Analysis of cis-Difluoroethylene Ozonide by Microwave Spectroscopy and ab Initio Techniques: An Unusual Conformational Potential

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(Received: September 22, 1983)

The microwave spectra of five isotopic species of cis-difluoroethylene ozonide (cis-3,3-difluoro-1,2,4-trioxolane) were assigned, including the parent, both the d1 and the d2 species, and the symmetric double-18O and the triple-18O species. A series of vibrational satellites also accompanied the ground-state transitions. The average structure consistent with this data was an ether oxygen envelope conformation having C3 symmetry, with the fluorines axial to the ring. Ab initio calculations were performed for selected values of the pseudorotational phase angle φ to provide additional insights. They indicated that the ether envelope corresponded to the minimum-energy conformer. The potential function vs. φ was relatively flat near the minimum and did not possess a low-energy path corresponding to the usual pseudorotation motion. Instead, the energy valley connecting puckered forms at 180, 90, and 270° terminates at the planar form. The ground-state conformation was discussed in terms of the balance between ring-substituent, substituent-substituent, and puckering forces. Stabilizing ring-substituent interactions dominate this interplay and are also reflected in long C-F and short C-O bond distances indicative of anomic interactions involving the fluorine substituents.

Introduction

Since first being reported in 1868, the reaction of ozone with alkenes in solution has been extensively studied by both experimental3 and theoretical4 means. While the mechanistic proposals have in general centered around that first put forth by Criegee3 and theoretical4 means. While the mechanistic proposals have in general centered around that first put forth by Criegee3 and theoretical4 means. While the mechanistic proposals have in general centered around that first put forth by Criegee3 and theoretical4 means. While the mechanistic proposals have in general centered around that first put forth by Criegee3 and theoretical4 means. While the mechanistic proposals have in general centered around that first put forth by Criegee3 and theoretical4 means. While the mechanistic proposals have in general centered around that first put forth by Criegee3 and theoretical4 means. While the mechanistic proposals have in general centered around that first put forth by Criegee3 and theoretical4 means. While the mechanistic proposals have in general centered around that first put forth by Criegee3 and theoretical4 means. While the mechanistic proposals have in general centered around that first put forth by Criegee3 and theoretical4 means. While the mechanistic proposals have in general centered around that first put forth by Criegee3 and theoretical4 means. While the mechanistic proposals have in general centered around that first put forth by Criegee3 and theoretical4 means. While the mechanistic proposals have in general centered around that first put forth by Criegee3 and theoretical4 means. While the mechanistic proposals have in general centered around that first put forth by Criegee3 and theoretical4 means. While the mechanistic proposals have in general centered around that first put forth by Criegee3 and theoretical4 means. While the mechanistic proposals have in general centered around that first put forth by Criegee3 and theoretical4 means. While the mechanistic proposals have in general centered around that first put forth by Criegee3 and theoretical4 means. While the mechanistic proposals have in general centered around that first put forth by Criegee3 and theoretical4 means. While the mechanistic proposals have in general centered around that first put forth by Criegee3 and theoretical4 means. While the mechanistic proposals have in general centered around that first put forth by Criegee3 and theoretical4 means. While the mechanistic proposals have in general centered around that first put forth by Criegee3 and theoretical4 mean

Scheme I

ozonide (6,7,8-trioxabicyclo[3.2.1]octane, CpO2).11

The four monocyclic ozonides have nonplanar structures with large dihedral angles (40°-50°) about the peroxy bond, while CpO2 is constrained by its bicyclo[3.2.1]octane structure to a C3 symmetry conformation with a peroxy dihedral angle of 0°. Comparison of the structural data has revealed an interesting interplay between lone-pair, bond dipole, and anomic interactions in determining the structure of the fluoro ozonides. The anomic effect can be viewed as a delocalization of electron density from an oxygen atom lone-pair orbital into an adjacent C-X (X = O, F) σ* orbital.12 This orbital overlap is maximized when the C-X bond lies in a plane perpendicular to the C-C-O-R (R = O or C) plane, giving rise to the observed axial fluorine fluorine conformation in FOz and the Q1 envelope conformation of 1,1-F2O3.13

The recent synthesis of cis-1,2-difluoroethylene ozonide (cis-3,3-difluoro-1,2,4-trioxolane, C-F2O)14 provides an opportunity to further explore the interactions which affect ozonide structures. The anomic effect should favor an O-ether (O2) envelope form with the fluorines axial. However, the dipole-dipole repulsion across the ring of the C-F and C-0-peroxy (C-O3) bonds as well as an axial O2 lone-pair interactions will tend to distort the ring away from the symmetric ether envelope form. A previous theoretical study of this system found a broad energy minimum for pseudorotational phase angles (φ) from 90 to 180°,15 i.e. from roughly a peroxy-twisted half-chair form similar to EtO to the O2 envelope with C3 symmetry. The calculated energy difference for the O2 envelope at φ = 108° and the Q1 envelope at φ = 180° was only 70 cal/mol.

(1) Portions of this work were presented as paper RB9, 37th Symposium on Molecular Spectroscopy, Ohio State University, Columbus, OH, 1982.
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However, the calculations lacked a full geometry optimized treatment.

This paper reports microwave (MW) data for several isotopic species and an improved theoretical investigation which indicates that the O envelope conformer is at the energy minimum. The evidence also points to a low-frequency vibrational motion and a relatively flat pseudorotational potential function associated with the ground-state species.

**Experimental Section**

**Instrumentation.** All microwave spectra were recorded on a Hewlett-Packard 8460A spectrometer using radio frequency--microwave double resonance method (RFMWDR), with a Tektronix SG503 oscillator, a buffered Mini-Circuits Lab SGA-3 mixer, and an ENI 406L amplifier as the radio frequency modulation source. The spectrometer cell was cooled with dry ice to between -40 and -60 °C. While the spectrometer's intrinsic resolution is about 0.01 MHz, the large line width of c-F$_2$O$_2$ (typically about 1 MHz hwhm at a pressure of 20–30 mtorr) and its crowded spectrum allowed a measurement accuracy of only 0.1–0.3 MHz. The decomposition half-life of c-F$_2$O$_2$ of ≤20 min and the very low synthetic yields (vide infra) made it impractical to employ computerized signal-averaging techniques to enhance the spectral sensitivity and resolution.

Infrared spectra were recorded with a Beckman 4240 spectrometer; far-IR spectra were recorded with a hybrid Digilab interferometer. Syntheses and product workups were carried out on a preparative vacuum line using standard high-vacuum techniques. Chromatographic separations were performed on a Varian Chromosorb W column. A sampling loop to permit the direct injection of samples from the vacuum line was used.

Syntheses. cis-Difluoroethylene ozonide was typically made by reacting 3 mmol of cis-difluoroethylene (c-DFE; PCR Inc.) in 20–25 mmol of chlorotrifluoromethane (Matheson) at -95 °C, with 0.15–0.20 mmol/min of O$_3$ in O$_2$ from a Welsbach T-408 ozonator for 10–15 min by using standard techniques. All reactants were dried by passage through at -78 °C trap.

Deuterated c-DFE was prepared by exchange with 1 M NaOD/D$_2$O in a stainless-steel bomb at 10 atm and 120 °C. Essentially complete exchange could be obtained in 2 days (as determined by gas-phase IR spectroscopy). c-F$_2$O$_2$-d$_2$ was prepared by ozonolysis of this material, while it was mixed 1:1 with n-DFE for the synthesis of c-F$_2$O$_2$-d$_3$. The latter reaction should yield a normal-d$_3$ ozonide ratio of 1:0:1 in the limit of no scrambling (see Scheme 1) and 1:2:1 for complete randomization. MW intensity measurements of the three species were roughly 1:2:1, indicative of considerable scrambling.

$^{18}$O-labeled species were made by using 98% $^{18}$O$_2$ (Mound Labs) in the ozone generator previously described. Triply substituted $^{18}$O ozonide was prepared from $^{18}$O$_2$. The $^{18}$O$_2$-$^{18}$O$_2$ species was made by adding 5 mmol of HCOF (prepared by the method of Olah$^{17}$) to the initial reaction mixture followed by 1.53 mmol of $^{18}$O$_2$. In this synthesis, the MW spectra of the $^{18}$O ozonide was several times weaker than those of the $^{18}$O$_2$-$^{18}$O$_2$ ozonide, indicative of considerable insertion of the added HCOF into the ozonide. This result (and the extensive deuterium scrambling mentioned above) indicates that the formation of the ozonide proceeds to a large extent via an "out-of-cage" Criegee mechanism.$^{66}$ Thus, the carbonyl oxide intermediate separates from the coproduced formyl fluoride and randomly recombines with the available aldehyde.

The reaction products were separated by trap-to-trap distillation through -78 and -196 °C traps. The major components of the -78 °C trap were cis-difluoroethylene oxide, trans-difluoroethylene oxide, and c-F$_2$O$_2$. The cis ozonide was purified by vapor-phase chromatography. The overall yield of c-F$_2$O$_2$ relative to ozone was typically 1–2%. Samples were stored under vacuum in liquid nitrogen.

To minimize the risk of explosions, ozone input was limited to 2 mmol in any reaction. All reactions were carried out inside a Plexiglas shield fitted with remote control handles to the stopcocks.

**Theoretical Methods.** The conformational features of c-F$_2$O$_2$ are best described by its ring-puckering coordinates,$^{18}$ namely the puckering amplitude $q$ reflecting the degree of nonplanarity of the five-membered ozonide ring and the pseudorotation phase angle $\phi$ defining the mode of ring puckering. Values of 0 and 180° correspond to the $\text{O}_2$ envelope forms having the F atoms in equatorial (0°) or axial positions (180°) (see Figure 1). $\text{O}_2$ envelope forms can be found at 72° (288°) and 108° (252°), and the $\text{O}_2\text{O}_2$ twist forms at 90° (270°), where the $\phi$ values in parentheses belong to the enantiomeric conformers. The conformational energy function is symmetrical to the line $q = 0$, $\phi = 0$; $q = 0$, $\phi = 180°$, which is the location of all $C_2$-symmetrical c-F$_2$O$_2$ forms in $\phi$, $\phi$ space.

Equilibrium geometries, relative energies, and the conformational behavior of c-F$_2$O$_2$ have been calculated with the aid of standard restricted Hartree–Fock theory employing Popie’s split valence 4–31G and augmented split valence 6–31G* basis sets.$^{19}$ Previous calculations indicated that there is a strong dependence of the conformational energy on the F positions.$^{15}$ The puckering amplitude, bond lengths, and angles couple strongly with changes of the conformational energy function is symmetrical to the line $q = 0$, $\phi = 0$; $q = 0$, $\phi = 180°$, which is the location of all $C_2$-symmetrical c-F$_2$O$_2$ forms in $\phi$, $\phi$ space.

Due to the computational demands of such an approach (calculations with 109 functions (6-31G* basis), optimization of 21 parameters), we have simplified calculations using the following procedure: (1) For given values of $\phi$ we have optimized the amplitude $q$, bond lengths, and bond angles with the 4-31G basis. (2) The semirigid pseudorotor model used in the first investigation of c-F$_2$O$_2$ was replaced by a flexible model$^{20}$ in which all parameters are relaxed for any change of $\phi$. (3) Previous calculations indicated that there is a strong dependence of the conformational energy on the F positions.$^{15}$ The puckering amplitude, bond lengths, and angles couple strongly with changes of the F positions which in turn depend on $\phi$. Therefore, the semirigid pseudorotor model used in the first investigation of c-F$_2$O$_2$ was replaced by a flexible model$^{20}$ in which all parameters are relaxed for any change of $\phi$.


Values are the CH bond lengths (R_{\text{CH}} = 1.09 \text{ Å}). (2) At the second stage of the investigation the puckering amplitude and the internal ring angles have been reoptimized with the 6-31G^* basis keeping all other parameters at 4-31G^* values. Theoretical values obtained in this way are known to provide a reasonable description of geometry and conformation of puckered rings.\textsuperscript{46,23,21}

### Results

#### Microwave Spectra

The Stark modulated spectrum of c-F_{2}Oz was very dense with no obvious patterns. Line widths were 1–2 MHz (fwhm) for sample pressures \(\geq 15\) mtorr, and many transitions appeared to be fully modulated with the Stark modulator output nominally at 0 V (actually ca. 20 V (base peak)). Due to the rich spectrum, Stark effects could not be clearly followed. This precluded the use of Stark splittings for spectral assignment and for measurement of the dipole moment.

The spectrum was greatly simplified by RFMWDR and found to consist of several series of \(\mu_0\)-dipole, Q-branch, K-doublet pairs, where the associated radio frequency transition is \(\mu_0\)-dipole allowed. One intense vibrational satellite series with a similar pattern was interwoven with the ground-state pattern. A second weaker vibrational satellite was eventually identified as well as a few of the more intense transitions in approximately the expected positions for a third higher satellite. However, the ozonide samples were depleted before the second and third series could be fully examined at high resolution. While more than 16 of the ground-state, Q-branch pairs could be seen, only three R-branch, K-doublet pairs occur between 26.5 and 40 GHz in the DR spectrum. No other R-branch lines could be unambiguously identified by Stark modulation. The assigned transitions of the ground vibrational state of c-F_{2}Oz are listed in Table I. The rotational and centrifugal distortion constants derived for the ground state are listed in Table II.

The centrifugal distortion analyses (\(P^0\) terms) were performed using a modified version of Kirchhoff’s program CDIST.\textsuperscript{22} The effects of centrifugal distortion led to shifts of up to 140 MHz at \(J = 31\). These are not unusually large effects, so it was puzzling that occasional transitions could not fit to better than 0.5–1.5 MHz by using the quartic centrifugal distortion treatment. (This held true also for the vibrational satellites and the enriched isotopic species.) In some cases this was obviously due to overlapping by weaker neighboring lines, but other deviate transitions appeared free of interference and had symmetric line shapes of ~1 MHz (hwhm). A missassignment of the Q-branch series by one or two units in \(J\) was explored but seemed improbable.

The possibility of a vibration–rotation perturbation arising from a small quartic–dipole minimum type of potential function was considered but rejected on the basis of the ab initio calculations described below. These calculations and the presence of a low-lying vibrational state in the MW spectra indicate that a rather low-frequency, presumably large-amplitude motion is associated with the ring pseudorotation coordinate. It appears that this motion is the likely origin for the small residual deviations in the spectral fit. The limited data set did not make it worthwhile to incorporate \(P^0\) distortion terms or other modeling schemes in order to further improve the fit.

The rotational and centrifugal distortion constants derived from the most intense vibrational satellite are listed in Table II as the \(v = 1\) state. For the \(v = 2\) state, no R-branch transitions could be assigned and only the \(A = C\) and \(J = C\) region were determined and the regular change in their values suggests the assignment to the second excitation of the same mode as the \(v = 1\) state. (The transition frequencies are available as supplementary tables.) Since the dipole moment was not determined, an estimate of the energy difference between the \(v = 0\) and 1 levels was made by measuring the change in relative intensity ratios of several pairs of transitions between 25 and \(-40\) °C. The results indicate that the first excited vibrational state lies 60 ± 50 cm\(^{-1}\) above the ground state. An effort was made to observe transitions associated with this mode using a far-IR spectrometer; however, the ozonide completely decomposed during the spectral acquisition period of 90 min. Strong HCOF bands were observed in the spectrum, and several weak features also occurred between 30 and 100 cm\(^{-1}\), but it was difficult to unambiguously assign them to the ozonide.

Spectra were assigned for the \(v = 0\) and 1 states of the di-deutero species and the \(v = 0\) states of the monodeuterio, triple-deutero, and double-\(^{18}\)O–\(^{18}\)O species by using the RFMWDR technique. Only one ground-state spectrum was found for the d_{2} ozonide species. This suggests that the ground state has \(C_{3v}\) symmetry since an asymmetric structure would give two distinguishable isomers, i.e. \(d_{\text{eq}}\) and \(d_{\text{diastere}}\). The transitions of the \(d_{1}\) species were roughly twice as intense as those of either the \(d_{2}\) or \(d_{3}\) species in that sample (vide synthesizes), which is also supportive of \(C_{3v}\) symmetry. The rotational and distortion constants obtained for all of the assigned species are listed in Table II. A complete list of the assigned transitions of all of the species is available (Tables S1–S7, supplementary material).

#### Conformation and Structure. Spectral Analyses

One test for the presence or absence of symmetry has already been seen in the qualitative appearance of the \(d_{1}\) ozonide spectrum. A further test of symmetry lies in the comparison of the hydrogen atom orbital contributions by Kraitchman’s method\textsuperscript{24} for single quadruplication (which is independent of symmetry) and by the Chutjian–Ngyaard

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\textsuperscript{22} W. H. Kirchhoff, J. Mol. Spectrosc., 41, 333–380 (1972). \(v_{\text{R}}\) is defined according to eq 13 rather than the alternative proposed by Watson.\textsuperscript{23}


observables was employed to estimate structural parameters. Often, a set of assumptions and weighting factors is added to the least-squares fitting as "pseudoexperimental" data to maintain the model's generality. One of these resultant fits, however, may be the method for symmetric double substitution (using the $d_2$ species). If the molecule has a plane of symmetry, then the two sets of coordinates should be essentially identical. The results shown in Table III, coincide within 0.0012 Å for the $a$ and $c$ coordinates and differ by only 0.0053 Å for the smaller and more uncertain $b$ coordinate. The excellent agreement confirms the $C_s$ symmetry of the ground state of c-F$_2$Oz.

Insufficient isotopic data are available to completely determine the structure by the Kraitchman and Chutjian methods, since carbon and fluorine substitution data are not available. (An enriched $^{13}$C synthesis was not practical given the low yields.) In principle, the structure can be calculated by a least-squares fit of the 14 Cartesian coordinates (assuming $C_s$ symmetry) to the 14 equations derived from the observed moments of inertia, the center of mass, and the product of inertia equations. This yields the $\nu_0^*$ or effective structure. In practice such a minimum data set often leads to implausible structures due to the cumulative errors introduced by neglecting small differences in the vibrational amplitudes of the isotopic species, differences in the set of transition used in calculating rotational constants, etc. It was therefore not surprising, given the evidence for low-frequency, large-amplitude motion, that such $\nu_0^*$ calculations would not successfully converge in this case.

An alternative procedure called the method of "predicate observables" was employed to estimate structural parameters.

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**TABLE II:** Rotational and Centrifugal Distortion Constants of c-F$_2$Oz

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>$\text{c-F}_2\text{O}_z$</th>
<th>$\text{c-F}_2\text{O}_z$</th>
<th>$\text{c-F}_2\text{O}_z$</th>
<th>$\text{c-F}_2\text{O}_z$</th>
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<tbody>
<tr>
<td>$A^\prime$/MHz</td>
<td>4256.68 (11)$^a$</td>
<td>4292.70 (15)</td>
<td>4219.33 (23)</td>
<td>4179.85 (16)</td>
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<tr>
<td>$B^\prime$/MHz</td>
<td>2923.67 (4)</td>
<td>2898.32 (4)</td>
<td>2843.41 (4)</td>
<td>2776.82 (5)</td>
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<tr>
<td>$C^\prime$/MHz</td>
<td>2347.38 (4)</td>
<td>2539.67 (3)</td>
<td>2209.95 (3)</td>
<td>2256.05 (5)</td>
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<tr>
<td>$r_\alpha$/kHz</td>
<td>-29.4 (4.6)</td>
<td>-29.2 (5.6)</td>
<td>-37.4 (4.3)</td>
<td>-37.2 (4.4)</td>
</tr>
<tr>
<td>$r_\beta$/kHz</td>
<td>-7.4 (1.5)</td>
<td>-6.5 (2.7)</td>
<td>-9.4 (1.4)</td>
<td>-8.8 (1.3)</td>
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<td>$\tau_{\alpha\alpha}$/kHz</td>
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<td>0.00</td>
<td>0.01</td>
<td>0.01</td>
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<td>-10.8 (6.5)</td>
<td>-10.5 (15)</td>
<td>-5.3 (7.7)</td>
<td>-7.0 (5.5)</td>
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<tr>
<td>$\tau_{\beta\beta}$/kHz</td>
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<td>-4.6 (1.3)</td>
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<td>-6.7 (1.0)</td>
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<td>$\tau_{\alpha\gamma}$/kHz</td>
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<td>-0.24 (1.1)</td>
<td>-2.5 (1.2)</td>
<td>-2.6 (1.0)</td>
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</table>

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**TABLE III:** Substitution Coordinates of the Hydrogen Atom

<table>
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<tr>
<th>coord</th>
<th>Kraitchman$^a$</th>
<th>Chutjian-Nygaard$^b$</th>
<th>K-CN</th>
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<tr>
<td>$\alpha$</td>
<td>±1.9651</td>
<td>±1.9649</td>
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<td>$\beta$</td>
<td>0.2662</td>
<td>0.2715</td>
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<tr>
<td>$\gamma$</td>
<td>1.0137</td>
<td>1.0149</td>
<td>-0.0012</td>
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</table>

$^a$ Calculated from the $d_a$ and $d_a$ species. $^b$ Calculated from the $d_a$ and $d_d$ species.

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**TABLE IV:** Comparison of Structural Parameters Obtained for c-F$_2$Oz and EtOza

<table>
<thead>
<tr>
<th>parameter</th>
<th>c-F$_2$Oz</th>
<th>EtOza</th>
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<tr>
<td>$\phi$</td>
<td>180</td>
<td>90</td>
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<tr>
<td>$\theta$</td>
<td>263.2</td>
<td>263.2</td>
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<tr>
<td>$\omega$</td>
<td>17.3</td>
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<tr>
<td>$\phi_{\text{eq}}$</td>
<td>153.3</td>
<td>153.3</td>
</tr>
</tbody>
</table>

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**Figure 2:** Theoretical pseudorotational potential between $\phi = 90$ and $270^\circ$. The solid line gives the energy change along the dashed line of Figure 4.

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(28) All structural calculations were performed with our extended version of Schwendeman's STRFIT program; R. Schwendeman in "Critical Evaluation of Chemical and Physical Structural Information", D. R. Lide and M. A. Paul, Eds., National Academy of Sciences, Washington DC, 1974, pp 74-115.
Theoretical inversion potential of the equilibrium form ($\phi = 180^\circ$, axial F atoms) of c-F$_2$O$_2$. $\phi = 0^\circ$ corresponds to the O$_e$ envelope with equatorially positioned F atoms.

Figure 3.


Dispersed structural details. Corrections to the moments of varying short value caused by the F substituents. These changes become even more parameters (see Discussion) but are not sufficient for estimating Also, there exists no minimum-energy path for pseudorotation no longer a preferred conformational mode of the ozonide ring.

$\Delta$E [KCAL/MOL]

0 2 4 6

$\phi = 0^\circ$ $\phi = 180^\circ$

0.4 0.2 0 0.2 0.4 q (K)

Figure 4. Qualitative conformational surface of c-F$_2$O$_2$ given by a contour line diagram. The center with $q = 0$ is the location of the planar form. The dashed line corresponds to the energetically most favorable conformational change of the equilibrium form.

Comparison of ab initio and experimental results obtained for c-F$_2$O$_2$ reveals that agreement is similar to the case of EtO$_2$, where extensive spectral data and ab initio calculations are available. The parameters obtained from spectral constants are essentially effective ($r_\alpha$) parameters and contain effects of averaging over the ground vibrational state. Thus, a comparison with the $r_\alpha$ values of the ab initio calculations can only be done qualitatively. On this basis, three observations can be made: (1) Both experiment and theory agree with regard to the overall shape of c-F$_2$O$_2$. This is reflected by the $q$, the $k$, and the substituent position angles listed in Table IV. Puckering is calculated to be somewhat larger than expected from spectroscopic data. (2) Calculated ring bond lengths are 0.01-0.03 Å longer than the experimental ones, which is consistent with results found for EtO$_2$ (Table IV). (3) Theory predicts the CO$_2$ length to be shorter than the CO$_2$ length, which is contrary to estimates from the spectroscopic measurements. Due to the lack of suitable reference data, this contradiction cannot be resolved at present.

Discussion

Both experiment and theory indicate that c-F$_2$O$_2$ adopts an O$_e$ envelope form in the ground state with both F atoms in axial positions. This conformation is the result of an interesting interplay of various electronic effects:

(1) The ozonide ring puckers in order to reduce $l$-$l$ electron repulsion in the peroxide bridge. This would be best accomplished with a twist puckering mode which allocates a large dihedral angle about the O$_2$O$_2$ bond. The same prediction can be made by examining the delocalized MOs of the ring. The antibonding character of the ozonide HOMO is strongly reduced for the O$_2$O$_2$ twist but not for the O$_e$ envelope forms.

(2) Interaction of the F substituents with the ring forces the molecule to deform to the O$_e$ envelope conformation. F is both a $\alpha$-acceptor and a $\pi$-donor substituent. Its donor capacity would lead to a population of the antibonding ozonide orbitals and hence to an overall destabilization of the molecule, provided its $2\pi$ orbitals could overlap with the ring position. This is possible in an equatorial but not in an axial position. Accordingly, a diaxial arrangement of the F substituents leads to the most stable while a diequatorial arrangement to the least stable c-F$_2$O$_2$.

The structural parameters corresponding to the minimum energy conformation are listed in Table IV, both for the flexible and semirigid pseudorotor model. Comparison of these data with the MW structure underlines the necessity of a full geometry optimization (flexible pseudorotor) and reveals structural changes caused by the F substituents. These changes become even more apparent when considering results obtained for EtO$_2$, which are also included in Table IV.

The puckering amplitude of c-F$_2$O$_2$ is reduced by almost 40% as compared to that of EtO$_2$. This is due to both the change of $\phi$ from 90° (EtO$_2$) to 180° and dipole–dipole repulsion between the CO bond moments across the ring. The decrease of the intrinsic structure of the ozonide HOMO is strongly reduced for the $\alpha$-F2O$_2$. This is due to both the change of $\phi$ from 90° (EtO$_2$) to 180° and dipole–dipole repulsion between the CO bond moments across the ring. The decrease of the center with $q = 0$ is the location of the planar form. The dashed line corresponds to the energetically most favorable conformational change of the equilibrium form.
conformers (Figure 3). As pointed out in the Introduction, this situation can be described in terms of localized orbitals via the anomeric effect: Both the \( \text{O}_2 \) and \( \text{O}_3 \) lp orbitals are almost coplanar (see dihedral angles in Table IV) with the CF bond and can therefore interact with the \( \sigma^*_{\text{CF}} \) orbital. This causes a shortening of the CO bonds and a lengthening of the CF bond.

The latter effect becomes obvious when comparing the CF bond lengths found for \( c\text{-F}_2\text{O}_2 \) (Table IV) with those of \( \text{CFH}_2 \left( R_{\text{CF}} = 1.332 \text{ Å}^{50} \right) \), where the O atoms of the \( \text{O}^-\text{CFH}^-\text{O}^- \) fragment are replaced by additional F atoms. The difference (0.04 Å) clearly reveals a lengthening of the CF bond in \( c\text{-F}_2\text{O}_2 \).

(3) Once the molecule is “locked” in the diaxial \( \text{O}_2 \) envelope form by strong ring–substituent interactions, puckering should increase in order to delocalize \( \text{O}_3 \) lp electrons into the \( \sigma^*\text{CO} \) orbitals and thus to reduce \( \text{p}^-\text{p}^-\text{repulsion} \) in the \( \text{O}_2\text{O}_3 \) bridge. Puckering, however, leads to an increase of across ring interactions between the F atoms. Both monopole–monopole as well as dipole–dipole interactions are repulsive. Lowering of these interactions can be achieved either by a rocking motion of the CFH groups, a flattening of the puckered ring, or a combination of both effects. The calculated as well as the spectroscopic rocking angles are small (1.0° vs. 2.5°) as are the wagging (0.1° vs. 0.6°) and bending angles (0.4° vs. 0.6°). Hence, a reduction in the destabilizing electrostatic interactions between the F atoms is solely achieved by decreased puckering, although this will lead to enhanced antibonding in the HOMO of the ozonide.

The balance between ring–substituent, substituent–substituent, and puckering forces determines the actual values of the geometrical parameters. Stabilizing ring–substituent interactions clearly dominate which becomes obvious when considering the formal reaction

\[
\text{F} + 2\text{CH}_4 \rightarrow \text{F}_2\text{O}_2 + 2\text{CH}_3\text{F}
\]

The calculated reaction energy of 35.1 kcal/mol is the sum of four terms: twice a contribution of 22 kcal/mol which is due to stabilization interactions between one F atom and the ring as obtained from the HF/6-31G* energy of monofluorozonide;\(^{15} \) a gain of about 4 kcal/mol caused by changing the puckering mode of the ozonide from \( \phi = 180° \) to \( \phi = 0° \) (3 kcal/mol);\(^{60} \) and increasing \( \phi \) from 0.28 to 0.35° (1 kcal/mol).\(^{60} \) A destabilization term due to F–F interactions, which can be evaluated from the following equation:

\[
35 = 2(22) - 4 + X \quad X = -5 \text{ kcal/mol}
\]

A similar value is obtained when relaxing the semirigid pseudorotor model. Therefore, it is reasonable to say that F–F interactions destabilize \( c\text{-F}_2\text{O}_2 \) by 5 kcal/mol.

It is interesting to note that energetic and geometrical results do not provide any indication that F–F interactions might be stabilizing. Through-space interactions between F atoms have been considered to stabilize in the case of 1,2-difluoroethylene \( (\text{F}_2\text{Et}) \) in order to rationalize the higher stability of its cis isomer as opposed to that of its trans isomer.\(^{52} \) In the equilibrium conformations \( c\text{-F}_2\text{O}_2 \) contains the CF bonds in almost the same geometrical arrangement as in \( c\text{-F}_2\text{Et} \) (F–F distance 2.84 Å\(^{52} \)) separated, however, by two bonds rather than one. The absence of stabilizing F–F interactions in \( c\text{-F}_2\text{O}_2 \) strongly suggests that these depend on the type and number of bonds connecting the F atoms (F–C–C–C–F in \( c\text{-F}_2\text{Et} \) as opposed to F–C–O–C–F in \( c\text{-F}_2\text{O}_2 \)); i.e., F–F attraction is a through-bond rather than a through-space phenomenon.\(^{33} \) Work is in progress to further scrutinize this conclusion.

The features of the calculated conformational energy surface reflect the dominance of substituent–ring interactions in the ring. A gradual change of \( \phi \) from 180° to 90° or 270° brings one F atom into an equatorial position (Figure 1 and ref 4c) and, hence, raises the energy. A situation where both F atoms are in an equatorial position \( (\phi = 0°) \) is energetically less favorable (due to \( \pi \)-donation) than a planar form with the F substituent in an inclinal position, which does not allow the F atoms to develop their full donor capacity. For each conformer in \( \phi, \phi \) space, opposing electronic effects determine geometry and stability as discussed for the equilibrium conformation. This leads to a conformational energy surface with potentially interesting dynamical effects. This was evident from the microwave spectrum which in fact motivated us to reexamine the energy surface by ab initio means for guidance on the presence of another low-energy form or for the presence of a small barrier at the \( C_2 \) (\( \phi = 180° \)) position. It would be interesting to obtain additional IR and MW data to further explore the vibration–rotation interaction effects associated with the pseudorotation coordinate. Unfortunately, the very inefficient syntheses of \( c\text{-F}_2\text{O}_2 \) and its instability make it a very difficult experimental system to acquire the extensive spectral data necessary for this task.

\( c\text{-F}_2\text{O}_2 \) is the second example of an ozonide possessing a stable \( \text{O}_2 \) envelope conformation. The only previous example, however, occurs in cyclopentene ozonide where the bicyclic ring system constrains the ozonide ring to the \( C_2 \)-symmetrical envelope form.\(^{11} \) The preference of a F substituent to adopt an axial position in the ozonide ring has already been demonstrated in vinyl fluoride ozonide\(^{6} \) and vinylidene fluoride ozonide.\(^{10} \) The geometrical data obtained in this work, in particular the spectrally derived CO and CF bond lengths, are very close to the \( r_p \) values derived from the MW data on vinyl fluoride ozonide.\(^{19} \) In essence, the spectral and ab initio geometry parameters of \( c\text{-F}_2\text{O}_2 \) most likely fit reasonable and systematic trends compared to the case for analogous systems.

In summary, \( c\text{-F}_2\text{O}_2 \) is an unusual species providing nonroutine challenges to a spectroscopic or ab initio analysis. By combining both approaches, its ground-state conformation was established and structural parameters were estimated. This provided insight on the interplay between various electronic interactions which give rise to the uncommon conformational potential function. One noteworthy finding has been the indication that the F–F through-space interactions are basically repulsive unlike other examples such as \( \text{cis-CHF}^-\text{CHF} \) where attractive or stabilizing F–F interactions occur which are apparently dependent on a through-bond mechanism.

**Acknowledgment.** This work was supported by Grants CHE-8005471 and CHE-8303615 from the National Science Foundation. Support at the Universität Köln was provided by the Deutsche Forschungsgemeinschaft and the Fond der Chemischen Industrie. All ab initio calculations were carried out at the Rechenzentrum der Universität Köln.

**Supplementary Material Available:** Tables S1–S7 listing transition frequencies for the ground and excited vibrational states (7 pages). Ordering information is given on any current masthead page.


\(^{31} \) The following absolute HF/6-31G* energies (in hartree) have been used to calculate the reaction energy: –502.25109 \( (c\text{-F}_2\text{O}_2) \), –4019517 \( (\text{CH}_4) \), –202516.22 \( (\text{EtO}_2) \), –1392146 \( (\text{CH}_3\text{F}) \).
