(Figure 11). It should, however, be recalled that an essential difference between blood and fluorinated liquids lies in the mechanism of dissolution, which is purely physical in the latter case (Henry's law is obeyed) and which results from O_2 binding to hemoglobin in the second case (hence a sigmoid shape of the uptake curve, cf. Figure 11). The uptake and release of oxygen is completely reversible, however, in both blood and fluorinated liquids, and the rate of exchange is very fast as shown by stopped-flow UV experiments.[20,60] As natural blood can release 5 vol % oxygen only in human breathing, this means that a similar release from fluorinated liquids involves an oxygen uptake of 5 vol %. This requires in turn a pressure of oxygen in touch with the liquid of about 500 and 350 torr for Fluosol DA 20% and 35% and of only 214 torr for microemulsion **4**, thus approaching in this case the partial pressure of oxygen in ordinary air (152 torr).

Conclusion

The pure surfactants synthesized in this work have allowed us to show the possibility of obtaining a novel class of true microemulsions (droplets less than 500 Å) using one nonionic surfactant only. These microemulsions are simply prepared by selecting appropriate surfactant-fluorocarbon pairs and mixing them in adequate molar ratio to an aqueous solution. High solubilization of fluorinated compounds are therefore possible, allowing in turn a high solubility of gases in the fluorinated microemulsion. On a fundamental point of view, a novel class of nonionic microemulsions is now available for all those working in this area. The structure of these aqueous microemulsions (in the water-rich region of the ternary-phase diagram) has been greatly elucidated by means of SANS experiments. A vast field of research seems now to be opened concerning the formulation of other fluorinated microemulsions along the lines of this work, the study of ternary-phase diagrams in their entirety with the corresponding structural determinations, and the numerous chemical and biochemical applications of these new materials.

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Registry No. 614, 82695-52-1; 615, 82576-80-5; 616, 82695-53-2; 715, 60331-77-3; 716, 82576-81-6; $C_6F_{13}CH{=}CHC_6F_{13}$, 56523-43-4; $C_8F_{17}C_2H_5$, 77117-48-7; $C_6F_{13}CH{=}CH_2$, 25291-17-2; $C_8F_{17}CH{=}CH_2$, 21652-58-4; $C_{10}F_{18}$, 306-94-5; oxygen, 7782-44-7.

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Microwave Spectra, Electric Dipole Moment, and Molecular Structure of *trans*-1,2-Difluoroethylene Oxide

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Abstract: The microwave spectra of the normal, oxygen-18, dideuterated, and carbon-13 isotopic species of *trans*-1,2-difluoroethylene oxide were assigned to determine the molecular structure. The partial r_s parameters are r(CO) = 1.395 (8) Å, r(CC) = 1.436 (4) Å, r(CH) = 1.098 (4) Å, and r(CF) = 1.363 (4) Å and θ(HCF) = 110.5 (4)° and θ(CCO) = 59.01 (42)°. The electric dipole moment was found to be 1.115 (3) D. The CC and CO ring bonds are shorter in *trans*-1,2-difluoroethylene oxide than in the corresponding cis isomer. However, the CF bond is longer in the trans form than in the cis isomer. The orientation of the HCF moiety with respect to the ring plane is very similar in the two isomers. These results are related to several theoretical studies of the 1,2-difluorocyclopropanes and 1,2-difluoroethylene oxides which predict the effect of fluorine substituents upon the molecular structure and the relative stabilities of the isomer pairs.

A number of experimental[3-5] and theoretical[6,7] studies of fluorinated cyclopropanes have provided data related to the effect of fluorine substitution upon the geometries. While the experimental data base is limited, the theoretical work has explained the observed structural effects[6,7] and also has offered a rationalization of an anomaly in the so-called "cis effect" for the 1,2-difluorocyclopropanes.[7] In this case, the trans isomer is more stable than the cis form[8] in spite of the fact that in the related unsaturated pair, 1,2-difluoroethylene, the cis form is more stable than the trans.[9]

Considerably less is known about the effect of fluorine substitution upon the structures of fluorinated oxiranes. A microwave study of the previously unknown compound, *cis*-1,2-difluoroethylene oxide, provided the first experimental structure of a fluorinated oxirane.[10] Recently, the geometry of perfluoroethylene oxide was determined by employing microwave techniques.[11] Both the CC and CO ring bonds in these oxiranes shorten relative to ethylene oxide.[10,11] These results are in contrast to theoretical predictions for 1,2-difluorocyclopropanes and 1,1,2,2-tetra-

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Table I. Rotational Transitions (MHz) and Rigid Rotor Fits of *trans*-CHFCHFO

	CHFCHFO		CDFCDFO	
transitions	ν_{obsd}	$\Delta\nu^a$	ν_{obsd}	$\Delta\nu^a$
$2_{11}-2_{20}$	33 454.21	−0.21	28 564.97	−0.13
$2_{12}-2_{21}$	34 526.99	−0.13	29 319.42	−0.06
$2_{02}-3_{13}$	30 666.75	0.24	28 876.84	0.19
$3_{12}-3_{21}$	32 953.37	−0.20	28 208.34	−0.14
$3_{13}-3_{22}$	35 073.01	−0.07	29 702.18	−0.06
$3_{03}-4_{14}$	36 768.70	0.27	35 043.27	0.23
$4_{13}-4_{22}$	32 329.30	−0.11	27 758.15	−0.05
$4_{14}-4_{23}$	35 804.07	−0.01	30 214.37	−0.01
$5_{14}-5_{23}$	31 618.52	−0.08	27 235.79	−0.02
$5_{15}-5_{24}$	36 722.75	0.40		
$5_{15}-6_{06}$	31 669.09	−0.30	31 914.73	−0.25
$6_{15}-6_{24}$	30 866.70	0.01	26 667.73	0.02
$6_{16}-6_{25}$			31 632.43	0.06
$7_{16}-7_{25}$	30 125.63	0.13		
$7_{17}-7_{26}$			32 541.28	0.12
$8_{18}-8_{27}$			33 585.05	0.10
$9_{19}-9_{28}$			34 764.77	0.06
$10_{1,10}-10_{29}$			36 080.82	−0.11

[a] $\Delta\nu = \nu_{obsd} - \nu_{calcd}$ obtained from rigid rotor fit.

fluorocyclopropane where only the CC bond located between fluorine-substituted carbons is expected to shorten significantly relative to cyclopropane.[6,7]

A recent theoretical study using the same approach as in the fluorinated cyclopropanes has rationalized the ring bond changes in *cis*-1,2-difluoroethylene oxide and predicted the ring bond lengths in perfluoroethylene oxide.[12] The theoretical results for perfluoroethylene oxide are in agreement with the experimental ring bond lengths.[11] In addition, the study predicted that *trans*-1,2-difluoroethylene oxide is more stable than the cis form due to greater electron delocalization in the cis isomer which will be reflected in distinct differences between the ring structures of the two geometrical isomers.[12]

Previously unknown, *trans*-1,2-difluoroethylene oxide was recently identified as a volatile product of the ozonolysis of 1,2-difluoroethylene.[13] Microwave studies of this compound were undertaken in order to determine the complete molecular geometry. These results will permit a critical comparison of the structures of *cis*- and *trans*-1,2-difluoroethylene oxide. In this work, the microwave spectra of the normal isotope and sufficient isotopic forms are assigned to permit calculation of a complete molecular structure for the trans isomer. The effects of fluorine substituents upon the ring structure are discussed and related to the cis form and to theoretical predictions for the 1,2-difluorocyclopropanes. Finally, theories concerned with the "cis effect"[7,8] are discussed and related to the structural results.

Experimental Section

Synthesis. The normal isotopic species of *trans*-1,2-difluoroethylene oxide was prepared by the ozonolysis of *trans*-1,2-difluoroethylene in CF_3Cl at −95 °C and purified by gas chromatography as described previously.[13] A previously prepared sample of *trans*-1,2-difluoroethylene-d_2 (96.7% d_2 isotope)[14] was ozonized to obtain a highly enriched sample of *trans*-1,2-difluoroethylene-d_2 oxide.[15] Oxygen-18-enriched *trans*-1,2-difluoroethylene oxide was obtained by ozonizing the *trans* olefin with oxygen-18-enriched ozone. A millimole-scale ozonator was used to produce oxygen-18 ozone from molecular oxygen (99.45 atom % $^{18}O_2$ gas; Prochem).[15]

Spectroscopy. A Hewlett-Packard 8400C microwave spectrometer was used to record the spectra of the normal, d_2, and oxygen-18 isotopic species in the 26.5–40.0-GHz range. Transition frequencies were measured at sample pressures of 45–60 mtorr (relative to air on a Hastings DV-3m vacuum gauge tube) to an accuracy of ±0.05 MHz. One Stark cell and one Stark modulator were used to measure the electric dipole moment of the normal isotopic species. The ground-to-base potentials were measured with a Keithley 177 Microvolt DMM voltmeter which was periodically calibrated to ±0.1% accuracy. Measurements of the $J = 2 \rightarrow 3$ Stark transitions of OCS and its known electric dipole moment were used to obtain the average spacing of the Stark septum in the cell.[16]

Table II. Rotational Transitions (MHz) and Rigid Rotor Fits of *trans*-CHFCHFO

	CHFCHF^{18}O		^{13}CHFCHFO	
transitions	ν_{obsd}	$\Delta\nu^a$	ν_{obsd}	$\Delta\nu^a$
$2_{11}-2_{20}$	30 642.75	−0.11	33 248.97	−0.16
$2_{12}-2_{21}$	31 854.36	−0.10	34 304.28	−0.08
$2_{02}-3_{13}$	29 468.81	0.29	30 553.11	0.21
$3_{12}-3_{21}$	30 086.38	−0.13	32 755.96	−0.13
$3_{13}-3_{22}$	32 473.57	−0.05	34 841.35	0.01
$3_{03}-4_{14}$	35 435.30	0.20	36 646.37	0.19
$4_{13}-4_{22}$	29 405.17	−0.08	32 140.97	−0.10
$4_{14}-4_{23}$	33 303.35	0.02	35 560.43	0.16
$5_{14}-5_{23}$	28 650.12	−0.05	31 440.02	−0.10
$5_{15}-5_{24}$	34 346.53	0.04	36 463.47	0.12
$5_{15}-6_{06}$	32 448.17	−0.28	31 590.39	−0.23
$6_{15}-6_{24}$	27 882.97	0.06	30 697.28	−0.02
$6_{16}-6_{25}$	35 606.07	0.05		
$7_{16}-7_{25}$			29 963.35	0.09
$7_{17}-7_{26}$	37 084.42	0.10		

[a] $\Delta\nu = \nu_{obsd} - \nu_{calcd}$ obtained from rigid rotor fit.

Table III. Rotational Constants (MHz) and Principal Moments of Inertia (μÅ^2) of *trans*-CHFCHFO

	CHFCHFO	CDFCDFO	CHFCHF^{18}O	^{13}CHFCHFO
A^a	14731.44 (3)	12977.85 (2)	13793.10 (2)	14650.15 (2)
B	3582.83 (2)	3457.81 (1)	3582.81 (1)	3569.90 (1)
C	3222.40 (2)	3204.69 (1)	3174.95 (1)	3215.36 (1)
$I_a{}^b$	34.3062	38.9417	36.6400	34.4965
I_b	141.0558	146.1558	141.0566	141.5667
I_c	156.8331	157.6998	159.1770	157.1765

[a] All rotational constants were obtained from rigid rotor fits of the transitions listed in Tables I and II; the uncertainty in parentheses is one standard deivation of the fit. [b] A conversion factor of 50 5379.05 MHz μÅ^2 was used.

The carbon-13 isotopic species was studied in natural abundance by utilizing a 10-ft Stark cell cooled to dry-ice temperature. This system was described previously.[11] It includes a Cromemco Z-2D computer system which allows signal averaging and frequency measurement. In all cases the carbon-13 transition frequencies were measured to an accuracy of ±0.05 MHz.

Spectra

Normal Isotope. The known molecular structure of *cis*-1,2-difluoroethylene oxide was used to provide a reasonable geometrical model of the trans isomer.[10] Microwave spectral calculations based on this model predicted that the trans isomer will exhibit a b-type spectrum which is characteristic of a nearly prolate top. In the region of 26.5–40.0 GHz, a few low-J R-branch transitions were predicted as well as numerous Q-branch transitions including the origin of the $K_{-1} = 1 \rightarrow 2$ series.

The experimental spectrum confirmed the predictions. An assignment was obtained once the lowest J members of the $K_{-1} = 1 \rightarrow 2$ Q-branch series were identified by their Stark effects and used in conjunction with several low-J R-branch transitions for spectral fitting. Weak vibrational satellites were observed for a number of ground-state lines. The observed ground vibrational state transitions are listed in Table I. Rigid rotor rotational constants obtained by a least-squares fit of the line frequencies and moments of inertia are given in Table III. Stark effects and line intensities are consistent with the assignment.

Relative intensity measurements demonstrated the expected presence of a C_2 symmetry axis in the molecule. *trans*-1,2-Di-

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Table IV. Stark Coefficients (MHz/V^2/cm^2) and Electric Dipole Moment of *trans*-CHFCHFO

transition	obsd[a]	calcd
2_{02}–3_{13} $m_J = 0$	-8.242×10^{-6}	-8.258×10^{-6}
2_{02}–3_{13} $m_J = 1$	-4.187×10^{-6}	-4.196×10^{-6}
2_{02}–3_{13} $m_J = 2$	8.021×10^{-6}	7.987×10^{-6}

$\mu_{\text{total}} = \mu_b = 1.115 \pm 0.003$ D

[a] The Stark coefficients were calculated by using the conversion factor 0.503 404 (MHz/D/V/cm).

fluoroethylene oxide has one pair of equivalent hydrogen nuclei and one pair of equivalent fluorine nuclei with nuclear spins of $^1/_2$. Bose–Einstein statistics apply which gives a 5/3 ratio in the intensity of transitions arising from symmetric to antisymmetric rotational states once other contributions to the intensities are considered. This ratio was observed for a number of transitions by using the method of Esbitt and Wilson for the intensity measurements.[17]

Enriched Isotopes. The d_2 and oxygen-18 isotopes were highly enriched, and the assignments presented no special problems. The transition frequencies and rigid rotor fits for these species are listed in Tables I and II. Least-squares fits of the transitions yielded the rigid rotor rotational constants in Table III. The assignments are supported by observation of the Stark effects, the expected isotopic shifts, and the line intensities.

Carbon-13 Isotope. The intensities of the normal isotope lines suggested that the carbon-13 species should be observable in 2% natural abundance. The d_2 and oxygen-18 isotopic data were combined with the moment of inertia relationships and one structural parameter in a least-squares fit to obtain a molecular structure.[17] Eight molecular structures were calculated in this way by using the values of different structural parameters. From these "fitted" structures, rotational constants were calculated for the normal and carbon-13 isotopes. Corrections were derived from the differences between the experimental and calculated rotational constants of the normal isotope and applied to the calculated rotational constants of the carbon-13 isotope. It was found that these corrected carbon-13 rotational constants for all eight structures predicted carbon-13 transition frequencies with a standard deviation of less than 2 MHz.

The carbon-13 lines were readily identified by their characteristic Stark effects by using the excellent predictions described above. The 13 transitions used in the rigid rotor fit are given in Table II. The rotational constants obtained from this fit are listed in Table III. The assignment was confirmed by the quality of the rigid rotor fit, the intensities of the transitions, observation of correct Stark effects, the predicted isotopic shifts, and the absence of nuclear spin statistics. No alternation of intensity of lines was observed for the carbon-13 species which is consistent with the absence of a C_2 symmetry axis. The lack of an intensity alternation for these assigned transitions also precludes the possibility that they originate from an excited vibrational state of the normal isotope.

Electric Dipole Moment

The electric dipole moment of the ground vibrational state of the normal isotope was determined by measurement of the Stark shifts for three transitions. A least-squares fit of the data to second-order perturbation theory gave the Stark coefficients listed in Table IV and a value of 1.115 ± 0.003 D for the b dipole component. The quality of the fit to one dipole component is consistent with the presence of a C_2 axis of symmetry in the molecule.

Structure

trans-1,2-Difluoroethylene oxide has ten unique atomic coordinates. The moment of inertia data from the four isotopic species can be combined with the first moment equation ($\sum_i m_i b_i = 0$) and the cross-product equation ($\sum_i m_i a_i c_i = 0$) to calculate the molecular structure in two different ways. With the exception of the small b carbon coordinate, the coordinates of the carbon, hydrogen, and oxygen atoms can be obtained by the substitution method.[18] This leaves the fluorine coordinates and the small b carbon coordinate to be calculated from the three second moment equations of the normal isotope, the first moment equation, and the cross-product equation.

Table V. Atomic Coordinates (Å) of *trans*-CHFCHFO

	r_s[a]	r_0
a(O)	0.0	0.0
b(O)	−1.0936	−1.0935
c(O)	0.0	0.0
a(C)	±0.5782	±0.5757
b(C)	0.1020	0.1016
c(C)	∓0.4259	∓0.4250
a(H)	±0.5739	±0.5627
b(H)	0.3172	0.3195
c(H)	∓1.5029	∓1.4885
a(F)	±1.8000	±1.8007
b(F)	0.3791	0.3792
c(F)	±0.1116	±0.1105

[a] The r_s coordinates include oxygen O, a and c carbon C and hydrogen H; the fluorine coordinates F and the b carbon coordinate were calculated from a least-squares fit of the three second moment, one first moment, and one cross-product equations.

Table VI. Structural Parameters of *trans*-CHFCHFO

	partial r_s	r_0
r(CO)	1.395 (8)	1.393 (2)
r(CC)	1.436 (4)	1.431 (2)
r(CH)	1.098 (4)	1.086 (1)
r(CF)	1.363 (4)	1.365 (2)
Θ(HCF)	110.5 (4)	110.7 (2)
Θ(CCO)	59.01 (42)	59.09 (1)

The structural fitting computer program STRFIT[19] was used to calculate the coordinates by the method described above. In this case the hydrogen coordinates were calculated from the d_2 species by using an adaptation of Chutjian's equations for double substitution[20] in which the species have C_2 symmetry.[21] The a and c coordinates of the carbon and the oxygen coordinate were calculated by the single substitution method.[18] Since the oxygen atom lies along the C_2 axis, the option was utilized in STRFIT to neglect the second and third factors in the Kraitchman equations. Hence, ΔP_{aa} and ΔP_{cc} were set to zero. Least-squares fitting of the b carbon and fluorine coordinates to the five moment relations gave the set of atomic coordinates listed in Table V. The molecular structure derived from these coordinates is listed in Table VI.

In order to get an estimate of the uncertainties derived from vibrational effects, a complete r_0 structure was obtained with STRFIT. The three second moment equations for the four isotopes as well as the first moment and cross-product equations were least-squares fit to give the atomic coordinates and structural parameters shown in Tables V and VI.

The errors in the structural parameters were estimated by using Costain uncertainties in the coordinates and the standard formula for propagation of random uncertainties in the distances and angles.[22] In the case of the small b carbon coordinate and small

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Table VII. Comparison of Structural Parameters for Fluorinated Oxiranes

	CH_2CH_2O[a]	cis- $CHFCHFO$[b]	trans- $CHFCHFO$[c]	CF_2CF_2O[d]
		Bond Lengths (Å)		
r(CO)	1.431 (1)	1.409 (4)	1.395 (8)	1.391 (2)
r(CC)	1.466 (2)	1.451 (3)	1.436 (4)	1.426 (4)
r(CH)	1.085 (1)	1.093 (4)	1.098 (4)	
r(CF)		1.345 (7)	1.363 (4)	1.329 (2)
		Bond Angles (deg)		
methylene (XCY)	116.6 (1)	111.0 (4)	110.5 (4)	109.0 (2)
		Distortion Coordinates (deg)[e]		
Φ_{rock}	0.0	−10.10 (81)	−8.70 (89)	0.0
Φ_{wag}	8.9	12.10 (81)	11.50 (89)	13.90 (45)
Φ_{twist}	0.0	−6.70 (81)	−3.50 (89)	0.0

[a] Structure from ref 23. [b] Structure from ref 10. [c] This work. [d] Structure from ref 11. [e] As defined in ref 7; $\Phi_{rock} = [\theta(XCC) + \theta(XCO)] - [\theta(YCC) + \theta(YCO)]$, $\Phi_{wag} = [\theta(XCC) + \theta(YCC)] - [\theta(XCO) + \theta(YCO)]$, and $\Phi_{twist} = [\theta(XCC) - \theta(XCO)] - [\theta(YCO) - \theta(YCC)]$ where X = Y = hydrogen for CH_2CH_2O, X = hydrogen and Y = fluorine for $CHFCHFO$, and X = Y = fluorine for CF_2CF_2O.

c fluorine coordinate, Costain uncertainties lead to unreasonable error estimates. The uncertainties in these coordinates were determined by calculating the propagated error from Costain uncertainties of all the other coordinates in the moment equations.[22] For the *b* carbon coordinate, the center of mass relation gives a propagated error of 0.0091 Å as compared to a 0.0192-Å propagated error from the *b* second moment equation. The *c* fluorine coordinate has a propagated error of 0.0005 Å from the *ac* cross-product relation and a propagated error of 0.0083 Å from the *c* second moment equation. Since the two coordinates were obtained from a least-squares fit of five moment equations, the standard deviation of these coordinates also provides an estimate of the uncertainties. The values of 0.0109 and 0.0017 Å for the *b* carbon and *c* fluorine coordinates, respectively, lie between the propagated errors described above. These values were used to obtain the errors for those structural parameters which depend upon these coordinates in the partial-Kraitchman structure listed in Table VI. The uncertainties for the complete r_0 structure are listed next to the r_0 parameters in Table VI. They are errors propagated from the standard deviations of the coordinates determined from the least-squares fit of all isotopic data.

Discussion

Ring Structure. Table VII compares the structural parameters of *trans*-1,2-difluoroethylene oxide with the known geometries of ethylene oxide, *cis*-1,2-difluoroethylene oxide, and perfluoroethylene oxide. The observed contraction of the CC and CO bonds in *trans*-1,2-difluoroethylene oxide relative to ethylene oxide is consistent with the trend found for the fluorinated oxirane series[10,11,23] as well as the general phenomenological observation that the introduction of fluorine in carbon compounds shortens the bonds adjacent to the CF bond.[24] In a structural study of *cis*-1,2-difluoroethylene oxide,[10] Gillies pointed out that this observed shortening of the CC and CO ring bonds was not consistent with theoretical predictions of ring bond lengths in fluorinated cyclopropanes.[6] Charge density difference plots predicted that fluorinated cyclopropanes substituted at the C_1 and C_2 carbons will have a shortened C_1C_2 bond but unchanged C_1C_3 and C_2C_3 bonds relative to cyclopropane.[6] The recent experimental study of perfluoroethylene oxide[11] and the present work on *trans*-1,2-difluoroethylene oxide demonstrate that all ring bonds contract in the fluorinated oxiranes. Hence, combination of the theoretical results on fluorinated cyclopropanes with the experimental studies on fluorinated oxiranes suggests that fluorination of cyclopropane does not generate the same ring bond length changes as does fluorination of ethylene oxide.

Comparison of the CC and CO bond lengths for *cis*- and *trans*-1,2-difluoroethylene oxide in Table VII shows that there is a shortening of the trans CC bond by 0.015 Å. The trans CO bond is numerically 0.014 Å shorter than the cis CO bond. However, the larger uncertainty in trans CO bond lengths indicates that there may not be as large a difference for the CO bond lengths. These CC and CO ring bond differences for the two isomers were predicted in a recent theoretical study by Deakyne and co-workers.[12]

This theoretical study used orbital compositions, overlap populations, charge distributions, orbital energy splitting diagrams, and charge density difference plots obtained from ab initio wave functions to determine the reason for the differences in fluorine substituent effects upon ring bonds in the oxiranes compared to the cyclopropanes. The analysis explained the observed shortening of all ring bonds in *cis*-1,2-difluoroethylene oxide and predicted an even more pronounced shortening of the ring bonds in perfluoroethylene oxide (CO bond of 1.39–1.40 Å and CC bonds of 1.44 Å). Recent experimental results for perfluoroethylene oxide (see Table VII) are in excellent agreement with these predictions for the CO ring bond.[11] The predictions also agree qualitatively with the observed CC bond, underestimating the amount of shortening by approximately 0.01 Å.

The CC bond in *trans*-1,2-difluoroethylene oxide was predicted to be shorter than the CC bond in the cis isomer due to two interactions between the fluorine substituents and the proper symmetry orbitals of ethylene oxide.[12] Similar considerations of fluorine interactions with the proper symmetry orbitals lead to opposing effects upon the CO bond strengths for both the cis and trans isomers. Hence, Deakyne concluded that this bond length will not differ by a lot for the two isomers. The experimental results in Table VII agree with these predictions for the CC bond length. As shown in Table VII, the CO bond is considerably shorter in the trans isomer. However, the experimental uncertainty is a factor of two larger which makes the agreement between the theoretical prediction and the observed CO bond length less certain.

HCF Group. The methylene group angle systematically shrinks in going from ethylene oxide to *cis*- and *trans*-1,2-difluoroethylene oxide to perfluoroethylene oxide (see Table VII). A similar effect is seen both for the cyclopropane series cyclopropane (θ(HCH) = 115.0°),[25] *cis,cis*-1,2,3-trifluorocyclopropane (θ(HCH) = 112.3°),[4] and 1,1-difluorocyclopropane (θ(FCF) = 108.4°)[3] and the fluorinated ethylene series.[26] The CF bond distance also shrinks with increasing fluorination from the 1,2-difluoroethylene oxides to perfluoroethylene oxide.[11] This trend has been observed for fluorinated methanes, aldehydes, ethylenes, ethanes, and silanes.[27] Curiously, the CF bond lengths are similar in *cis,cis*-1,2,3-trifluorocyclopropane and 1,1-difluorocyclopropane.

Table VII shows that the CF bond length in *trans*-1,2-difluoroethylene oxide is more than 0.01 Å longer than the CF bond in the cis isomer. The study by Deakyne on the fluorinated oxiranes did not perform geometry optimization, and it cannot be used to explain this difference.[12] However, Skancke and Boggs found that the optimized CF bonds in *cis*- and *trans*-1,2-difluorocyclopropane are identical.[7] This result seemed puzzling, and they noted that the overlap populations for the cis and trans forms are 0.42 and 0.39, respectively, which suggests greater partial double bond character of the CF bond in the cis form.[7] Since theoretical studies of the 1,2-difluorocyclopropanes and 1,2-difluoroethylene oxides[12] both find the trans isomer more stable than the cis due to greater delocalization in the cis form (see the section Cis Effect in the Discussion section of this paper), the CF bond in *trans*-1,2-difluorocyclopropane is expected to be longer

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(23) Hirose, C. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1311.

(24) See ref 4 for a number of examples.

(25) Bastiansen, O.; Fritsch, F. N.; Hedberg, K. *Acta Crystallogr.* **1964**, *17*, 538.

(26) Kollman, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 4363.

(27) See ref 4 and 11 for a summary of these examples.

than the cis CF bond. Experimental structures of the 1,2-difluorocyclopropanes are needed to resolve this problem.

A comparison of the distortion coordinates for *cis*- and *trans*-1,2-difluoroethylene oxide reveals little difference in Φ_{rock} and Φ_{twist} angles while Φ_{wag} is almost identical. These results demonstrate that the HCF moiety is oriented in the same way with respect to the CCO ring plane for both isomers. The same conclusion is drawn from a comparison of the OCCH and OCCF dihedral angles for the cis and trans isomers. These are ∠OCCH = 257.6° and 256.4° and ∠OCCF = 104.2° and 103.2°, respectively, for the cis and trans isomers.

Cis Effects. Structural comparisons between *cis*- and *trans*-1,2-difluoroethylene oxide are relevant to rationalizations of the "cis effect".[8,9] Some disubstituted ethylenes are examples of this effect in which the cis isomer is more stable than the trans contrary to the general rule of the trans form being more stable than the cis isomer. A well-studied example is found for the 1,2-difluoroethylenes where the cis form is 1080 cal/mol more stable than the trans form.[9]

Explanations of the cis effect have focused on either factors which lead to extra stabilization of the cis isomer or factors which destabilize the trans form. Skancke and Boggs have discussed the literature involving the 1,2-difluoroethylenes.[7] Factors which stabilize *cis*-1,2-difluoroethylene are expected to give rise to structural effects in the isomers. Epiotis cited the small FCF angle in 1,1-difluoroethylene and the enhanced stability of *cis*-1,2-difluoroethylene as support for a molecular orbital model which concludes that lone-pair interactions between non-bonded fluorines lead to attractive forces.[28] However, Skancke and Boggs have noted that differences in the CCF angles for *cis*- and *trans*-1,2-difluoroethylene are in the wrong direction in order to offer support for this explanation of the cis effect.[7] In addition, Kollman finds that differences in the electronegativity of hydrogen vs. fluorine and the resultant changes in CX bonding orbitals explain the XCX angle effects without invoking fluorine lone-pair interactions.[26]

Bingham has proposed that the cis effect of ethylenes results from more destabilization of the trans form rather than greater stabilization of the cis form.[29] The argument is that the fluorine lone-pair orbital and the π bonding orbital interact to form delocalized antibonding and bonding molecular orbitals. For the 1,2-difluoroethylene isomers, these two orbitals are occupied and the delocalization leads to destabilization of both forms since the antibonding orbital is more antibonding than the bonding orbital is bonding. However, electron delocalization is greater through the elongated, trans form than in the bent, cis isomer.[30] Hence, the total interaction leads to a larger destabilization of the trans isomer. Skancke and Boggs pointed out that photoelectron spectra, NMR chemical shifts, and force constant data support this explanation.[7]

The 1,2-difluorocyclopropanes exhibit anomalous behavior compared to the 1,2-difluoroethylenes.[9] In this case, the cis isomer is less stable than the trans in spite of the unsaturated character of cyclopropane. Ab initio geometry optimization and Mulliken population analysis of the two isomers support the Bingham proposal for the cis effect.[7] The Mulliken population analysis suggests a greater delocalization of charges for the cis isomer. The longer C_2C_3 bond in the cis isomer is in accord with greater delocalization in this form.[7]

Experimentally, the relative stabilities of *cis*- and *trans*-1,2-difluoroethylene oxide are not known. However, Deakyne's theoretical work on these isomers indicates that the trans isomer is more stable than the cis form due to a more delocalized charge distribution in the latter.[12] The theoretical results are consistent with the Bingham proposal for the cis effect. In addition, the charge density difference maps predict the same ring bond effects for *cis*- and *trans*-1,2-difluoroethylene oxide[12] as the complete geometry optimization methods found for *cis*- and *trans*-1,2-difluorocyclopropane.[5] The experimental gas-phase structures of *cis*- and *trans*-1,2-difluoroethylene oxide presented in the present work compare well with Deakyne's results. While experimental structures of *cis*- and *trans*-1,2-difluorocyclopropane are needed to verify Skancke and Boggs' work, the combined results on the fluorinated cyclopropane and oxirane pairs offer strong evidence in support of the Bingham explanation of the cis effect.

Furthermore, the HCF groups are oriented in approximately the same way with respect to the oxirane ring (see Table VII and the section on the HCF group) for both *cis*- and *trans*-1,2-difluoroethylene oxide. If there is an attractive interaction between the vicinal fluorines in the cis isomer, then differences in the orientation of the HCF group are expected for the cis and trans pairs. The fact that there are not argues against the explanation of the cis effect by Epiotis.[28]

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Registry No. *trans*-1,2-Difluoroethylene oxide, 80397-37-1; *trans*-1,2-difluoro-1,2-dideuterioethylene oxide, 91606-63-2; *trans*-1,2-difluoroethylene oxide-^{18}F, 91606-64-3; *trans*-1,2-difluoroethylene oxide-^{13}C, 91606-65-4.

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(29) Bingham, R. C. *J. Am. Chem. Soc.* **1976**, *98*, 535.
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