When the iodide of **1** was found to be too insoluble for low-temperature ^{13}C NMR work, the fluoroborate was prepared by trituration of the iodide with silver oxide and 40% tetrafluoroboric acid, washing the solids formed with acetone, concentration, and recrystallization from acetone (mp 262-263 °C dec).

1,1,2-Trimethylhexahydropyridazinium Tetrafluoroborate (2). A solution of 0.54 g (4.74 mmol) of **5** in methylene chloride was added over 10 min to a vigorously stirred suspension of 0.71 g (4.79 mmol) of trimethyloxonium tetrafluoroborate in 5 mL of methylene chloride. After the solution was stirred overnight the solvent was removed by rotary evaporation, giving 0.9 g of residue. Crystallization from ethanol-ethyl acetate gave 0.8 g (78%) of **2**: mp 274-275 °C dec;[15] ^1H NMR (acetone-d_6) δ 1.5-2.2 (m, 4 H), 2.75 (s, 3 H), 2.95-3.2 (m, 2 H), 3.3 (s, 6 H), 3.6-3.9 (m, 2 H); IR (KBr) 2860-3000, 1430-1500, 1020-1150 (BF_4^-) cm^{-1}.

1,1,2-Trimethyl-1,2,3,6-tetrahydropyridazinium Tetrafluoroborate (3). This was prepared and purified as for **2**, from 0.7 g (4.73 mmol) of trimethyloxonium tetrafluoroborate and 0.53 g (4.7 mmol) of **6**, giving 0.82 g (81%) of **3**; mp 218-219 °C dec;[15] ^1H NMR (CD_3CN) δ 2.7 (s, 3 H), 3.08 (s, 6 H), 3.51 (m, 2 H), 4.00 (m, 2 H), 5.8 (m, 2 H); IR (KBr) 3020, 2940, 1630, 1080 (BF_4^-) cm^{-1}.

Variable-Temperature NMR Experiments

Solutions of **1** and **2** were approximately 0.5 M in substrate in acetone-d_6. A mixed solvent of 7:3 v/v acetone-d_6/acetonitrile-d_3 was required for the 0.25 M sample of **3** employed. The coalescence temperature data were recorded and analyzed, as in previous work,[1,3] on a Varian XL-100 spectrometer operating in the FT mode. Total line shape analysis used program NMRSIM (written by M. Chen), and activation parameters and statistical error parameters employed program DEEJAY written by G. R. Weisman. Computations were carried out on a Harris/7 computer.

The measurements of broadening at C_6 at various temperatures were carried out on a JEOL FX-200 spectrometer operating in the FT mode. The experiments on **2** (300 mg in 2.5 mL of acetone-d_6) were measured with a digital resolution of 0.06 Hz per point, and those on **3** at 0.10 Hz per point. Spectra were determined every 5 °C between -55 and -90 °C to find the point of maximum broadening, the peak width at half-height was measured visually from expanded spectra for C_6 and nonbroadened peaks, and the temperature of maximum broadening (±2 °C) was determined from a plot of the difference vs. temperature.

Acknowledgment. We thank the National Institutes of Health for financial support under Grant GM25428 and the National Science Foundation Major Instrument program for funds used in the purchase of the spectrometers employed in this work. We also thank David F. Hillenbrand for help in using the NMR equipment.

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[15] A satisfactory C, H, N analysis was obtained from Spang Microanalytical Laboratories, Eagle Harbor, MI.

Fluoromethyl Formate. Synthesis, Microwave Spectrum, Structure, Dipole Moment, and Anomeric Effect

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Abstract: Eleven isotopic species of fluoromethyl formate have been synthesized. They were obtained via the decomposition of vinyl fluoride ozonide. The isotopic enrichments were consistent with the postulate that this ozonide upon decomposition produces some fluoromethyl alcohol which reacts further to give fluoromethyl formate. The isotopic species were identified by microwave spectroscopy. Transition assignments were made and rotational and centrifugal distortion constants were determined. Two excited vibrational states of the normal species were also assigned. Principal axes dipole moment components of $|\mu_a| = 0.10$ D, $|\mu_b| = 2.09$ D, and $|\mu_c| = 0.80$ D were determined. These gave a molecular dipole moment of 2.24 (2) D. The structure was determined and detailed parameters were obtained. The heavy atoms (exclusive of fluorine) have the usual cis ester configuration but slight deviations from exact planarity apparently occur ($\tau(OCO_eC)$ is 1.5 ± 1°). The fluorine orientation is approximately perpendicular to the formyl ester plane ($\tau(FCO_eC)$ is 84 ± 1°). This structure and its relationship to the anomeric effect are discussed.

Introduction

Recently, a simple but new compound, fluoromethyl formate (FMF), was identified in our laboratory[1] as a product from the decomposition of 3-fluoro-1,2,4-trioxolane, i.e., vinyl fluoride ozonide (VFO). During the characterization of FMF, we realized that the fluoromethyl group had an exaggerated gauche conformation and estimated that the FCOC dihedral angle was probably 85-90°. This conformation attracted our interest and it motivated us to obtain more detailed bond distances and angles which are reported herein.

This conformation was interesting for at least three reasons. (1) It contrasted with several other recent microwave (MW) reports involving CH_2F groups where the CF bond was coplanar with an adjacent carbonyl group (*cis-* and *trans*-fluoroacetic acid,[2] *cis-* and *trans*-fluoroacetyl fluoride,[2] *trans*-fluoromethylacetone,[3] and *cis,trans*-1,3-difluoromethylacetone.[4,5] (2) The internal rotation angle of the CH_2F groups deviated markedly from the canonical value of 60° for a gauche conformation. (3) The conformation could be correlated to the anomeric effect.[7]

This last reason made it especially attractive to obtain more precise structural parameters. The CH_2F-O- moiety (more specifically, the compound CH_2FOH) has been a prototypal model for extensive MO analyses of the anomeric effect.[7a,8] So far

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[1] Mazur, U.; Lattimer, R. P.; Lopata, A.; Kuczkowski, R. L. *J. Org. Chem.* **1979**, *44*, 3181-3185.

[2] Van Eijck, B. P.; Brandts, P.; Maas, J. P. M. *J. Mol. Struct.* **1978**, *44*, 1-13.

[3] Saegebarth, E.; Krisher, L. C. *J. Chem. Phys.* **1970**, *52*, 3555-3562.

[4] Finnegan, D. J.; Gillies, C. W.; Suenram, R. D.; Wilson, E. B.; Karlsson, H. *J. Mol. Spectrosc.* **1975**, *57*, 363-376.

[5] Reference 4 suggests, along with the gas-phase IR data,[6] that a gauche,gauche form may be more stable than the cis,trans configuration whose MW spectrum was assigned for $CH_2FC(O)CH_2F$.

[6] Crowder, G. A.; Cook, B. R. *J. Mol. Spectrosc.* **1968** *25*, 133-137.

[7] The literature on the anomeric effect is extensive. Two recent reports which contain excellent summaries and lists of references are (a) Wolfe, S.; Whangbo, M.-H.; Mitchell, D. J. *Carbohydr. Res.* **1979**, *69*, 1-26. (b) Szarek, W. A.; Horton, D. Eds.; "Anomeric Effect, Origin and Consequences", ACS Symposium Series No. 87; American Chemical Society: Washington, D.C., 1979.

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detailed experimental data have not been available for the geometrical parameters of this unit.

In order to obtain the structural parameters for FMF, the syntheses of a variety of isotopic species and assignment of their microwave (MW) spectra were necessary. These isotopic analyses provided an auxiliary impetus to the investigation since they could provide information by the technique of isotopic tracers about the curious production of FMF from VFO. It was previously suggested that the synthesis could proceed from reaction of some simple decomposition products of VFO such as HF, H_2CO, HCOF, and possibly HCOOH via the unstable fluoromethyl alcohol, CH_2FOH.[9] This scheme will be discussed subsequently.

Experimental Section

Synthesis. All the isotopic species of FMF were prepared by decomposition of an appropriately labeled sample of VFO. The ozonide was prepared by ozonolysis of neat vinyl fluoride or from mixtures of vinyl fluoride or *cis*-1,2-difluoroethylene with added H_2CO or HCOF. The ozonolysis reactions were run using standard techniques at -115 °C[1,9] with exceptions as noted below.

The VFO was isolated by distilling the ozonolysis products for 20 min through traps held at -78 and -196 °C. The -78 °C trap contained VFO which was allowed to warm to room temperature for 20 min, giving products including FMF as previously discussed.[9] The FMF was isolated by distilling off the CO_2 and SiF_4 with the sample held at -115 °C. The remaining products were then cryopumped into a 3 mm i.d. × 5 cm long capillary tube which was constructed as a bypass inlet to a Varian 920 GLC unit. The material was then quickly vaporized to 25 °C, and the flow was diverted to sweep the material onto a 10 ft × $^3/_8$ in. i.d. (30% DC710 on 80/100 Chromsorb W) Al column. Fractions were collected in U-traps at -196 °C. No decomposition of FMF was noted on the GLC or after isolation.

Isotopic Species. Enriched starting materials were used to prepare samples of VFO labeled at sites predictable by the Criegee mechanism for ozonide formation.[9] The analysis of the enrichment in the subsequent FMF was obtained by MW spectroscopy which can determine the site(s) of enrichment as well as set sensitive limits (≤1%) for the absence of a isotopic species whose spectrum has been assigned. This isotopic information will be noted below where it has implications regarding the mechanism of formation of FMF.

$DC(O)OCD_2F$. The enriched C_2D_3F (~95% D) was prepared by exchange of C_2H_3F with excess NaOD by a procedure described previously.[9]

$DC(O)OCH_2F$. This material was obtained by ozonizing a mixture of CH_2CDF and CH_2CHF. The mixture was obtained by stopping the NaOD exchange reaction before deuteration at the β-carbon sites occurred.[9] Another route to this species involved the reaction of 15 mmol of C_2H_3F, 2 mmol of DCOF, and 1.5 mmol of O_3. The D-enrichment in the CH_2F group of FMF was essentially negligible for both of these syntheses.

$HC(O)OCD_2F$. Mixtures of C_2D_3F and HCOF were ozonized. This also produced FMF-d_3, but no substantive production of FMF containing CHDF or CH_2F groups was observed.

HC(O)OCHDF. A mixture of *cis*-CHF═CHF (5 mmol) and HDCO (98% D, Merck Co., 3 mmol) in 15 mmol of CF_2Cl_2 solvent was ozonized (3 mmol of O_3) at -115 °C. Good yields of VFO were obtained as discussed previously.[9] No $DC(O)OCH_2F$ was detected from this synthesis.

$HC(O)O^{13}CH_2F$. Mixtures of *cis*-CHF═CHF and $H_2{}^{13}CO$ (90% ^{13}C, Merck Co.) in CF_2Cl_2 were ozonized. $H^{13}C(O)OCH_2F$ was not observed by this procedure.

$H^{13}C(O)OCH_2F$. Mixtures of C_2H_3F and $H^{13}COF$ were ozonized. No $HC(O)O^{13}CH_2F$ could be detected in this synthesis. The $H^{13}COF$ used here and the DCOF used in the $DC(O)OCH_2F$ synthesis (cf. above) were prepared from DCOOH or $H^{13}COOH$ (99% D and 90% ^{13}C, respectively, Merck Co.) by the method of Olah and Kuhn.[10] Formyl fluoride was purified from HCl by a combination of trap-to-trap distillation and distillation from KOH pellets at -78 °C.

Table I. Assigned Transitions for the Normal Isotopic Species of Fluoromethyl Formate (in MHz)

transition	Obsd	centrifugal[a] distortion	Dev[b]
3(1,3)-2(0,2)	27 215.68	-0.02	0.07
4(0,4)-3(1,3)	22 141.95	-0.57	-0.07
4(1,4)-3(0,3)	33 212.79	-0.16	0.09
4(1,3)-3(0,3)	39 184.19	-2.20	0.12
5(1,5)-4(0,4)	39 040.83	-0.50	0.02
5(0,5)-4(1,4)	29 854.83	-4.73	-0.10
6(0,6)-5(1,5)	37 494.30	-7.46	-0.04
7(1,6)-6(2,5)	34 430.21	-21.29	-0.08
9(2,7)-8(3,6)	32 564.40	-51.00	0.05
7(1,6)-7(0.7)	18 838.83	-10.78	-0.03
8(1,7)-8(0,8)	22 639.22	-19.33	-0.15
9(1,8)-9(0,9)	26 950.23	-30.83	0.02
10(1,9)-10(0,10)	31 648.07	-44.81	0.04
11(1,10)-11(0,11)	36 590.76	-60.42	0.09
2(2,1)-2(1,2)	23 800.90	-1.06	-0.01
3(2,2)-3(1,3)	24 720.10	-0.38	-0.19
4(2,3)-4(1,4)	25 956.54	0.21	-0.11
5(2,4)-5(1,5)	27 515.00	0.44	-0.05
6(2,5)-6(1,6)	29 398.50	-0.03	0.01
7(2,6)-7(1,7)	31 605.05	-1.59	-0.00
8(2,7)-8(1,8)	34 126.84	-4.65	-0.03
9(2,8)-9(1,9)	36 949.28	-9.58	0.01
3(2,1)-3(1,2)	21 307.54	0.23	0.01
4(2,2)-4(1,3)	20 503.56	1.78	-0.00
5(2,3)-5(1,4)	19 767.48	3.50	0.03
6(2,4)-6(1,5)	19 247.84	4.91	0.02
7(2,5)-7(1,6)	19 085.22	5.19	0.02
8(2,6)-8(1,7)	19 399.13	3.31	-0.03
9(2,7)-9(1,8)	20 285.98	-2.03	0.01
10(2,8)-10(1,9)	21 821.54	-12.43	0.00
11(2,9)-11(1,10)	24 060.28	-29.38	-0.01
12(2,10)-12(1,11)	27 025.71	-54.12	-0.00
13(2,11)-13(1,12)	30 697.15	-87.55	-0.01
14(2,12)-14(1,13)	35 002.12	-126.97	-0.02
15(2,13)-15(1,14)	39 820.52	-171.39	-0.01

[a] The calculated shift due to centrifugal distortion effects.
[b] Deviation = ν(obsd) − ν(calcd) where ν(calcd) = ν(rigid rotor) + ν(cent. dist).

$HC(^{18}O)^{18}OCH_2F$. Enriched ozone was employed. It was prepared from 98% $^{18}O_2$ (BioRad Co.) using a special apparatus. High voltage from a neon-sign transformer was applied to aluminum foil jacket electrodes on a static ozone generator.[11] The ozone was collected on ~3 g of silica gel (Grace Davison Chemical Co., Grade 40, 6–12 mesh) suspended on a glass frit near the bottom of the generator which was cooled to -78 °C. The O_3 production was followed by monitoring the O_2 vapor pressure as it was displaced by O_3 on the silica gel. After the O_3 formation was completed, it was carried into the standard ozonolysis reactor by a stream of dry N_2, simultaneous with slow warming of the silica gel.

$HC(^{18}O)OCH_2F$ and $HC(O)^{18}OCH_2F$. These two species were prepared in approximately the statistically expected amounts by synthesizing O_3 from $^{18}O_2$ (60 atom %) in the static ozone generator.

Spectrometer. The microwave spectra were recorded using a Hewlett-Packard 8460A MRR spectrometer in the region of 18–40 GHz. Pressures of 20–60 mTorr and ambient temperatures were typically used. Frequency measurements were accurate to at least 0.05 MHz. A limited amount of work was also performed with a 80-kHz Stark-modulated spectrometer, which had a klystron source and oscilloscope display.

Spectra. The microwave spectra of the normal species was dominated by strong *b*-dipole, Q-branch series for the ground state and several vibrational satellites, characteristic of a prolate asymmetric top with $\kappa = -0.8492$ and $(A - C)/2 = 3966.99$ MHz. These series were of the type $J'_{K'_{-1},K'_{+1}} \leftarrow J''_{K''_{-1},K''_{+1}}$, where $K'_{-1} \leftarrow K''_{-1}$ were $4 \leftarrow 3$, $3 \leftarrow 2$, $2 \leftarrow 1$, and $1 \leftarrow 0$. Both Q- and R-branch transitions were identified by their frequency, intensity, and Stark effects. Centrifugal distortion effects were apparent. The transitions were therefore fit to three rotational constants and five linear combinations of the τ's using the procedure and program written by Thomas.[12,13] Following common practice, the linear com-

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Table II. Rotational and Centrifugal Distortion Constants (in MHz) for Fluoromethyl Formate

isotope	A	B	C	τ_{aaaa}'	τ_{bbbb}'	τ_{cccc}'	$\tau_{aabb}' = \tau_{aacc}'$	τ_{bbcc}'	no. trans in fit	av dev of fit
$HC(O)OCH_2F$	11195.15	3359.40	3261.16	−0.33584	−0.05505	−0.01212	0.07246	−0.02918	60	0.09
$DC(O)OCH_2F$	10854.59	3728.83	3164.46	−0.28797	−0.04702	−0.01113	0.05653	−0.02548	25	0.05
$HC(O)OCD_2F$	10339.05	3704.13	3179.02	−0.24720	−0.03705	−0.00267	0.05649	−0.01635	15	0.01
$DC(O)OCD_2F$	10042.61	3580.70	3084.60	−0.20109	−0.03823	−0.00904	0.03819	−0.02120	33	0.05
$HC(^{18}O)^{18}OCH_2F$	10460.70	3729.97	3109.02	−0.32147	−0.05348	−0.01166	0.06796	−0.02827	50	0.04
$HC(O)^{18}OCH_2F$	10766.38	3858.67	3223.94	−0.34085	−0.05643	−0.01292	0.06901	−0.03000	27	0.04
$HC(O)OCFHD_8$	10736.89	3798.04	3253.07	−0.31144	−0.04858	−0.01184	0.06398	−0.02804	38	0.07
$HC(O)CFHD_7$	10756.82	3762.19	3186.11	−0.26617	−0.05014	−0.01034	0.05494	−0.02498	25	0.02
$HC(O)^{13}CFH_2$	11102.75	3826.02	3242.34	−0.33854	−0.05333	−0.01188	0.06962	−0.02824	30	0.04
$HC(^{18}O)OCH_2F$	10885.14	3730.08	3145.00	−0.33574	−0.05406	−0.01305	0.06980	−0.02939	27	0.03
$H^{13}C(O)OCH_2F$	11161.13	3810.76	3226.14	−0.38518	−0.05191	−0.01140	0.07399	−0.02711	22	0.07

bination of the τ's which has $\tau_{aabb'} - \tau_{aacc'} = 0$ was chosen.[12] The agreement between the observed and calculated transition frequencies for the R-branch and two Q-branch series are listed in Table I. The entire list of assigned transitions for the normal and the isotopic species is available (Tables S1–S11: Supplementary Material). The effective rigid rotor rotational constants and centrifugal distortion parameters derived for the ground vibrational states of the 11 isotopic species are listed in Table II. The uncertainties in the rotational constants are estimated to be ±0.05 MHz. The distortion constants have uncertainties that are difficult to estimate, especially in cases where the number of transitions is small. They are probably accurate to about 10–20%.

Excited Vibrational States. Transitions for two states excited by one vibrational quantum (hereafter, ω_a and ω_b) were measured and rotational and centrifugal distortion constants were determined (Tables S12–S14: Supplementary Material).

The rotational constants for ω_a were 11442.4, 3803.6, and 3235.5 MHz. It was 96 ± 6 cm^{-1} above the ground state. This was determined from the integrated intensities (peak height × half-width at half-height) using three sets of transitions along with computed line strengths for the ground state and ω_a.

Only Q-branch transitions were assigned for ω_b resulting in reliable values for $\kappa = -0.85042$ and $(A - C)/2 = 3971.5$ MHz. It was 232 ± 18 cm^{-1} above the ground state by comparison of peak heights for four sets of transitions. Since rotational constants and dipole moments were not precisely known for ω_b, they were assumed equal to the ground state in order to obtain the energy difference.

It is thought that ω_a and ω_b arise from excited vibrational states and are not a different conformer owing to the similarity of rotational constants, distortion constants, and dipole moment components to those of the ground state. They probably correspond to the torsional modes about the $O-CH_2F$ and $HC(O)-OCH_2F$ bonds. The study was not extensive enought to rule out the presence of torsional splittings for some of the excited-state transitions such as observed for the gauche form of 3-fluoropropene.[15] However, there were no readily notable "low barrier" effects except for perhaps a somewhat greater shift in the rotational constants for ω_a than ordinarily expected.

All strong lines in the spectra with resolvable Stark effects were assigned to either the three energy levels mentioned (ground, ω_a, ω_b) or to weaker vibrational satellites which were nearly coincident with ground-state transitions. The implications this has on the possible existence of other low-energy conformers will be noted in the Discussion.

Dipole Moment. The quadratic Stark coefficients were measured for nine transitions (Table S15: Supplementary Material). They were analyzed by the method of Golden and Wilson.[16] A minimum of five sets of $\Delta\nu$ (Stark shift) vs. ϵ^2 (electric field) data was used to determine the least-squares value of each Stark coefficient. The electric field was determined by sequential Stark shift measurements on OCS which was simultaneously in the Stark cell with FMF. The $|M| = 0, 1; J = 2 \leftarrow 1$ transitions of OCS were used in the electric field determination.[17] The dipole moment components were $|\mu_a| = 0.10 \pm 0.02$ D, $|\mu_b| = 2.09 \pm 0.01$ D, and $|\mu_c| = 0.80 \pm 0.01$ D. This gave a total dipole moment of 2.24 ± 0.02 D.

Table III. Principal Axis Coordinates (Å) for Fluoromethyl Formate

atom[a]	a	b	c
H_1	1.9804	−0.8966	−0.8266
C_2	1.2792	−0.2754	−0.2469
O_3	1.5039	0.8159	0.1790
O_4	0.1118	−0.9519	−0.1185
C_5	−0.9188	−0.2725	0.5545
F	−1.5796	0.5466	−0.3227
H_7	−1.6027	−1.0264	0.9230
H_8	−0.5351	0.3010	1.3636

[a] See Figure 1 for atom numbering.

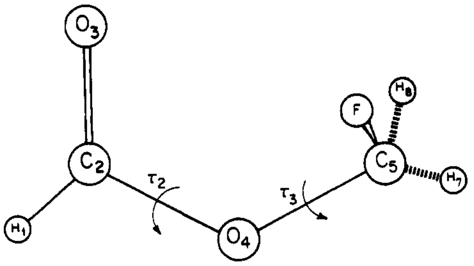

Figure 1. Atom numbering and approximate conformation for fluoromethyl formate.

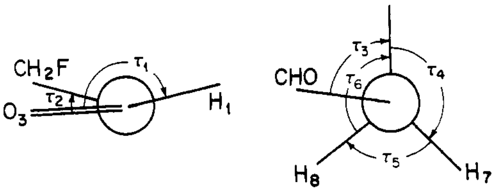

Figure 2. Dihedral angles viewed down C_2O_4 axis (left) and O_4C_5 axis (right). Not to scale.

The dipole moment components of the vibrationally excited state ω_a were also determined by the above procedure (Table S15: Supplementary Material). This resulted in $|\mu_a| = 0.13 \pm 0.02$ D, $|\mu_b| = 1.99 \pm 0.01$ D, $|\mu_c| = 0.83 \pm 0.01$ D, and a total dipole moment of 2.16 ± 0.02 D.

Structure Calculation. FMF has no symmetry elements and so 18 parameters are necessary to completely define the structure. There are 33 moments of interia and 3 center-of-mass and 3 product-of-interia relationships available to determine the parameters. Depending on the choice of isotopic moments and the procedure for analysis, small but nonnegligible differences will occur between structures calculated differently.[18,19] This arises from vibration–rotation interactions which complicate the interpretations of experimental I's rather than from the smaller (usually negligible) contributions from experimental uncertainty.

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(13) As a check on the fitting procedure, the normal species transitions were also analyzed using a computer program obtained from Professor R. Schwendeman which employs the form of Hamiltonian given by Watson.[14] This reproduced the rotational constants to within ±0.03 MHz.

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Table IV. Structural Parameters for Fluoromethyl Formate

bond, Å		bond angle, deg		dihedral angle,[a] deg
H_1C_2	1.100 (3, 10)[b]	$H_1C_2O_3$	125.7 (3, 10)	$\tau_1 = O_3C_2O_4H_1$, 179.0 (10, 20)
C_2O_3	1.194 (15, 3)	$O_3C_2O_4$	125.8 (3, 10)	$\tau_2 = O_3C_2O_4C_5$, 1.5 (10, 5)
C_2O_4	1.355 (20, 3)	$H_1C_2O_4$	108.5 (15, 3)	$\tau_3 = C_2O_4C_5F$, 83.9 (10, 8)
O_4C_5	1.404 (3, 20)	$C_2O_4C_5$	115.8 (3, 5)	$\tau_4 = FO_4C_5H_7$, 118.3 (5, 15)
C_5F	1.369 (10, 12)	O_4C_5F	109.6 (3, 10)	$\tau_5 = H_7O_4C_5H_8$, 120.2 (10, 10)
C_5H_7	1.082 (15, 10)	$O_4C_5H_7$	106.8 (7, 15)	$\tau_6 = H_8O_4C_5F$, 121.5 (15, 8)
C_5H_8	1.066 (10, 15)	$O_4C_5H_8$	111.1 (10, 3)	
		FC_5H_7	109.2 (10, 5)	
		FC_5H_8	109.8 (15, 10)	
		$H_7C_5H_8$	110.2 (7, 3)	

[a] Dihedral angles are illustrated in Figure 2 and defined according to Wilson, Decius, and Cross, "Molecular Vibrations", McGraw-Hill Co., New York, 1955, p 60. [b] Uncertainty estimates are not symmetrical. Within the parentheses, the (plus, minus) deviations are listed for the last parameter digits given.

Table V. Dihedral Angles for Fluoromethyl Groups

compound	technique	dihedral angle,[a] X-C-O-A, deg	ref
$CH_2FOC(O)H$	MW	83.9 (1.0)	
CH_2FOCH_3	MW	69	*d*
	MO	64, 67[b]	*e*
CH_2ClOCH_3	MW	69.6 (2.0)	*f*
	MO	74, 79[b]	*e*
CH_2BrOCH_3	MW	77.5	*g*
CH_2FOH	MO	~60	*h*
		dihedral angle F–C–C=O, deg	
$CH_2FC(O)OH$	MW	0, 180[c]	*i*
$CH_2FC(O)F$	MW	0, 180[c]	*i, j*
$CH_2FC(O)CH_3$	MW	180	*k*

[a] X = F or Cl. A = C or H. cis (or syn) = 0°. [b] Standard geometry and optimized geometry, respectively. [c] Two low-energy conformers; 0° is more stable. [d] Reference 33. [e] Reference 7b. [f] M. Hayashi and H. Kato, *J. Mol. Spectrosc.*, *76*, 412–429 (1979). [g] M. Hayashi, K. Kuwada, and H. Imaishi, *Chem. Lett.*, 913–918 (1974). [h] Reference 8. [i] Reference 2. [j] E. Saegebarth and E. B. Wilson, Jr., *J. Chem. Phys.*, 46, 3088–3098 (1967). [k] Reference 3.

After examining the results from 14 different calculations, it was concluded that the best structure evaluation resulted from a least-squares fitting procedure using all 39 relationships employing either moments of inertia or planar moments of inertia.[18] Such a procedure led to the highest consistency. It employed all the data and appeared to minimize the problems that are well known to occur owing to small coordinates for atoms near to a principal axis. It also distributed the vibration–rotation effects over the entire data set so that they presumably did not accumulate unduly in any single structural parameter. Such a derived structure is called a r_0 or effective structure; it is probably close to the so-called r_z or average structure.[18]

The atom coordinates that resulted from the least-squares fitting procedure of all the moments of inertia are listed in Table III. The program STRFIT was used.[19] The derived bond distances and angles are listed in Table IV. Several projections of the structure are illustrated in Figures 1 and 2. The fit to the observed moments was good (δ_{rms} = 0.009825 amu·Å^2), and the largest deviations occurred for ($I^B_{obsd} - I^B_{calcd}$) for the parent (+0.0099), $^{13}C_F$ (−0.0110), *gem*-d_2 (+0.0073), $^{18}O_{ester}$ (−0.0166), and di-^{18}O (−0.0175) isotopic species.

The uncertainties that are listed in Table IV are partly subjective. They resulted from consideration of the differences for structures derived by the other calculation procedures, the Costain error estimate,[18] the problems associated with small atom coordinates (for example, the ester oxygen *a* and *c*), and the method used for locating the fluorine atom for which no substitution data existed.[20]

It was also considered whether large amplitude vibrational motions could affect the estimated dihedral angle and orientation of the CH_2F group. This usually becomes evident in serious differences for structures derived with different isotopic data. Therefore, the five D_n species provided insight on this question. The hydrogen coordinates in the principal axes system of the normal species could be calculated from differences in moments of inertia using only the normal isotopic data and various combinations of the deuterium data. Both Schwendeman's[19] and Typke's[26] programs were employed. The calculations (11 variations) all led to substitution coordinates or pseudo-Kraitchman[19] coordinates which were within 0.01 Å of those in Table III. Using a different approach, bond shrinkage corrections[19,27] were also applied to the D_n moments of inertia before determining the r_0 structure. This did not affect the structure in Table IV except for changes in all three CH bonds of about 0.007–0.01 Å. It was concluded that abnormal vibrational motions involving the H atoms were not a problem in deriving the structure.

Discussion

Structure. Formate Group. The details of the FMF structure are shown in Table IV and in the two figures. The dihedral angles indicate that the formyl hydrogen (H_1), fluoromethyl carbon (C_5), and the fluorine atoms are all on the same side of the plane defined by the CO_2 fragment. The $C_2O_4C_5F$ dihedral angle (83.9°) indicates that the O_4C_5F plane is nearly perpendicular to the CO_2 plane and tilted toward the carbonyl oxygen.[21]

The formate group (HC(O)O) and the $O_3C_2O_4C_5$ group both appear to have small deviations from strict planarity. However, the position of the light H atom is not well determined by the data. A planar formate group resulted from some structure calculations and cannot be strongly ruled out. The nonplanarity of the $O_3C_2O_4C_5$ group seems more definite since none of the structure calculations resulted in a planar group. In this case, all four atoms are heavy, and small deviations from planarity will affect the moments more readily. Of course, the orientation of the CH_2F group introduces asymmetric electronic interactions and there is no symmetry reason for the HC(O)OC atoms to be constrained to a common plane.

The orientation of C_5 cis (syn) to the carbonyl is consistent with results for most carboxylic esters. This field has been reviewed[22] and a number of recent conformational studies have been made by Bohn.[23] The preference for a cis configuration has also been documented by MO calculations for simple esters.[24]

The bond lengths and angles in the HC(O)O group of FMF are close (±0.01 A, ±1°) to the values in methyl formate[25] except for C_2–O_4 (1.334 (10) Å). The small lengthening of this bond in FMF (1.355 Å) suggests a decreased interaction of the ester oxygen with the HC(O) group. This would correlate with the increased interaction of this oxygen with the CH_2F group (anomeric effect) to be discussed below.

Conformation and Anomeric Effect. Fluoromethyl Group. There have been a few experimental determinations of the dihedral angle, F–C–O–A (and XCOA) involving a CH_2F (or CH_2X) group. There have also been several estimates by ab initio MO calculations. Table V summarizes these results along with several dihedral angles for CH_2F groups attached to a carbonyl carbon. It is seen that molecules with the CH_2F–O– group have a gauche (or synclinal) configuration while those with the CH_2F–C(O)–

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(20) For example, the Kraitchman single substitution procedure or the pseudo-Kraitchman procedure[19] (fitting to differences in moments, $I_{parent} - I_{subst.}$) deviated as much as 0.02–0.04 Å for bond distances $C_{(2)}$–$O_{(3)}$, $C_{(1)}$–$O_{(3)}$, and $C_{(1)}$–F. This is traceable to errors involved in determining several small coordinates involving these atoms. The substitution procedure is known to break down in such cases, and it is reasonable to weight such structures less.

(21) A more precise phraseology is that the planes defined by $C_{(2)}O_{(4)}C_{(5)}$ and $O_{(4)}C_{(5)}F$ are nearly perpendicular (83.9°). The small tilting of the $O_{(4)}C_{(5)}F$ plane from 90° to 83.9° is toward the carbonyl side of the $C_{(2)}$-$O_{(4)}C_{(5)}$ plane. Following the IUPAC nomenclature, the CH_2F group is synclinal to the $C_{(2)}O_{(4)}$ bond.

(22) Jones, G. I. L.; Owen, N. L. *J. Mol. Struct.* **1973**, *18*, 1–32.

(23) The most recent study in this series is Thomas, L. P.; True, N. S.; Bohn, R. K. *J. Phys. Chem.* **1980**, *84*, 1785–1789.

(24) (a) John, I. G.; Radom, K. *J. Mol. Struct.* **1977**, *36*, 133–147. (b) Lester, D. A.; Owen, N. L.; Palmieri, P. *Ibid.* **1976**, *31*, 411–413.

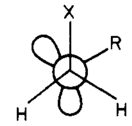
(25) Curl, R. F., Jr. *J. Chem. Phys.* **1959**, *30*, 1529–1536.

(26) Typke, V. *J. Mol. Spectrosc.* **1978**, *69*, 173–178.

(27) Laurie, V. W.; Herschbach, D. R. *J. Chem. Phys.* **1962**, *37*, 1687–1693.

group often (but not always[5]) prefer a cis or trans (i.e., syn periplanar or anti periplanar) configuration. The interactions which lead to this contrast can be analyzed by an MO procedure such as described by Epiotis et al.[28] For the $CH_2FC(O)$ system, the planar heavy atom arrrangement results from π interactions involving suitable filled orbitals of the F and CH_2 group with the empty π^* orbital of the carbonyl. In the case of the CH_2FO system, the important interaction involves n_{oxygen} and σ^*_{CF}. The gauche conformation results from the overlap of these σ orbitals.

This n-σ^* interaction has become a widely accepted rubric for interpreting the anomeric effect,[7] i.e., structure and conformational effects arising when a carbon is covalently bonded to two or three more electronegative atoms particularly when one of them is an oxygen or nitrogen.[29] For many chemists, the interaction is often visualized by a CX bond antiperiplanar to a sp^3 lone pair on oxygen or sulfur. This lines up the n–σ^* orbitals and rationalizes a gauche conformation with a nominal 60° dihedral angle between CX and OR. The high value of 84° for the dihedral angle in FMF may therefore appear curious, and this should be more fully analyzed by MO calculations.



However, calculations for some simpler species suggest how the anomeric effect contributes to determining this angle. In both CH_2FOH[7a] and CH_2FOCH_3[8b] the orbital interactions involving the oxygen atom and the CF bond have energy minima at $\sim 90°$[30] although the overall energy minima are at $\tau \sim 60°$ and 67°, respectively. The positions of the overall minima are determined by all the electronic interactions and contain the influence of the additional factors such as steric effects, dipole–dipole effects, etc., which collectively determine the equilibrium dihedral angles. Extending these concepts to FMF, the exaggerated gauche conformation would naturally result from a strengthening of the orbital or anomeric interaction which prefers a conformational minimum near $\tau_3 = 90°$ and/or changes in the other factors which lead to a minimum at a smaller τ. Obviously the carbonyl bond is the perturbation which leads to the contrast between FMF and compounds like CH_2FOH perhaps because of its high polarity or its ability to also interact with the ester n_O.

Regular changes in the O–C(X) and C–X bond lengths are also often associated with the anomeric effect.[7a,8b,31,32] The O–C(X) bond is usually shorter, and this trend is also apparent in FMF where the O_e–C(F) bond distance of 1.404 Å can be compared to 1.437 Å in methyl formate.[25] From the interaction of σ^*_{CF}, a long CF bond might also be expected as suggested by theoretical calculations for CH_2FOH[7a] and CH_2FOCH_3[8b] and the limited amount of experimental data for CH_2FOCH_3 (1.394 Å)[33] and for a pyranosyl fluoride with an axial CF bond (1.389 Å).[34] However, there does not appear to be a lengthening effect in FMF. Its CF bond distance falls between CH_3F (1.383 Å)[35] and CH_2F_2 (1.357 Å).[36] The implications of this are unclear and speculation seems unwarranted without any MO data. However, it has already been pointed out that the variations in the two-bond distances associated with the anomeric interaction arise from competing effects and in some cases both bonds have become shorter.[7a]

The values for the CH parameters of the CH_2F group are also curious but they may not be germane to the anomeric interaction. It is interesting that the relationship of Flood, Pulay and Boggs[37] for the HCO angles in methanol as a function of dihedral angle when applied to FMF predicts valence angles of $O–C–H_7 = 107.3°$ and $O–C–H_8 = 112.3°$, in good agreement with the values in Table V. This would imply that bond–bond interactions between the O_4–C_2 and C–$H_{7,8}$ bonds are factors in determining these angles.[38]

Dipole Components. The observed dipole components ($|\mu_a|$, $|\mu_b|$, $|\mu_c|$) = (0.10, 2.09, 0.80 D) can be approximately reproduced by a model which vectorily sums the group moments arising from the formate and fluoromethyl fragments. The group moments for these fragments were estimated from methyl formate[25] and ethyl fluoride.[40] The dipole moment of methyl formate was transferred to the principal axes system of the FMF with the same orientation relative to the CO_2 group in both species. Likewise the dipole moment of ethyl fluoride was used with the same orientation relative to the CCF and OCF planes in both species. The dipole components from methyl formate (1.397, 1.207, 0.067) and ethyl fluoride (−1.090, 1.235, −0.994) sum to give values (0.307, 2.442, −0.927) which roughly reproduce the observed values. This suggests that (in the coordinate scheme of Table III) the negative end of the μ_b and μ_c components are along the $+b$ and $-c$ directions, respectively, while the low μ_a component is due to the cancellation of two relatively large, opposing components. The approximate agreement furnished by this model intimates that the electronic effects on the bonding associated with the anomeric effect probably has only a small effect (≤20%) on the dipole moment.

Other Conformers. The model just discussed can also be used to estimate the dipole components for other conformers of FMF. This is helpful to explore if any conformers could be present in appreciable concentrations but which might have accidentally small dipole components. Such isomers could go undetected in the assignment of a MW spectrum since the intensity of a transition is proportional to the square of the dipole component involved.

Since only cis esters (i.e., syn, $\tau_2 = 0$) have been generally observed, the discussion can be restricted to forms involving rotation about the O_e–C(F) bond ($\tau_2 = 0$, τ_3 variable). It can be seen qualitatively in Figure 1 that the rotation which brings the CF bond syn ($\tau_3 = 0°$) to the C_2O_4 bond should increase the dipole moment while an anti orientation ($\tau_3 = 180°$) should decrease it. Calculations substantiate this and lead to small values for the dipole components of an anti conformer (0.32, 0.41, 0.00 D, respectively).

Because of the extensive assignment work on the MW spectra of FMF, it is reasonable to assume that a conformer would have been detected if its strongest transitions were about $^1/_{15}$th the

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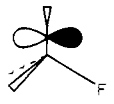
(28) Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R.; Bernardi, F. "Structural Theory of Organic Chemistry"; Springer-Verlag: Berlin, 1977.

(29) The term "anomeric effect" was originally coined in carbohydrate chemistry and refers to the tendency of an electronegative substituent at C-1 of a pyranoid ring to assume the axial rather than equatorial orientation. However, the interpretation of this phenomenon has extended its usage to many other systems, including noncyclic compounds. See ref 7.

(30) The strong interaction at 90° can be visualized using the orbital decomposition of Wolfe et al. for CH_2FOH.[7a] The two lone pairs on the oxygen are considered energetically different; i.e., one more s-like, the other more p-like. For $\tau = 90°$, the p-orbital lone pair is perpendicular to the COH plane and eclipses the CF bond.



(31) Jeffrey, G. A.; Pople, J. A.; Radom, L. *Carbohyd. Res.* **1972**, *25*, 117–131.

(32) Romers, C.; Altona, C.; Buys, H. R.; Havinga E. *Top. Stereochem.* **1969**, *4*, 39–97.

(33) Nakagawa, J.; Hayashi, M. *Chem. Lett.* **1976**, 349–350.

(34) The compound is 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl fluoride. The result is taken from Table 3 in ref 8b where it is attributed to Kothe, G.; Luger, P.; Paulsen, H. *Acta Crystallogr.*, in preparation. See also Paulsen, H.; Luger, P.; Heiker, F. R., Chapter 5, ref 7b.

(35) Clark, W. W.; DeLucia, F. C. *J. Mol. Struct.* **1976**, *32*, 29–36.

(36) Hirota, E.; Tanaka, T. *J. Mol. Spectrosc.* **1970**, *34*, 222–230.

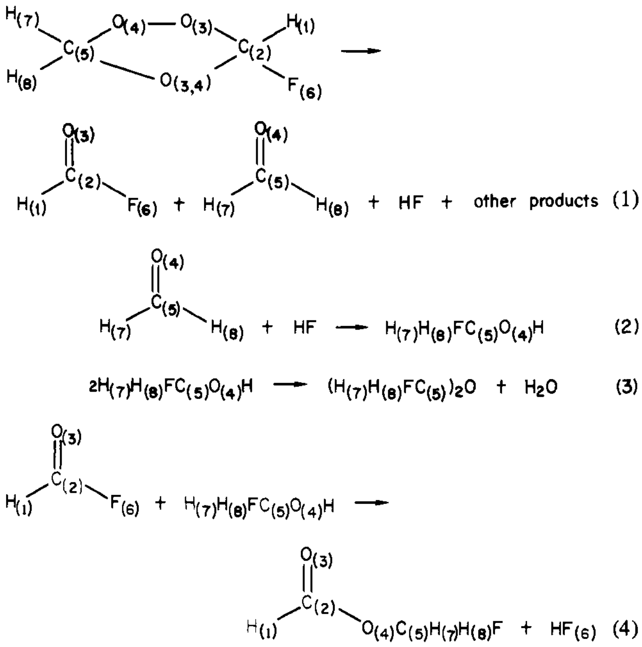
(37) Flood, E.; Pulay, P.; Boggs, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 5570–5574.

(38) Their model also predicts differences between the CH bond lengths of about 0.005–0.010 Å. This is smaller than the differences of 0.016 Å in FMF although the error estimates make the significance of this large difference debatable. Also, it has been recently shown that when harmonic corrections are made to moments of inertia, an apparent difference between CH bond distances can sometimes be removed although nonequal bond angles still persist.[39]

(39) Zeil, W.; Christen, D. *J. Phys. Chem.* **1980**, *84*, 1790–1792.

(40) Kraitchman, J.; Dailey, B. P. *J. Chem. Phys.* **1955**, *23*, 184–190.

Scheme I



intensity of the assigned form. Hence, any conformer such as the syn species which has dipole components equal to or greater than the observed form must be at least 1.7 kcal higher in energy.

The possibility of an anti form which is low in energy is more difficult to exclude. The estimated dipole components and sensitivity limits make it unlikely that an anti conformer exists which is more than 0.2 kcal lower than the assigned form. However, an anti form of nearly the same or moderately higher energy cannot be definitively eliminated. This, however, would be surprising since MO calculations on related systems (CH_2FOH, CH_2FOCH_3)[7a,8a,b,e] indicate that the anti form is higher by 3–12 kcal.

Synthesis. The curious synthesis of FMF can be rationalized if the decomposition of VFO producs HCOF, H_2CO, and HF which react according to Scheme I to produce FMF and bis(fluoromethyl) ether, $(CH_2F)_2O$. The decomposition of VFO produces only minor amounts of isolatable HCOF, H_2CO, and HF (detected as SiF_4), and the yields of FMF and $(CH_2F)_2O$ are also typically below 5%.[1] The major products are CO_2 (~40%) and a viscous residue which has not been completely characterized. Owing to the lack of precise information on a sizable fraction of the products, it is speculative to discuss a detailed mechanism for the decomposition of the VFO such as that described for the primary ozonide of ethylene.[41] Nevertheless, it is attractive to propose that the simple products HCOF, H_2CO, HF, and perhaps some HCOOH as well are involved in the production of the small amounts of FMF and $(CH_2F)_2O$. Three additional facts have a bearing on this proposal. (1) The two reported syntheses of $(CH_2F)_2O$ involve HF and $(CH_2O)_n$.[42] (2) The isotopic labeling in FMF reported here (vide supra) are in perfect agreement. For example, ^{13}C enrichment at C_2 or C_5 in VFO leads exclusively to enrichment at C_2 or C_5, respectively, in FMF in accordance with reactions 2 and 4. The same tracking occurs for deuterium enrichment at the sites H_1, H_7, and H_8 for VFO and FMF. (3) The bis(fluoromethyl) ether produced from decomposition of VFO with deuterium enrichment at H_1 contains no D-labeling[9] consistent with reaction 3.

This proposal could be considered on very firm ground if the ester and ether could also be produced from mixtures of HF, H_2CO, and HCOF (or HCOOH). Such syntheses using mixtures of aqueous HF, H_2CO, and HCOOH have not been successful.[9] However, the attempts were a poor reflection of the actual reaction conditions and concentrations during decomposition of VFO, and so the negative results are not considered a categorical impairment to the proposed scheme.

Acknowledgment. This work was supported by Grants CHE76-09572 A01 and CHE-8005471 from the National Science Foundation. We are grateful to Mr. Kurt Hillig for assistance with the O_3 generator and for other informative discussions, to Mr. Donald Borseth for checking the centrifugal distortion calculations, and to Dr. Ursula Mazur for discussions on various experimental aspects during the early stage of this study.

Supplementary Material Available: Tables S1–S11, transition frequencies for the 11 isotopic species; Tables S12–S14, frequencies and rotational constants for the excited vibrational states; Table S15, Stark coefficients (16 pages). Ordering information is given on any current masthead.

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(41) (a) Herron, J. T.; Huie, R. E. *J. Am. Chem. Soc.* **1977**, *99*, 5430–35. (b) Martinez, R. I.; Huie, R. E.; Herron, J. T. *Chem. Phys. Lett.* **1977**, *51*, 457–60.

(42) (a) Weinmayer, V. *J. Org. Chem.* **1963**, *28*, 492–494. (b) Olah, G. A.; Mateescu, G. D. *J. Am. Chem. Soc.* **1971**, *93*, 781–782.