solutions from the results of Pellin et al.[34] and the data in Figures 8 and 9. The magnitude of these internal conversion rates for the linked pair in its folded configuration in methylene chloride suggests that charge transfer (CT) rather than molecular motion is involved in the relaxation process. In this connection it is of interest to note that Netzel et al.[51,52] postulated the formation of charge-transfer states on photoexcitation of the asymmetric species, cofacial diporphyrins, in solutions of methylene chloride and methylene chloride + 0.1 M $[N(C_2H_5)_4]Cl$. For the latter solution the charge-transfer state was represented as $Cl^-Mg^{+}\cdot H_2^{-}\cdot$,[51] with a lifetime for this state of 630 ± 20 ps. It was suggested that complexation of the central Mg by Cl^- reduced the electrostatic attraction between the $Mg^{+}\cdot$ and $H_2^{-}\cdot$ relative to the CT product formed when the Cl^- ion is absent. The lifetime of the CT product in methylene chloride has been reported to be $\tau = 380 \pm 40$ ps, corresponding to $k_{ic} \cong 2.6 \times 10^9\ s^{-1}$;[51] and $\tau \cong 200$ ps, corresponding to $k_{ic} = 5 \times 10^9\ s^{-1}$.[52,53] No specific role was assigned to methylene chloride by these workers. It is difficult to account for our observations without concluding that there are strong specific interactions between the methylene chloride and the linked Pchlide *a* macrocycles.

Registry No. P700, 53321-11-2; bis(pyrochlorophyllide *a*)ethylene glycol diester, 67582-80-3.

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A Microwave Study of Perfluoroethylene Oxide

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Abstract: Assignment of the microwave spectra of the normal, oxygen-18, and carbon-13 isotopic species of perfluoroethylene oxide has given a complete structure. The molecular parameters are r(CO) = 1.391 (2) Å, r(CC) = 1.426 (4) Å, r(CF) = 1.329 Å (2), θ(CCO) = 59.17 (8)°, and θ(FCF) = 109.01 (19)°. The dipole moment was found to have a value of 0.576 (5) D. A vector analysis of a number of fluorinated oxiranes indicated that the oxygen atom is at the negative end of the molecule. Microwave spectra of three low-lying vibrational states were assigned, and their energies were determined from relative intensity measurements to be 226 (17) and 306 (17) cm^{-1} for the symmetric vibrations and 182 (23) cm^{-1} for the asymmetric vibration. The shortening effect of fluorine substituents upon the ring bonds which was established earlier for *cis*-1,2-difluoroethylene oxide is also found with perfluoroethylene oxide. However, the vicinal fluorine–fluorine nonbonded distance is almost 0.2 Å longer than the value of 2.7 Å consistently observed for other fluorocarbons. Structural trends established both theoretically and experimentally for the oxiranes and other fluorocarbons are used to predict unknown structures of fluorinated oxiranes.

A number of experimental and theoretical investigations into the structure of substituted three-member ring systems have been conducted.[1-14] Microwave spectroscopy has been used to determine the structures of some fluorinated three-member ring systems, including cyclopropanes[1-5] and oxiranes.[6-9] These systems provide data for testing the various theoretical approaches used to predict substituent effects on structure.

In their work on cyclopropanes, Deakyne, Allen, and Craig[10] found that charge density difference plots could be used to qualitatively predict the changes in ring geometry with fluorine substitution. This technique was found to be useful since Mullikan overlap populations did not predict bond lengths well and correlation diagrams are complicated for large systems. Their treatment explained for the first time several observed changes in the cyclopropane ring of 1,1-difluorocyclopropane and *cis*,-*cis*-1,2,3-difluorocyclopropane. In addition, they proposed a simple additivity principle that allows the prediction of ring bond changes for multiply substituted systems from the changes for less substituted systems.

By this method the effect of 1,1,2,2-tetrafluoro substitution was determined from the experimentally observed changes upon 1,1-difluoro substitution. No change in the C(1,2)–C(3) bond is predicted. The C(1,2)–C(3) bond of *cis*-1,2-difluorocyclopropane was also predicted to remain unchanged. Skancke and Boggs[12] used ab initio calculations to predict the structures of *cis*- and *trans*-1,2-difluorocyclopropane, and they also predict a virtually unchanged C(1,2)–C(3) bond length. This is contrary to the commonly observed shortening of carbon–carbon bonds adjacent to the site of fluorine substitution. Only a partial structure of 1,1,2,2-tetrafluorocyclopropane has been reported,[3] and the question of C(1,2)–C(3) bond length change has not been resolved.

The structure of *cis*-1,2-difluoroethylene oxide was determined by microwave spectroscopy and compared with the structure of ethylene oxide.[6] It was found that all the ring bonds shorten and

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Table I. Rotational Transitions (MHz) of the Normal Isotopic Species of CF_2CF_2O

transition	ν_{obsd}	$\nu_{obsd} - \nu_{calcd}$[a]
$2_{11}-3_{21}$	19470.80	0.07
$2_{20}-3_{22}$	23 896.67	0.04
$2_{21}-3_{31}$	24 008.20	0.04
$3_{03}-4_{13}$	23 323.70	0.06
$3_{21}-4_{31}$	28 235.29	0.04
$3_{22}-4_{32}$	28 725.93	0.03
$3_{30}-4_{40}$	32 619.61	−0.05
$3_{31}-4_{41}$	32 635.41	−0.02
$4_{04}-5_{14}$	29 630.63	0.02
$4_{13}-5_{23}$	29 109.70	0.01
$4_{14}-5_{24}$	31 693.40	0.04
$4_{22}-5_{32}$	32 426.19	0.04
$4_{23}-5_{33}$	33 622.18	0.02
$4_{31}-5_{41}$	37 108.29	−0.02
$4_{32}-5_{42}$	37 211.51	−0.04
$5_{14}-6_{24}$	34 579.02	−0.07
$5_{05}-6_{15}$	36 201.21	0.01
$5_{23}-6_{33}$	36 646.20	−0.06
$5_{15}-6_{25}$	37 557.82	−0.05

[a] ν_{calcd} obtained from a rigid rotor fit.

the F–C–H group tilts slightly which places the fluorine atoms closer together. In the same work it was found that an extension of Hoffman's electron donor–acceptor scheme to oxiranes does not satisfactorily explain the observed changes in the ring bonds. Although the treatment of cyclopropane by Deakyne, Allen, and Craig was not directly applicable, it was suggested that a similar approach may explain ring bond changes on fluorine substitution in the oxiranes.[6]

Recently, Deakyne, Cravero, and Hobson[11] have used a combination of overlap density difference plots obtained from ab initio wave functions to examine substituent effects in the oxiranes. They are able to rationalize the observed effect on the ring bonds of *cis*-1,2-difluoroethylene oxide. For perfluoroethylene oxide, they predict that the C–O and C–C bonds will shorten.

The study of the microwave spectrum of perfluoroethylene oxide was undertaken to determine the molecular structure, and hence the effect of increasing fluorination upon the ring bonds in the oxirane series. In the course of this investigation, the electric dipole moment of perfluoroethylene oxide was determined. The vibrational energies and symmetries of the lowest three vibrational states were determined. From isotopic data a complete structure of perfluoroethylene oxide has been determined and interpreted in terms of the known structures of similar molecules and theoretical work of current interest.

Experimental Section

The normal isotope of perfluoroethylene oxide was synthesized by the reaction of perfluoroethylene with ozone at 273 K with use of techniques developed in this laboratory.[15] The major products, perfluoroethylene oxide and carbonyl fluoride, and unreacted perfluoroethylene and ozone were collected in a 77 K trap after distillation of $CF_2ClCFCl_2$ solvent through 178 K and 142 K traps. Aqueous KI was used to remove carbonyl fluoride and ozone. The resulting CO_2 was adsorbed onto Ascarite. Addition of bromine removed the unreacted olefin. The known gas-phase IR spectrum was used to characterize perfluoroethylene oxide.[16] A millimole scale ozonator was used to produce oxygen-18 ozone from a small amount of 99.45 atom % O-18 enriched molecular oxygen, obtained from Prochem. The isotopically enriched ozone was adsorbed onto silica gel, and the reaction and workup were then carried out as for the normal isotope.

A Hewlett-Packard 8460A spectrometer was used to observe the spectrum of the normal isotope in the region from 18 to 40 GHz. The dipole moment was determined by using one Stark modulator and an HP3440A digital voltmeter to measure the ground-to-base voltage of the applied square wave. The J = 2–3 transition of OCS was used to calibrate the Stark cell.[17] The oxygen-18 isotopic species was examined with an HP-8400C microwave spectrometer in the region 26.5 to 40 GHz. Transition frequencies were measured to an accuracy of 0.05 MHz.

Table II. Rotational Transitions (MHz) of the Oxygen-18 Isotopic Species of CF_2CF_2O

transition	ν_{obsd}	$\nu_{obsd} - \nu_{calcd}$[a]
$3_{21}-4_{31}$	27 684.77	0.09
$3_{22}-4_{32}$	28 140.66	0.06
$3_{30}-4_{40}$	31 886.89	−0.01
$3_{31}-4_{41}$	31 901.15	−0.04
$4_{13}-5_{23}$	28 620.80	0.01
$4_{04}-5_{14}$	29 071.69	0.05
$4_{14}-5_{24}$	31 091.24	0.07
$4_{22}-5_{32}$	31 854.79	0.02
$4_{23}-5_{33}$	32 972.82	0.01
$4_{31}-5_{41}$	36 341.10	−0.03
$4_{32}-5_{42}$	36 435.16	−0.03
$5_{14}-6_{24}$	33 980.70	−0.03
$5_{05}-6_{15}$	35 498.80	−0.04
$5_{23}-6_{33}$	36 041.01	−0.06
$5_{15}-6_{25}$	36 843.34	−0.02
$5_{24}-6_{34}$	38 014.62	−0.02

[a] ν_{calcd} obtained from a rigid rotor fit.

Table III. Rotational Transitions (MHz) of the Carbon-13 Isotope of CF_2CF_2O

transition	ν_{obsd}	$\nu_{obsd} - \nu_{calcd}$[a]
$3_{22}-4_{32}$	28 708.44	−0.07
$3_{30}-4_{40}$	32 615.84	0.05
$4_{04}-5_{14}$	29 562.94	0.04
$4_{22}-5_{32}$	32 402.94	0.04
$4_{23}-5_{33}$	33 590.83	−0.06
$5_{14}-6_{24}$	34 507.49	0.01
$5_{05}-6_{15}$	36 119.58	−0.02

[a] ν_{calcd} obtained from a rigid rotor fit.

Table IV. Rotational Constants of CF_2CF_2O[a]

	CF_2CF_2O	$CF_2CF_2O^{18}$	$^{13}CF_2CF_2O$
A	4336.504 (3)[b]	4234.506 (4)	4336.697 (8)
B	2553.987 (3)	2518.130 (3)	2547.489 (6)
C	1949.829 (8)	1949.794 (9)	1946.067 (19)

[a] Obtained from a least-squares fit of the transitions listed in Tables I, II, and III to a rigid rotor model. [b] Error is one standard deviation of the fit.

The carbon-13 isotopic species was studied in natural abundance. In order to increase the system sensitivity, the R-band source of the HP-8400C spectrometer was coupled to a 10-ft Stark cell cooled to dry ice temperature. The system employed 95-kHz Stark modulation and utilized the HP 422A crystal with a 95-kHz tuned preamplifier and an HR-8 lock-in amplifier. A Cromemco Z-2D computer was used to determine the frequencies of weak transitions with an accuracy of 0.05 MHz.

Results

Analysis of Spectra. The spectrum of perfluoroethylene oxide is sparse with relatively weak c-type transitions. The low J transitions of the normal and oxygen-18 isotopic species were identified by their Stark effect. The 19 transitions used in the least-squares fit of the normal isotopic rotational constants are given in Table I. Sixteen transitions were observed for the fit of the oxygen-18 rotational constants. These frequencies are presented in Table II. The assignments of both species were confirmed by relative intensities and the goodness of the rigid rotor fits. Table IV lists the rotational constants obtained from these fits.

Several vibrational satellites of the normal isotope were observed, and the rotational spectra and symmetry of the strongest three were assigned. The transition frequencies and the rotational constants obtained from the rigid rotor fit for these three excited vibrational states are given in Table V. The energy and symmetry

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Table V. Rotational Transitions and Constants (MHz) for Vibrational Satellites of CF_2CF_2O

transition	V(1)	V(10)	V(100)
$3_{22}-4_{32}$	28 731.40	28 715.03	28 735.63
$3_{21}-4_{31}$	28 241.65	28 242.74	28 229.57
$3_{30}-4_{40}$	32 630.92		
$3_{31}-4_{41}$			32 617.29
$4_{13}-5_{23}$	29 105.60	29 013.77	29 189.64
$4_{04}-5_{14}$		29 467.89	
$4_{14}-5_{24}$	31 691.46		
$4_{22}-5_{23}$	32 430.92	32 421.19	32 430.95
$4_{23}-5_{33}$	33 625.43	33 581.81	33 656.24
$5_{05}-6_{15}$	36 191.46	36 001.43	
$5_{14}-6_{24}$	34 571.17	34 425.34	34 706.89
$5_{23}-6_{33}$	36 648.32	36 612.40	
constants[a]			
A	4 338.173 (5)[b]	4 341.072 (7)	4 332.915 (6)
B	2 553.035 (3)	2 540.444 (4)	2 565.080 (4)
C	1 949.315 (9)	1 949.100 (11)	1 950.198 (15)

[a] Rotational constants obtained from least-squares fit to a rigid rotor model. [b] Error represents one standard deviation of the fit.

of the vibrational states were determined from the relative intensities of selected transitions at dry ice and room temperatures.[18] These results are presented in Table VI. Each value represents the average taken for three transitions. The errors of the resulting energies are derived from the standard deviation of all the relative intensity measurements. The vibrational assignment[16] predicts that 5 normal modes will be populated to greater than 2% of the ground state at dry ice temperature and 10 normal modes will be populated to greater than 2% at room temperature. Nevertheless, the spectrum is not crowded and it seemed possible to observe the C-13 spectrum in natural abundance of 2%.

Because of the high degree of symmetry in the molecule, the partial structure obtained from the rotational constants of the normal and oxygen-18 isotopic species left only the *a* coordinates of the carbon and fluorine atoms not uniquely determined. Since the *a* coordinate of the carbon atom is one-half the carbon–carbon bond distance, a reasonable value could be chosen and the *a* coordinate of the fluorine atoms was calculated. From this structure, rotational constants were calculated for the normal and carbon-13 isotopes, and a correction was derived from the experimental and calculated values for the normal isotope. The carbon-13 spectrum was then predicted from the corrected rotational constants. Frequency measurements were made for all weak lines near the predicted frequency. Stark effects were used to aid in the identification of the transitions. Intensity measurements at different temperatures were used to rule out weak vibrational satellites. The seven transitions used in the rigid rotor fit are given in Table III. The rotational constants obtained from this fit are presented in Table IV.

Structure. The C_{2v} symmetry of the molecule is confirmed by a number of pieces of experimental evidence. The presence of only *c*-type transitions indicates that the molecule has a C_2 axis of symmetry. With use of the notation $K_{-1}K_1$, transitions of the type ee–oe and eo–oo are allowed.[19] From the spin statistics, it is found that equivalent nuclei cause a change in the population of states that are symmetric to 180° rotation.[18] Therefore, since transitions of the type ee–oo were less intense than predicted, the two pairs of trans fluorine atoms and the two carbon atoms must be equivalent. The calculated statistical weights of 10 to 6 were in agreement with the experimental results as can be seen in the analysis of the vibrational states. The negligible change in the *C* rotational constant between the normal and O-18 isotopic species indicates that the oxygen atom lies on the *c* axis. The small change in the *A* rotational constant between the normal and carbon-13 isotopes indicates that the carbon atoms lie very close to the *a* axis of the molecule.

The program STRFIT developed by Schwendeman[20] was used to calculate the structure of the molecule in three different ways. The atomic coordinates were fit to the second moments of the three isotopic species and the only nontrivial center of mass condition along the *c* acix by a least-squares routine, giving the r_0 structure presented in Table VII. The errors given are the uncertainty of the fit. Since no isotopic substitution is possible for the fluorine atoms, only a partial r_S structure is possible. Because the carbon atom lies so close to the *a* axis, the Kraitchman calculation for C-13 substitution does not give a real value for the *c* coordinate of the carbon atoms, and so only the isotopic substitution of the oxygen atom is used in the second structure. The resulting structure, designated r_S(I) in Table VII, is derived from the oxygen coordinates determined by substitution and the other atomic coordinates fit to the second moments of the normal and C-13 isotopic species, and the nontrivial center of mass condition. In the third structure the *c* coordinate of the carbon atoms was set to zero, and the coordinates of the oxygen and the carbon atoms were determined by the Kraitchman method. The fluorine coordinates were then fit to the normal isotopic second moments and the center of mass condition. This structure is designated r_S(II) in Table VII. The errors given for the partial substitution structures reflect the Costain uncertainty[21] of the values obtained by the Kraitchman method, or the uncertainty of the least-squares fit if this value is larger. Table VIII gives the structural parameters of the molecule determined from each set of coordinates. The errors are carried through the calculations from the uncertainty of the atomic coordinates.

Dipole. The electric dipole moment was determined by measurement of the Stark shifts for four transitions. Stark coefficients were determined by a least-squares fit of the data to second-order perturbation theory.[22] The Stark coefficients and the resulting dipole are given in Table IX. The fit to only one dipole component is consistent with the symmetry of the molecule.

The structure and electric dipole moments of a number of oxiranes are known. Gas-phase dipole moments and structures of ethylene oxide,[8,9] *cis*-1,2-difluoroethylene oxide,[6] *trans*-1,2-difluoroethylene oxide,[7] and perfluoroethylene oxide have been determined and are compiled in Table X. A vector analysis requires the assumption that the bond moments do not change significantly as the substituents of the molecule are changed. From the five dipole components, and the structures of the four molecules, five equations in the C–O, C–F, and C–H bond moments can be written. The values of the bond moments presented in Table X were obtained from the best least-squares fit of the four equations. The calculated dipole moments were obtained from these bond moments. The signs of the dipole were chosen to give a reasonable fit. The results agree with the direction of the dipole determined for ethylene oxide by the Zeeman effect.[23] In all four cases the oxygen atom is at the negative end of the molecule.

Discussion

Ring-Bond Effects. The ring bond lengths of ethylene oxide and perfluoroethylene oxide are summarized in Table XI. Deakyne, Cravero, and Hobson[11] predicted that for tetrafluoro substitution all bonds in the oxirane ring will shorten approximately twice as much as in the case of *cis*-difluoro substitution. The predictions are confirmed. Since the methods used have been found to work well for the oxiranes, it seems possible that there is some peculiarity in the cyclopropane ring that results in the unique structural changes predicted by Deakyne, Allen, and Craig[10] and Skancke and Boggs[12] for the C(1,2)–C(3) bond of 1,2 symmetrically fluorinated cyclopropanes.

The ring bond lengths show a nearly linear change from ethylene oxide to *cis*-1,2-difluoroethylene oxide to perfluoroethylene oxide (Table XI). This is consistent with the additivity principle proposed by Deakyne, Allen, and Craig,[10] based on the

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Table VI. Symmetry Assignment of Vibrational Satellites

	relative intensity				vibrational assignment		
	300 K	200 K	E_{vib}, cm^{-1}	SYM		E_{vib}, cm^{-1}	SYM
V(1) ee–oe	0.2386[a]	0.1035			V_5	318	A_1
oo–eo	0.2320	0.1026	306 (17)[b]	A			
V(10) ee–oe	0.2710	0.1767			V_{15}	180[c]	B_2
oo–eo	0.6281	0.3693	182 (23)	B			
V(100) ee–oe	0.3474	0.1874			V_8	190[c]	A_2
oo–eo	0.3373	0.2007	226 (17)	A			

[a] Average of measurements for three transitions. [b] Error is one standard deviation of the individual measurements. [c] Not measured for vibrational assignment.

Table VII. Atomic Coordinates of CF_2CF_2O (Å)

	r_O	r_S(I1)	r_S(11)
a(O)	0.0	0.0	0.0
b(O)	0.0	0.0	0.0
c(O)	1.1944 (6)	1.1943	1.1943
a(C)	0.7102 (18)	0.7129 (15)	0.7129
b(C)	0.0	0.0	0.0
c(C)	0.0006 (24)	0.0002 (2)	0.0
a(F)	1.4427 (3)	1.4422 (3)	1.4422 (12)
b(F)	1.08173 (1)	1.08173 (1)	1.08175 (1)
c(F)	0.2512 (7)	0.25132 (3)	0.2514 (47)

Table VIII. Structural Parameters of CF_2CF_2O[a]

	r_O	r_S(1)	r_S(11)
C–O	1.390 (3)	1.391 (2)	1.391 (2)
C–C	1.420 (3)	1.426 (3)	1.426 (4)
C–F	1.330 (1)	1.329 (2)	1.329 (2)
F---F	2.885 (1)	2.884 (2)	2.884 (2)
F---F	2.163 (1)	2.163 (2)	2.164 (2)
∠CCO	59.28 (13)	59.17 (8)	59.17 (8)
∠FCF	108.82 (13)	109.01 (19)	109.01 (19)

[a] Distances in Å, angles in deg.

Table IX. Stark Coefficients and Dipole Moment of CF_2CF_2O

	MHz/(v/cm)**2	
transitions	observed	calculated
4_{04}–5_{14} (M = 1)	6.6946E-06	6.7324E-06
4_{04}–5_{14} (M = 2)	2.6355E-05	2.6462E-05
4_{04}–5_{14} (M = 3)	5.8400E-05	5.9344E-05
3_{22}–4_{32} (M = 2)	−9.1232E-07	−8.8936E-07
$\mu_c = \mu_t$ = 0.576 (5) D[a]		

[a] Error represents one standard deviation of the fit.

Table X. Bond Moments and Dipole Moments of Some Oxiranes

bond (δ^+–δ^-)	dipole, D
C–O	0.92
C–F	1.34
H–C	0.33

molecule	component, D	obsd (ref)	calcd
CF_2CF_2O	μ_c	−0.576 (this work)	−0.568
cis-CHFCHFO	μ_c[a]	−2.55 (6)	−2.70
	μ_b	1.36 (6)	1.37
trans-CHFCHFO	μ_b	−1.115 (7)	−1.165
CH_2CH_2O	μ_b	−1.88 (19)	−1.84

[a] Component not used in the fit.

Table XI. Comparison of Structural Parameters for the Oxirane Series

	bond lengths, Å			methylene angle, deg
	C–O	C–C	C–F	
CH_2CH_2O	1.431	1.466		116.9
cis-CHFCHFO	1.409	1.451	1.345	111.0
CF_2CF_2O	1.391	1.426	1.329	109.0

Table XII. Predicted Structures of Some Fluorinated Oxiranes

	C(1)–O	C(2)–O	C–C	C–F	C–H	methylene angles	
CF_2CH_2O	1.39	1.43	1.45	1.32	1.08	109[b]	117[c]
$CHFCH_2O$	1.41	1.43	1.46	1.34	1.08	112[d]	117[c]
$CHFCF_2O$	1.41	1.39	1.44	a	1.08	112[d]	109[b]

[a] 1.32 for CF_2 and 1.34 for CHF. [b] F–C–F. [c] H–C–H. [d] H–C–F.

Table XIII. Fluorine–Fluorine Nonbonded Distances (Å)

molecule	geminal	vicinal	ref
CF_2CF_2	2.19	2.74	28
$CHFCF_2$	2.20	2.75	27
cis-CHFCHF		2.74	27
cis-CHFCHFO		2.72	6
CF_2CF_2O	2.16	2.88	this work

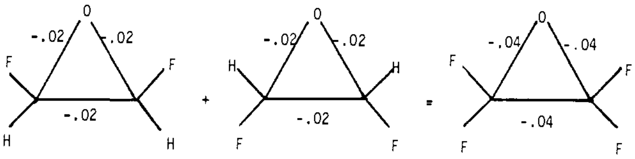

Figure 1. Additivity principle used to predict changes in ring bonds of CF_2CF_2O.

idea that each substituent causes the same shift in the electron distribution relative to the substitution site. Figure 1 illustrates how the ring bond length changes observed for the cis epoxide can be added together to predict the changes for the perfluoro epoxide. The actual effect of each fluorine atom is not totally determined since a small change in the bond opposite the substitution site would be hidden by the large change caused by the substituent adjacent to that bond. With use of the additivity principle and the experimentally determined structural changes for *cis*-1,2-difluoroethylene oxide and perfluoroethylene oxide, ring structures of other fluorinated oxiranes can be reasonably predicted. The ring bond lengths obtained in this way for the two unknown species, 1,1-difluoroethylene oxide and fluoroethylene oxide, and the known species, trifluoroethylene oxide,[24] are given in Table XII.

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[24] Agopovich, J. W.; Gillies, C. W. *J. Am. Chem. Soc.* **1980**, *102*, 7572–4.

Fluorine–Fluorine Nonbonded Distances. The structures of a number of fluorinated molecules have been determined. The geminal and vicinal fluorine–fluorine distances for these molecules are given in Table XIII. The geminal F–F distance for the molecules listed is consistent with the value for perfluoroethylene oxide. For all other cases available, the distance between vicinal fluorine atoms is very close to 2.7 Å, the sum of two fluorine van der Waals radii. In perfluoroethylene oxide this same distance is more than 0.1 Å larger. Hence perfluoroethylene oxide does not fit in with the other fluorocarbons listed in Table XIII. This result as well as previous structural effects noted in related fluorocarbons[6,25] argue against the idea of an intramolecular bond between vicinal fluorine atoms.[26]

Vibrational States. Craig[16] used infrared spectra to assign the normal modes of perfluoroethylene oxide. He was not able to observe the spectrum below 200 cm^{-1}. The two normal modes in this region were assigned on the basis of combination bands, and by analogy to the more definitive vibrational assignment of 1,1,2,2-tetrafluorocyclopropane. The energies and symmetries of the two lowest energy vibrational states have been measured for the first time. The energy and symmetry of the lowest vibrational state measured in the vibrational assignment were also determined in this work. The possibility that this third assigned vibrational state is the second excitation of one of the lower vibrational states was considered, but ruled out on the basis of two pieces of evidence. First, the rotational constants do not change linearly with the vibrational quantum number. Second, no other vibrational satellites are found which could be assigned to the observed 318-cm^{-1} vibration.

The symmetry assignments are based on the nuclear spin statistics. In the A_1 and A_2 vibrational states the ee and oe rotational levels have a statistical weight of 10 while the oo and eo levels have a weight of 6. In the B_1 and B_2 states the weights are reversed. The ground state must be an A_1 vibrational state. Therefore, if the rotational transitions between ee and oo levels have the same intensity relative to the ground state as the oo–eo transitions, then the excited vibrational state must be an A_1 or A_2 species. If, on the other hand, the ratio of the relative intensities for the ee–oe transitions to the oo–eo is (6/10):(10/6), then it must be a B_1 or B_2 vibration. The results are presented in Table VI.

The values obtained for the vibrational frequencies are in fair agreement with the vibrational assignment. For the previously unobserved transitions, the results indicate that the actual values may be higher than predicted in the vibrational assignment. This trend is even more significant if the difference in the observed energies of the V(1) state are the result of a systematic error, possibly caused by poor temperature control.

Structure Trends. The angle of the methylene group changes systematically from ethylene oxide to *cis*-1,2-difluoroethylene oxide to perfluoroethylene oxide. The values of the methylene group angles in difluoromethane are 113.7, 108.7, and 108.3 for the H–C–H, H–C–F, and F–C–F groups, respectively. The trend toward a smaller angle with increased fluorination is the same for the oxirane series (Table XI).

The carbon–fluorine bond length shortens with increased fluorination from the 1,2-difluoroethylene oxides to perfluoroethylene oxide (Table XI). This same trend has been observed in many fluorocarbons such as the fluorinated methanes, ethanes, ethylenes, and silanes.[27-28] Extrapolation from the values for the fluorinated oxiranes along the trend established by the fluorinated ethylenes gives the predicted fluorine–carbon bond lengths in Table XII.

The structural trends can be explained in terms of the changes in hybridization of the carbon atom. The differences in electronegativities of fluorine and hydrogen atoms cause a change in hybridization which results in a decrease in the bond angle and a shortening of the bonds. Both the X–C–X bond angle and the C–F bond length changes are consistent with the changes in hybridization determined for the fluorinated ethylenes by Kollman.[25]

Conclusion

The effect of perfluoro substitution on the oxirane ring has been determined. The changes of the bond lengths throughout the molecule are consistent with recent predictions based on ab initio calculations and the experimentally observed trends in *cis*-1,2-difluoroethylene oxide. The vicinal fluorine–fluorine distance is different from previously observed values, which provides evidence that lone electron pair attraction is not significant in determining the geometry of the fluorinated oxiranes. Previously unmeasured vibrational frequencies have been observed, and symmetry assignments are consistent with the vibrational assignment.

It has been shown that some of the changes in structure observed for the series of fluorinated ethylene oxides can be explained in terms of the effect of electronegative substituents on the hybridization of the carbon atoms. The shortening of the carbon bond and the closing of the methylene angles with increased fluorination are consistent with this explanation and the experimentally observed trends in other molecules.

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Registry No. CF_2CF_2O, 694-17-7; CF_2CF_2O (^{18}O isomer), 89043-69-6; CF_2CF_2O (^{13}C isomer), 89043-70-9.

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