

Transition	Obs.	Obs. – Calc.[b]	Transition	Obs.	Obs. – Calc.[b]
1(1, 1)-2(2, 0)	36705.11	0.01	9(1, 9)-10(1, 10)	35681.88	0.02
1(1, 0)-2(2, 1)	36394.71	−0.01	9(3, 6)-10(3, 7)	37644.27	−0.02
2(1, 1)-2(2, 0)	28609.54	0.02	9(3, 7)-10(3, 8)	37563.26	0.01
3(1, 2)-3(2, 1)	28187.43	0.01	9(5, 5)-10(5, 6)	37500.43	0.01
4(1, 4)-4(2, 3)	30585.97	0.00	10(0, 10)-11(0, 11)	39858.46	−0.03
4(1, 3)-4(2, 2)	27660.66	0.00	10(1, 10)-10(2, 9)	37638.42	−0.06
5(0, 5)-6(1, 6)	29113.60	0.02	10(1, 10)-11(1, 11)	39200.69	0.02
6(0, 6)-7(1, 7)	31954.39	0.00	12(2, 11)-13(1, 12)	31709.35	−0.02
7(3, 4)-8(3, 5)	30053.02	0.00	13(2, 12)-14(1, 13)	36962.17	0.02
8(0, 8)-9(0, 9)	32911.77	−0.01	14(4, 10)-13(5, 9)	34221.88	0.00
8(3, 5)-9(3, 6)	33841.50	−0.05	14(0, 14)-14(1, 13)	32309.49	0.05
8(5, 4)-9(5, 5)	33742.23	0.00	17(3, 15)-18(2, 16)	34324.96	0.00
8(6, 3)-9(6, 4)	33729.03	0.00	18(1, 17)-18(2, 16)	31393.79	0.00
8(7, 2)-9(7, 3)	33720.11	−0.02	19(2, 17)-19(3, 16)	37474.25	0.01
9(4, 5)-10(4, 6)	37532.98	−0.03	20(1, 19)-20(2, 18)	36584.66	−0.01
9(0, 9)-10(0, 10)	36400.05	0.05	20(2, 18)-20(3, 17)	37026.99	−0.00
9(1, 8)-10(1, 9)	38632.76	0.02	22(2, 20)-22(3, 19)	37046.78	0.02

[a] All frequencies in MHz. [b] Computed from constants of Table 2.

TABLE 2

Rotational and centrifugal distortion constants for normal and monosubstituted isotopic species of difluoropropadienone in the ground vibrational state[a,b]

	Normal	1-^{13}C	^{18}O
A	11558.126(4)	11550.113(4)	11554.468(4)
B	2023.911(1)	2004.106(1)	1913.832(1)
C	1720.649(1)	1706.141(1)	1640.344(1)
τ'_{aaaa}	−60.7(4)	−61.7(4)	−62.0(5)
τ'_{bbbb}	−2.67(2)	−2.63(2)	−2.41(2)
τ'_{cccc}	−1.35(1)	−1.33(1)	−1.25(1)
τ'_{bbcc}	−1.21(2)	−1.20(2)	−1.17(2)
$\tau'_{aabb}+\tau'_{aacc}$	−41.3(1)	−40.1(1)	−38.5(1)

[a] Rotational constants in MHz; centrifugal distortion constants in kHz. [2] Uncertainties in the final digits are the standard deviations based on the fit of the data in Tables 1, 3 and 4.

RFMDR transitions of several $K_{-1}=3$ and $K_{-1}=4$ R-branch lines. High-K and low-K lines of the same R-branch clusters were observed subsequently without too much difficulty. Following these a-type assignments, which provided relatively precise B and C rotational constants but an imprecise A rotational constant, a search was undertaken for low-J, b-type R-branch and Q-branch lines. Such transitions should, of course, be present for a permanently bent C_s molecule, or for an interconverting bent molecule such as propadienone. After some initial difficulty caused by the dense background of impurity lines, the $1 \rightarrow 2$ b-type lines were observed and identified by their characteristic fast first-order Stark effects (for $M=1$ components) caused by near-degenerate levels connected by the μ_a component of the electric dipole moment. Subsequently, numerous high-J, a- and b-type P-, Q- and R-branch transitions were easily assigned and measured. Table 1 presents a list of 34 assigned transitions for the normal isotopic species which lead to the rotational and P^4 centrifugal distortion constants [15] given in Table 2. A more extensive list of 81 lines has actually been measured. The more extensive tally leads to some improvement in the precision of the centrifugal distortion constants but has a minor effect on the rotational constants; therefore, we present the abridged list for conciseness and efficiency.

It should be mentioned that there was no evidence of nuclear-spin statistical-weight intensity alternations in the ground vibrational state which should be present if the molecule is of rigid C_{2v} structure; nor was there evidence of any tunneling splitting of the ground state into substates with alternating statistical-weight factors as observed for propadienone [2]. In particular, the b-

TABLE 3

Microwave spectrum of 1-^{13}C isotopomer of difluoropropadienone[a]

Transition	Obs.	Obs. − Calc.[b]	Transition	Obs.	Obs. − Calc.[b]
1(1,1)-2(2,0)	36661.02	0.02	9(3,7)-10(3,8)	37216.48	−0.05
1(1,0)-2(2,1)	36356.18	0.00	9(3,6)-10(3,7)	37293.35	0.03
2(1,1)-2(2,0)	28644.65	0.01	9(4,5)-10(4,6)	37186.67	0.01
3(1,2)-3(2,1)	28229.33	0.01	9(5,5)-10(5,6)	37155.29	0.02
4(1,4)-4(2,3)	30586.50	0.02	10(0,10)-11(0,11)	39521.80	−0.01
4(1,3)-4(2,2)	27710.31	−0.01	10(1,10)-10(2,9)	37513.01	−0.03
5(0,5)-6(1,6)	28967.25	−0.03	10(1,10)-11(1,11)	38862.74	0.00
6(0,6)-7(1,7)	31786.74	−0.01	12(2,11)-13(1,12)	31062.78	−0.04
7(3,4)-8(3,5)	29774.82	0.01	13(2,12)-14(1,13)	36269.46	−0.02
8(0,8)-9(0,9)	32628.92	0.01	14(4,10)-13(5,9)	34804.16	0.00
8(3,5)-9(3,6)	33527.27	0.01	14(0,14)-14(1,13)	31871.15	0.03
8(5,4)-9(5,5)	33431.90	0.01	17(3,15)-18(2,16)	33298.68	0.02
8(6,3)-9(6,4)	33419.15	0.01	18(1,17)-18(2,16)	31049.74	−0.00
8(7,2)-9(7,3)	33410.59	0.03	19(2,17)-19(3,16)	37618.81	−0.06
9(0,9)-10(0,10)	36090.14	0.00	20(1,19)-20(2,18)	36067.71	−0.03
9(1,8)-10(1,9)	38275.53	0.00	20(2,18)-20 (3,17)	37126.86	0.00
9(1,9)-10(1,10)	35373.33	0.01	22(2,20)-22(3,19)	37018.35	0.04

[a]All frequencies in MHz. [b]Computed from constants of Table 2.

TABLE 4

Microwave spectrum of ^{18}O isotopomer of difluoropropadienone[a]

Transition	Obs.	Obs. − Calc.[b]	Transition	Obs.	Obs. − Calc.[b]
1(1,1)-2(2,0)	36582.70	0.03	9(3,7)-10(3,8)	35639.30	0.04
1(1,0)-2(2,1)	36303.40	−0.05	9(3,6)-10(3,7)	35697.82	−0.02
2(1,1)-2(2,0)	28927.48	0.08	9(4,5)-10(4,6)	35611.43	0.05
3(1,2)-3(2,1)	28543.55	−0.01	9(5,5)-10(5,6)	35585.08	−0.03
4(1,4)-4(2,3)	30709.26	−0.01	10(0,10)-11(0,11)	37991.53	−0.02
4(1,3)-4(2,2)	28060.81	−0.03	10(1,10)-10(2,9)	37053.63	−0.03
5(0,5)-6(1,6)	28347.08	−0.04	10(1,10)-11(1,11)	37327.50	0.02
6(0,6)-7(1,7)	31071.23	0.01	12(2,11)-13(1,12)	27972.75	0.00
7(3,4)-8(3,5)	28509.71	−0.04	13(2,12)-14(1,13)	32963.34	0.01
8(0,8)-9(0,9)	31341.80	0.00	14(4,10)-13(5,9)	37816.92	0.00
8(3,5)-9(3,6)	32098.30	−0.02	14(0,14)-14(1,13)	29871.15	0.01
8(5,4)-9(5,5)	32020.05	−0.01	17(3,15)-18(2,16)	28372.15	−0.01
8(6,3)-9(6,4)	32009.19	−0.01	18(1,17)-18(2,16)	29613.48	−0.01
8(7,2)-9(7,3)	32001.73	−0.01	19(2,17)-19(3,16)	38587.45	0.01
9(0,9)-10(0,10)	34680.85	0.02	20(1,19)-20(2,18)	33817.99	0.01
9(1,8)-10(1,9)	36647.35	0.02	20(2,18)-20(3,17)	37906.48	0.01
9(1,9)-10(1,10)	33971.64	0.02	22(2,20)-22(3,19)	37235.68	−0.01

[a]All frequencies in MHz. [b]Computed from constants of Table 2.

type transitions, which for an interconverting molecule should appear as doublets separated by approximately twice the tunneling frequency, were not split in the ground state. Thus the spectra data for difluoropropadienone in the ground vibrational state show that it behaves like an "ordinary" semi-rigid molecule of C_s symmetry, rather than like a molecule such as propadienone which tunnels between C_s conformations through a C_{2v} barrier.

Spectra of the 1-^{13}C and ^{18}O isotopic species were assigned easily using the tried and tested procedures described for the normal isotopomer. Tables 3 and 4 present the experimental frequency measurements for the same set of transitions as used for the normal isotopomer; the rotational and centrifugal distortion constants are again summarized in Table 2. It should be noted that the quality of the spectral fits is very high for all three isotopomers. It is interesting to observe also that the A rotational constants change by a relatively small amount on isotopic substitution, a result that is attributable to the small values of the b coordinate of the substituted atoms.

DIPOLE MOMENT MEASUREMENTS

The electric dipole moment was determined by measurement of the quadratic Stark effect and use of the theory of Golden and Wilson [16]. Table 5 presents the experimental values of the Stark coefficients ($\Delta\nu/\epsilon^2$) for four independent M components. Least-squares analysis of the data provided the μ_a and μ_b components (actually only the magnitudes, since the signs are undetermined) and consequently the total μ_T as summarized in Table 5. For the planar asymmetric rotor we have constrained $\mu_c=0$. In addition to the second-order Stark measurements we have also measured and analyzed the nearly

TABLE 5

Dipole moment measurements and results

Transition	M	$(\Delta\nu/\epsilon^2)\times10^5$	
		Obs.[a]	Calc.[a]
$1_{10}\rightarrow2_{21}$	0	0.1154	0.1154
$1_{11}\rightarrow2_{20}$	0	−0.2902	−0.2902
$6_{15}\rightarrow7_{16}$	3	0.2587	0.2547
$6_{15}\rightarrow7_{16}$	4	0.1852	0.1906

$\mu_a=0.418(13)$ D[b]
$\mu_b=0.525(3)$ D
$\mu_c=0$ (by symmetry)
$\mu_T=0.671(12)$ D

[a] Units are MHz V^{-2} cm^2. [b] Uncertainties represent the standard deviations.

first-order Stark shifts of the $M=1$ components of the $1_{10} \rightarrow 2_{21}$ and $1_{11} \rightarrow 2_{20}$ transitions. The nearly degenerate 1_{10} and 1_{11} states and the 2_{20} and 2_{21} states are coupled by the μ_a component of the dipole moment. These off-diagonal matrix elements dominate the Stark effect at low voltages and consequently provide an independent means for evaluating μ_a [17]. At an electric field of 109.3 V cm^{-1}, the $M=1$ components of the $1_{11} \rightarrow 2_{20}$ and $1_{10} \rightarrow 2_{21}$ lines are shifted by +5.26 MHz and −5.29 MHz, respectively. From these results we obtain $\mu_a = 0.415 \pm 0.001$ MHz by numerical solution of the simple 2×2 matrices. This value is in excellent agreement with the second-order result given in Table 5. Consequently, we prefer to report the second-order results which have statistical uncertainties that more accurately reflect our experimental errors over a range of electric field strengths.

MOLECULAR STRUCTURE

The microwave data available for difluoropropadienone are not sufficiently extensive to perform a complete structural determination, but they do permit a reasonably accurate delineation of the principal geometrical features. First, all the evidence for the three isotopomers is consistent with the molecule being planar as observed for propadienone [2]. In particular, the inertial defect values $(I_c - I_a - I_b)$ for the normal, 1-^{13}C and ^{18}O species are 0.2850, 0.2846 and 0.2879 amu Å^2, respectively. These values are rather large, but are reasonable for a molecule such as difluoropropadienone, which has relatively low-frequency in-plane vibrations and relatively large moments of inertia about the b and c axes. The value can also be rationalized by comparison with related planar molecules. Thus for formaldehyde (CH_2O) the inertial defect Δ has the value 0.0574 [18], whereas for propadienone (H_2C_3O) the value doubles to 0.1151 [4]. For difluoroformaldehyde, Δ has the value 0.1556 [18], and so based on an analogy with the protonated species it is not surprising to find that Δ approximately doubles for difluoropropadienone. In addition, we find no evidence for the existence of c-type transitions or a measurable μ_c out-of-plane component of the electric dipole moment.

The normal and isotopic data permit an immediate determination of the r_s coordinates [19] of the carbonyl carbon and oxygen atoms and thus the r_s value of the C=O bond length. The value obtained, 1.161 ± 0.007 Å (where the uncertainty is estimated by Costain's rule [20]), is nearly identical to the value (1.162 ± 0.002) reported for propadienone [4].

More general structural information is available by least-squares fitting of the rotational constant data. Of the nine experimental rotational constants only six can be considered independent by virtue of the rigid-rotor planarity condition. We have chosen the six A and B rotational constants (actually the I_a and I_b moments of inertia) as the independent data for fitting purposes. Constraining the molecular structure to planarity, a total of nine structural parameters (five bond distances and four bond angles) are needed to completely define the structure (see Fig. 1). We have chosen to use ab initio theory to reduce the number of variables. For this purpose, the HF/6-31G* [1] results have been used to fix the differences in the two C–F bond lengths and the differences in the two C=C bond lengths. In addition, the two F–C=C angles have been fixed at the ab initio values, leaving a total of five independent parameters (including the C=O distance) to be fitted to the six experimental moments of inertia. The results of this determination are summarized in Table 6 together with the ab initio results and the experimental parameters for propadienone. The uncertainties that are listed are the standard deviations of the least-squares fit. They should not be considered as measures of the parameter accuracies, since the parameter values depend on the imposed constraints. However, the statistical uncertainties do indicate the internal consistency of the structure based on the assumed model.

It is observed from Table 6 that the partially constrained, least-squares structure is in very good agreement with the ab initio predictions and shows a close analogy with the experimental results for propadienone [4]. There can be no doubt that the molecule is strongly bent — indeed the C=C=C angle is markedly smaller than the corresponding value for propadienone. We have investigated the structure under a variety of constraints and assumptions in addition to those of Table 6. Under all plausible assumptions the C=C=C group is strongly bent. In particular, if the molecule is constrained in the least-squares fit to be a linear cumulenone with C_{2v} symmetry, the resulting structural parameters are completely implausible. It is less certain that the C=C=O moiety is non-linear, although all of our fitting attempts gave the non-linear configuration as in Fig. 1. In summary, the structure given in Table 6 must surely be

TABLE 6

Structural results[a]

Parameter[b]	Present work	Ab initio[e]	Propadienone[f]
$R(C_3F_1)$	1.311 ± 0.001[d]	1.289	-
$R(C_3F_2)$	1.320[c]	1.298	-
$R(C_2C_3)$	1.314 ± 0.002	1.305	1.322
$R(C_1C_2)$	1.309[c]	1.300	1.320
$R(C_1O)$	1.159 ± 0.002	1.137	1.163
$\angle F_1C_3C_2$	124.5[c]	124.5	117.2[g]
$\angle F_2C_3C_2$	127.3[c]	127.3	121.0[g]
$\angle C_3C_2C_1$	130.6 ± 0.4	132.8	144.5
$\angle C_2C_1O$	170.5 ± 0.6	172.1	169.4

[a] Units are Å and degrees. [b] Refer to Fig. 1 for parameter identification. [c] Constrained by: $R(C_2C_3) = R(C_1C_2) + 0.005$, $R(C_3F_2) = R(C_3F_1) + 0.009$, $\angle F_1C_3C_2 = 124.5°$, $\angle F_2C_3C_2 = 127.3°$. [d] Standard deviations of the least-squares fit. [e] Ref. 1. [f] Ref. 4. [g] HCC angles.

a correct qualitative representation of the equilibrium structure and should provide a reasonably accurate quantitative representation.

VIBRATIONAL SATELLITES

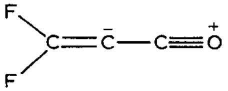
Although we did not perform extensive studies of vibrational satellite structure because of the very dense spectrum, it was possible to identify the two most intense series of satellites of the 7→8, 8→9 and 9→10 double-resonance lines. Relatively crude intensity measurements indicated that the satellites corresponded to vibrational frequencies of approximately 190 cm^{-1} and 270 cm^{-1}, presumably assignable to the lowest frequency in-plane and out-of-plane vibrational modes. These values are approximately twice as large as those predicted by the earlier HF/6-31G* ab initio calculations [1].

DISCUSSION

Although we have not been able to derive a complete set of structural parameters, the available microwave data for difluoropropadienone show unambiguously that it is a planar molecule with a strongly non-linear cumulenone chain, similar to that reported earlier for the parent propadienone species [4]. Unlike the parent molecule the difluoro species is confined to a relatively deep C_s potential well and does not tunnel rapidly through the C_{2v} conformation, at least not in the lower vibrational state(s). This is not surprising, since the potential barrier is predicted to be substantially higher in the difluoro species, and the reduced mass for the tunneling motion is expected to be larger. In addition, it appears that the difluoro species is even more strongly bent ($\angle C_3C_2C_1$ is smaller) so that the C_s minimum is even further from the C_{2v} potential barrier. All three of these factors mitigate against a facile tunneling interconversion. It is not possible, however, to exclude the possibility of tunneling in higher vibrational states, and indeed the general theory for a molecule of this type (as discussed thoroughly by Brown et al. [2]) suggests that tunneling should occur for states nearer to the top of the barrier. We were not able to probe high vibrational states due to the severe spectral congestion. Presumably the 190 cm^{-1} vibrational satellites observed for the *a*-type *R*-branch lines correspond to transitions in the first excited state pair of still nearly degenerate vibrational levels. The *b*-type lines, which should show the tunneling frequency (splitting) directly [2], could not be identified in the dense spectrum, but it seems likely that the tunneling splitting would not be large enough to observe. Using a simple theory described earlier [21], we estimate that the tunneling splitting will be reduced by a factor of approximately 10^6–10^7 in difluoropropadienone compared with propadienone. Consequently, the tunneling splitting is unlikely to be evident until the $v=2$ or $v=3$ pairs of states are reached.

The structure reported in Table 6 is in generally good agreement with the

HF/6-31G* ab initio results, although the experimental values of the C–F and C=O bond distances are each approximately 0.02 Å longer. A portion of this discrepancy is probably related to the fact that the reported experimental structure is essentially an r_0 structure [20] and thus is likely to yield distances that are somewhat longer than the r_e values. Table 6 also shows that the experimental values of the parameters of the difluoro species correspond closely to those of propadienone. The major difference appears in the $C_1C_2C_3$ angle, which is 14° smaller in the difluoro molecule. According to the arguments of Brown [22], this suggests that the resonance structure of the form



plays an even more important role in difluoropropadienone than in propadienone.

The molecular electric dipole moment of 0.671 D is substantially smaller than the value (1.15 D) obtained from the HF/6-31G* computations [9]. This result parallels that for the parent propadienone molecule, for which the experimental ab initio 6-31G* values of μ are 2.30 D [23] and 2.73 D [7], respectively. It is interesting to note that the difluoropropadienone moment is also significantly smaller than the 0.951 D value in $O=CF_2$ [24]. In contrast, the propadienone dipole moment is nearly identical to that of $O=CH_2$, which has an experimental value of 2.33 D [25]. Brown [22] has argued that the alternation in the magnitudes of the dipole moments of the series formaldehyde, ketene, propadienone and butatrienone can be rationalized by considering the occurrence and importance of ionic resonance structures analogous to that above. These arguments are compatible with our observations since an increased importance of the resonance structure given above would lead to a decreased dipole moment compared with carbonyl fluoride.

In summary, the experimental work confirms the highly non-linear cumulenone chain in difluoropropadienone and shows it to be non-inverting in the lowest vibrational state. The unusual electronic structure of the molecule is further highlighted by the relatively small value of the electric dipole moment.

ACKNOWLEDGMENTS

We thank the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research at both the Pennsylvania and Kansas laboratories, and the National Science Foundation for partial support of the work performed in the former laboratory under grant CHE 88-22674.

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