This suggests that an oxy-bridged structure is a contributing factor to the bonding in **3**.

Acknowledgment. We thank the Rutgers Research Council and the Center for Computer and Information Services, Rutgers University, for partial financial support. We also thank Professor J. San Filippo, Jr. for helpful discussions.

Registry No. 3, 63181-01-1; $Mo(CO)_6$, 13939-06-5; Ph_2C_2, 501-65-5.

Supplementary Material Available: Listing of structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Rutgers, The State University of New Jersey. (b) The Weizmann Institute of Science.

(2) (a) W. Hübel and R. Merényi, *J. Organomet. Chem.*, **2**, 213 (1964); (b) A. Efraty, J. Potenza, L. Zyontz, J. Daily, and M. H. A. Huang, *ibid.*, in press.

(3) J. Potenza, P. Giordano, D. Mastropaolo, and A. Efraty, *Inorg. Chem.*, **13**, 2540 (1974).

(4) Program ABSORB, written by P. Coppens and R. F. Stewart, was used.

(5) To calculate the *E* map, program REL (R. E. Long, Ph.D. Dissertation, UCLA, 1965) was used; additional programs used are given in ref 3.

(6) S. J. LaPlaca and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965).

(7) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England.

(8) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(9) P. Ganis, G. Avitabile, W. Mechlinski, and C. P. Schaffner, *J. Am. Chem. Soc.*, **93**, 4560 (1971).

(10) Supplementary material.

(11) (a) $[Ph_4C_4Mo(CO)_2Br]_2$ (2.954 (1) Å), M. Mathew and G. L. Palenik, *Can. J. Chem.*, **47**, 705 (1969); *J. Organometal. Chem.*, **61**, 301 (1973); (b) $[Mo_2(CO)_{10}]^{2-}$ (3.123 (7) Å), L. B. Handy, J. K. Ruff and L. F. Dahl, *J. Am. Chem. Soc.*, **92**, 7312 (1970); (c) $[C_5H_5Mo(CO)_3]_2$ (3.235 (1) Å), R. D. Adams, D. M. Collins, and F. A. Cotton, *Inorg. Chem.*, **13**, 1086 (1974).

(12) (a) $Mo_2[CH_2SiMe_3]_6$ (2.167 Å), F. Huq, W. Monat, A. Shortland, A. C. Skapski, and G. Wilkinson, *Chem. Commun.* 1079 (1971); (b) $[C_5H_5Mo(CO)_2]_2$ (2.448 (1) Å), R. J. Klingler, W. Butler, and M. D. Curtis, *J. Am. Chem. Soc.*, **97**, 3535 (1975).

(13) F. A. Cotton, *Chem. Soc. Rev.*, **4**, 27 (1975).

(14) W. G. Sly, *J. Am. Chem. Soc.*, **81**, 18 (1959).

(15) K. Nicholas, L. S. Bray, R. E. Davis, and R. Pettit, *Chem. Commun.*, 608 (1971).

(16) W. I. Bailey, Jr., F. A. Cotton, J. D. Jamerson, and J. R. Kolb, *J. Organomet. Chem.*, **121**, C23 (1976).

(17) F. A. Cotton and J. G. Norman, Jr., *J. Coord. Chem.*, **1**, 161 (1971).

(18) F. A. Cotton, Z. C. Mester, and T. R. Webb, *Acta Crystallogr., Sect. B*, **30**, 2768 (1974).

(19) F. L. Bowden and A. B. P. Lever, *J. Organomet. Chem. Rev., Sect. A*, **3**, 227 (1968).

(20) P. M. Maitlis, *Adv. Organomet. Chem.*, **4**, 95 (1966).

(21) G. M. Whitesides and W. J. Ehmann, *J. Am. Chem. Soc.*, **91**, 3800 (1969).

(22) A. A. Pasynokii, K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, **185**, 610 (1969).

(23) V. W. day, R. O. Day, J. S. Kristoff, F. J. Hirsekorn, and E. L. Muetterties, *J. Am. Chem. Soc.*, **97**, 2571 (1975).

(24) J. P. Collman, R. G. Finke, P. L. Matlock, R. Wahren, and J. I. Brauman, *J. Am. Chem. Soc.*, **98**, 4685 (1976).

(25) 2-Propene-2,3-diol-1-one: C═O = 1.240 (2) Å; C–OH = 1.351 (2), 1.322 (2) Å; D. Semminsen, *Acta Chem. Scand., Ser. B*, **28**, 141 (1974).

(26) *p*-Benzoquinone: C═O = 1.222 (8) Å; J. Trotter, *Acta Crystallogr.*, **14**, 553 (1961).

(27) 2-Hydroxyl-4-methoxybenzophenone: C(aliph)–O = 1.435 (5) Å; C(arom)–O = 1.356 (5) Å; B. W. Liebich and E. Parthé, *Acta Crystallogr., Sect. B*, **30**, 2522 (1974).

Contribution from the Departments of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109,
and Kansas State University, Manhattan, Kansas 66506

Molecular Structures of CF_3OOH, CF_3OOF, and CF_3OOCl by Gas-Phase Electron Diffraction

C. J. MARSDEN, D. D. DESMARTEAU,[1] and L. S. BARTELL*

Received February 28, 1977 AIC70154C

Structural characteristics of the present molecules are consistent with previous chemical evidence differentiating the substances from each other and from other peroxides. Whereas the hydride and chloride are typical peroxides, the fluoro derivative departs significantly in the direction of the unusual substance FOOF as revealed by the rather short O–O and long O–F and C–O bonds. It was observed that O–O bond lengths in peroxides are strongly correlated with the force constants for internal rotation about the peroxide bonds. The trifluoromethyl groups have unexceptional structures, tilts, and, except for the chloro derivative, conformations. It appears in the case of CF_3OOCl that $CF_3 \cdots Cl$ steric interactions introduce a hump in the expected minimum of the CF_3 torsional potential function at the staggered conformation, giving rise to two distinct conformers. Structural parameters ($\pm 3\sigma$) for CF_3OOX (X = H, Cl, F) were determined to be r_g(O–O) = 1.447 (8), 1.447 (15), 1.366 (33) Å; r_g(O–X) = 0.974 (42), 1.699 (6), 1.449 (15) Å; r_g(C–O) = 1.376 (10), 1.372 (22), 1.419 (24) Å; ∠O–O–X = (100.0, assumed), 110.8 (1.2), 104.5 (4.5)°; and ∠O–O–C = 107.6 (0.8), 108.1 (4.0), 108.2 (1.2)°. Values of other structural parameters are tabulated together with observed amplitudes of vibration as well as calculated amplitudes and shrinkage corrections derived with the aid of a normal-coordinate treatment.

Introduction

Highly fluorinated peroxides are a small but most interesting class of compounds.[2] Although the first two examples, CF_3OOCF_3[3] and FOOF,[4] were prepared in 1933, further well-characterized examples did not appear until the 1950's. At present, the number of such compounds is over 100 and some general synthetic methods have been found which could make their number much larger.

It turns out that the first two examples represent extremes in this class of compounds. Both O_2F_2 and $CF_3O_2CF_3$ are unusual compounds, O_2F_2 for its unusual structure, low thermal stability, and extreme reactivity and $CF_3O_2CF_3$ for its high thermal stability, unusual decomposition equilibrium, and rather low reactivity. While both compounds are formally derivatives of H_2O_2, where hydrogen is replaced by an electronegative atom or group, they have little other similarity. The oxygen–oxygen bond in $CF_3O_2CF_3$ closely resembles that in H_2O_2,[5] whereas the bond in O_2F_2 is considerably shorter and not greatly different from that in molecular oxygen.[6] Several rationales have been invoked to account for structural variations among the compounds, but a quantitative treatment has not yet appeared.[7]

Three important compounds that can be viewed as intermediate between H_2O_2 and O_2F_2 are CF_3OOH,[8,9] CF_3OOCl,[10,11] and CF_3OOF.[12,13] These molecules can in principle

---

*To whom correspondence should be addressed at The University of Michigan.

Table I. Observed NMR and Vibrational Data for Peroxides

	ϕ^{*a}		ν, cm^{-1}		
Compd	CF_3	OF	OO	OX	Ref
CF_3OOH	72.3		865	3575	9, 17
CF_3OOCl	69.9		828	665	10, 17
CF_3OOF	68.9	−292	873	760	12, 17, 18
CF_3OOCF_3	69.0		886		19, 20
CF_3OCl	64.0			780	15, 17
CF_3OF	72.3	−147.1		882	15, 17
O_2F_2		−82.5	1306	621, 615	21, 22
H_2O_2			880	3599, 3608	23

[a] ^{19}F chemical shift in ppm relative to $CFCl_3$ as an internal standard.

provide considerable insight into the factors affecting the nature of the oxygen–oxygen bond in peroxides. The chemistry of CF_3OOX (X = H, Cl, F) indicates that the hydride and chloride are unremarkable. Trifluoromethyl hydroperoxide is very acidic but otherwise like organic hydroperoxides. The chloro derivative has low thermal stability but otherwise resembles other hypochlorites, especially CF_3OCl, to which it readily decomposes. The fluoro derivative is less similar to CF_3OF in its reactions and exhibits much greater reactivity.[14-16] Comparisons among the thermal decomposition patterns of the three show that CF_3OOF at least formally resembles O_2F_2.

$$CF_3OOH \rightarrow COF_2 + HF + O_2/2$$

$$CF_3OOCl \rightarrow CF_3OCl + O_2/2$$

$$CF_3OOF \rightarrow CF_4 + O_2$$

Vibrational spectroscopy and NMR provide further suggestive comparisons[17-23] among CF_3OOX, H_2O_2, and O_2F_2. Pertinent data are summarized in Table I. Taken at face value, the data suggest that the CF_3 peroxides are rather like H_2O_2 and that the OX bonds (X = Cl, F) are similar to those in CF_3OX. On the other hand, chemical evidence suggests some similarity between CF_3OOF and O_2F_2. In order to provide a more definitive basis for comparison, detailed structural information is needed. Gas-phase electron diffraction is well suited to this task and the present paper reports the structures of CF_3OOX (X = H, Cl, F).

Experimental Section

Samples of CF_3OOH,[9] CF_3OOF,[14] and CF_3OOCl[11] were prepared and purified following standard procedures. Electron diffraction patterns were recorded on 4 × 5 in. Kodak electron image plates, using the diffraction unit at the University of Michigan[24] equipped with an r^3 sector, at the 21-, 11-, and 7-cm distances. Incident electrons were accelerated through 40 kV. All samples were maintained at −196 °C when not in use. Since CF_3OOCl reacts extremely readily with many different substances, the nozzle and inlet system were seasoned with two bursts of vapor prior to recording any diffraction patterns for CF_3OOCl. Experimental conditions are given in Table II. Photographic plates were developed at 20 °C for 3 min using Kodak HRP developer to which antifog solution had been added. All photographic solutions were continually agitated with bursts of nitrogen gas. An automated recording microphotometer, with digital output, measured the absorbance of the plates at $^1/_8$ mm intervals, while they were spun about the center of the diffraction pattern. Absorbances were converted to exposures by the following relationship[25]

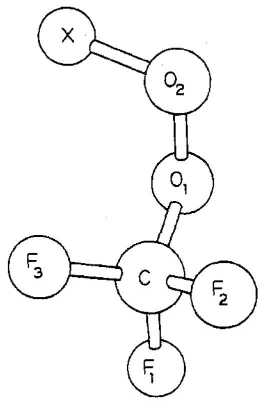

Figure 1. A view of the molecule CF_3OOX (X = H, F, or Cl) showing the atomic labeling scheme adopted.

$$E = A(1 + 0.116A + 0.0179A^2 + 0.00312A^3)$$

in which E and A are respectively the exposure and the absorbance. Experimental intensities, obtained by averaging data from the number of plates for each distance listed in Table II, were leveled after applying corrections for extraneous scattering and for irregularities in the sector opening. Atomic elastic and inelastic scattering factors used for carbon, oxygen, chlorine, and hydrogen were those of Schafer, Yates, and Bonham,[26] but those for fluorine were taken from the data of Cox and Bonham.[27] Molecular parameters were refined by a least-squares process which imposed geometrical self-consistency on the internuclear distances, comparing values of the reduced molecular intensity $M(s)$. Intensity data for the three camera distances were initially treated separately until the individual background functions had been established. The three data sets were blended together once acceptable matching of $M(s)$ had been obtained for the overlapping regions. Indices of resolution for the 21-, 11-, and 7-cm data were CF_3OOH 0.89, 0.92, 0.95; CF_3OOF 0.90, 0.90, 0.86; and CF_3OOCl 0.87, 0.92, 0.89. The composite data sets, covering the range $4.0 \leq s \leq 49.7$, were interpolated in units of $\Delta s = \pi/10$. Diagonal weight matrices were used, whose elements were proportional to the scattering variable s, but the uncertainties quoted have been augmented to take the correlation between neighboring data points ($\gamma \approx 1$ Å[24]) into account. Radial distribution functions were calculated using a damping factor of $\exp(-0.0015s^2)$. Asymmetry constants[28] were taken to be 2.5 for the O–H distance, 2.0 for all other bonded distances, and 1.0 for all nonbonded distances. Approximate shrinkage corrections, calculated by the program MSAV written by R. L. Hilderbrandt from force fields discussed elsewhere,[29] were applied; they are listed in Table III.

Structure Analyses

A view of the molecule CF_3OOX (X = H, F, or Cl) is shown in Figure 1. In the general molecular model adopted, we assumed only that the CF_3 group possesses local C_{3v} symmetry and that its axis lies in the O_2O_1C plane. Ten geometrical parameters are required to define the structure. We chose these to be the O_2–X, O_1–O_2, C–O_1, and C–F bond lengths, the X–O_2–O_1, O_2–O_1–C, and F–C–F bond angles, the X–O_2–O_1–C dihedral angle, and angles of twist and tilt for the CF_3 group. The angle of twist defines the rotation of the CF_3

Table II. Experimental Conditions for Recording Diffraction Patterns

	CF_3OOH			CF_3OOF			CF_3OOCl		
Camera distance, cm	21.112	11.083	6.540	21.115	11.083	6.535	21.115	11.081	6.537
Reservoir temp, °C	−45	−45	−45	−120	−120	−120	−78	−78	−78
Nozzle temp, °C	27	27	27	27	27	27	27	27	27
Vapor pressure, Torr	22	22	22	18	18	18	30	30	30
Exposure time, s	3-5	16-24	40-60	5-8	18-32	36-60	3-5	10-18	36-50
Beam current, μA	0.70	0.36	0.36	0.68	0.36	0.36	0.38	0.37	0.36
Pt nozzle diameter, mm	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Nozzle-beam distance, mm	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
No. of plates	5	5	5	5	5	4	4	5	5

Table III. Approximate Shrinkage Corrections Applied to CF_3OOX, in Å

	CF_3OOH	CF_3OOF	CF_3OOCl
$X\cdots O_1$	0.0093	0.0114	0.0073
$F_1\cdots F_2$	0.0023	0.0021	0.0021
$O_2\cdots C$	0.0074	0.0061	0.0051
$O_1\cdots F_1$	0.0015	0.0009	0.0006
$O_1\cdots F_2$	0.0028	0.0022	0.0028
$O_1\cdots F_3$	0.0053	0.0044	0.0057
$X\cdots C$	0.0266	0.0208	0.0146
$O_2\cdots F_1$	0.0152	0.0139	0.0131, 0.0135[a]
$O_2\cdots F_2$	0.0063	0.0061	0.0041, 0.0078
$O_2\cdots F_3$	0.0083	0.0086	0.0099, 0.0060
$X\cdots F_1$	0.0297	0.0301	0.0266, 0.0224
$X\cdots F_2$	0.0522	0.0328	0.0212, 0.0260
$X\cdots F_3$	0.0047	0.0084	0.0089, 0.0066

[a] The second entry refers to the distances in the second, less abundant, conformer.

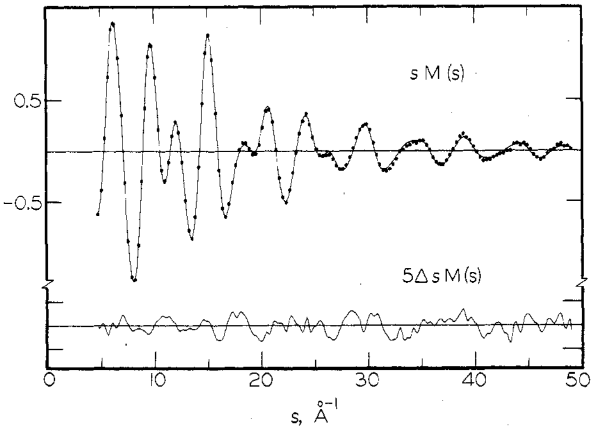

Figure 2. Observed and calculated molecular intensity function $sM(s)$ for CF_3OOH: filled circles are experimental points; smooth line is theoretical curve. $\Delta = sM(s)_{\text{exptl}} - sM(s)_{\text{calcd}}$.

group about its threefold axis away from the conformation in which it staggers the O_1–O_2 bond. A positive rotation implies that F_3 is closer to O_2 than is F_2. The angle of tilt denotes the deviation of the threefold axis of the CF_3 group away from the C–O_1 direction; if that angle is positive, F_1 is closer to O_2 than are F_2 and F_3. It was evident at the outset that difficulty would be experienced in refining all ten parameters simultaneously by least squares, due to the extensive overlapping of internuclear distances in the radial distribution function. These difficulties were reduced to manageable proportions with the availability of calculated amplitudes of vibration for all internuclear distances, except those involving torsional motion around the O–O bond for CF_3OOCl.

A. CF_3OOH. Experimental and final calculated molecular intensities are presented in Figure 2. The radial distribution function displayed in Figure 3 has only four main features, since the bonded distances (excluding O_2–H) all lie under one peak, as do the 1,3 nonbonded distances (excluding $O_1\cdots H$). Scattering due to atom pairs involving hydrogen is very weak, and we thought it unprofitable to attempt to determine two of the three parameters defining the hydrogen atom's position. The H–O_2–O_1 bond angle and the H–O_2–O_1–C dihedral angles were fixed at apparently reasonable values. Such constraints are not expected to influence the results derived for the other parameters to any significant extent. Attempts to refine the angle of twist of the CF_3 group showed that its value was close to zero and very strongly correlated with that of the $O_2\cdots F_2,F_3$ amplitude of vibration ($\rho = 0.97$), as anticipated, since virtually no information can be obtained from the positions of the $H\cdots F$ peaks. Accordingly, the angle of twist was fixed at zero, and the $O_2\cdots F_2,F_3$ amplitude allowed to refine.

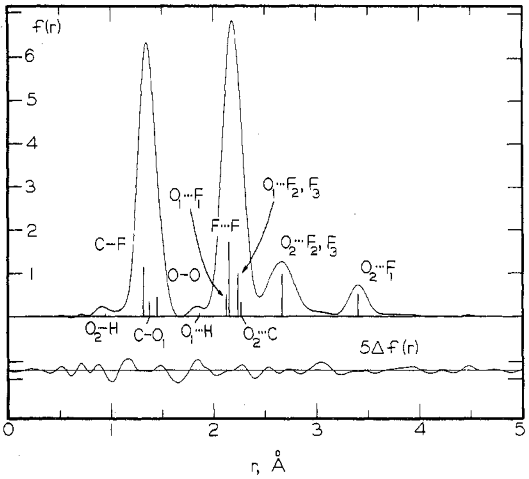

Figure 3. Experimental radial distribution function for CF_3OOH. $\Delta = f(r)_{\text{exptl}} - f(r)_{\text{calcd}}$.

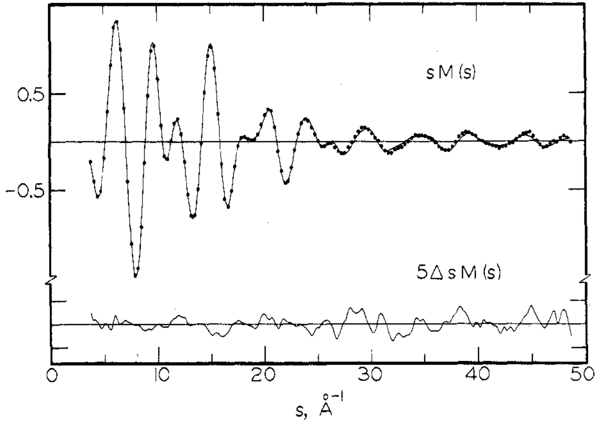

Figure 4. Observed and calculated molecular intensity function $sM(s)$ for CF_3OOF: filled circles are experimental points; smooth line is theoretical curve for minimum I (see text). $\Delta = sM(s)_{\text{exptl}} - sM(s)_{\text{calcd}}$.

With these constraints applied, all 11 parameters (seven geometrical, four amplitudes) converged satisfactorily without any instability. The standard deviations obtained are naturally larger than could be expected for molecules with no overlapping distances, although not excessively so. Experimental values of the amplitudes of vibration are all pleasingly close to those calculated spectroscopically. The angle of tilt is small, yet appears to be well determined. Refinements in which the tilt angle was fixed at zero gave residuals almost three times higher than when it was free to refine. Despite its evident correlation with the $F\cdots F$ amplitude of vibration, we feel that the tilt angle is demonstrably nonzero. Only one least-squares minimum was found, although extensive searches were made for others. Final parameter values are listed in Table IV. The correlation matrix, presented in Table V, contains only two elements numerically greater than 0.7.

B. CF_3OOF. Experimental and final calculated molecular intensities are displayed in Figure 4, and the radial distribution function is shown in Figure 5. The problems caused by parameter correlation are much more acute for CF_3OOF than for CF_3OOH. Ten geometrical parameters must be extracted from the five distinct peaks and two poorly defined additional features visible in Figure 5. It proved impossible to find a stable least-squares minimum starting from CF_3OO parameter values close to those obtained for CF_3OOH. Two minima were eventually located. Minimum I is characterized by an O_1–O_2 bond appreciably shorter than that in CF_3OOH, whereas the C–O_1 bond is somewhat longer, and the O_2–F_4 distance is greater than that found in OF_2.[30] For minimum II, the O_1–O_2

Table IV. Structural Parameters for CF_3OOH and CF_3OOCl[a]

	CF_3OOH			CF_3OOCl		
Parameter description and no.	r_g, Å, or $\angle_\alpha$, deg	l_α, Å	Calcd amplitude, Å	r_g, Å, or $\angle_\alpha$, deg	l_α, Å	Calcd amplitude, Å
$r(O_2\text{-}X)\ r_1, l_1$	0.974 (42)	0.070^b	0.070	1.699 (6)	0.050 (8)	0.051
$r(O_1\text{-}O_2)\ r_2$	1.447 (8)	0.052^b	0.052	1.447 (15)	0.053^b	0.053
$r(C\text{-}O_1)\ r_3$	1.376 (10)	0.047^b	0.047	1.372 (22)	0.048^b	0.048
$r(C\text{-}F)\ r_4, l_2$	1.324 (4)	0.045 (5)	0.044	1.323 (7)	0.045 (9)	0.044
$\angle(O_2\text{-}O_1\text{-}C)\ \angle_1$	107.6 (0.8)			108.1 (4.0)		
$\angle(F_1\text{-}C\text{-}F_2)$	109.2 (0.7)			110.0 (1.8)		
$\angle$tilt $\angle_3$	4.8 (0.9)			5.1 (2.5)		
$\angle(X\text{-}O_2\text{-}O_1)\ \angle_4$	100.0^b			110.8 (1.2)		
$\angle\tau(X\text{-}O_2\text{-}O_1\text{-}C)$	95.0^b			93.2 (7.0)		
$\angle$twist $\angle_6, \angle_7$	0.0^b			−15.5 (3.6) and +23.6 (7.5)[c]		
$r(F_1\cdots F_2)\ l_3$	2.160	0.058 (5)	0.054	2.166	0.062 (14)	0.054
$r(O_1\cdots F_1)$	2.142	0.062^b	0.062	2.122, 2.126[d]	0.064^b	0.064
$r(O_1\cdots F_2)$	2.239	0.059^b	0.059	2.238, 2.198[d]	0.062^b	0.062
$r(O_1\cdots F_3)$	2.239	0.059^b	0.059	2.203, 2.244[d]	0.062^b	0.062
$r(O_2\cdots C)$	2.271	0.065^b	0.065	2.277	0.064^b	0.064
$r(O_2\cdots F_2)\ l_4$	2.666	0.109 (8)	0.122	2.538, 2.869[d]	0.11^b	0.127
$r(O_2\cdots F_3)\ l_4$	2.666	0.109 (8)	0.122	2.793, 2.480[d]	0.11^b	0.128
$r(O_2\cdots F_1)\ l_5$	3.410	0.063 (12)	0.065	3.383, 3.361[d]	0.060 (25)	0.069
$r(X\cdots O_1)\ l_6$	1.802	0.104^b	0.104	2.586	0.071 (15)	0.067
$r(X\cdots C)$	2.598	0.20^b	0.20	3.239	0.15^b	0.12
$r(X\cdots F_1)\ l_7$	3.662	0.17^b	0.17	4.388, 4.056[d]	0.10 (4)	0.12, 0.16[d]
$r(X\cdots F_2)\ l_8$	3.273	0.23^b	0.23	3.717, 4.185[d]	0.13 (5)	0.20, 0.16[d]
$r(X\cdots F_3)\ l_9$	2.630	0.31^b	0.31	3.047, 2.897[d]	0.18 (7)	0.20, 0.20[d]
$\sigma(I)/\bar{I}^e$	7.36×10^{-4}			8.86×10^{-4}		

[a] Uncertainties in parentheses, in units of least significant digit quoted, are 3σ. σ includes random errors and our estimates of possible systematic errors and of the effects of correlation between neighboring data points ($\gamma \approx 1$ Å). [b] Parameter not varied in least-squares refinements. [c] Two torsional conformers were found for CF_3OOCl, with twist angles of −15.5° (66%) and + 23.6° (34%). Other parameters assumed equal. [d] The second entry refers to the less abundant conformer. [e] Mean fractional standard deviation of diffraction intensity points.

Table V. Matrix of Correlation Coefficients[a] for CF_3OOH

	r_1	r_2	r_3	r_4	$\angle_1$	$\angle_2{}^b$	$\angle_3$	l_2	l_3	l_4	l_5	R
σ	0.0087	0.0018	0.0024	0.00070	0.20	0.14	0.24	0.00060	0.00091	0.0022	0.0032	0.0036
r_1	100	7	1	6	−8	4	2	−5	−7	<1	<1	−6
r_2		100	−46	50	−44	21	34	37	−9	7	3	47
r_3			100	−87	1	−44	−9	−72	−19	−13	1	−4
r_4				100	−24	59	17	63	1	8	−1	5
$\angle_1$					100	−30	−36	−1	29	1	−16	−18
$\angle_2$						100	−39	38	28	4	<1	−3
$\angle_3$							100	11	−57	2	<1	21
l_2								100	16	10	1	26
l_3									100	2	1	2
l_4										100	−1	3
l_5											100	8
R												100

[a] Units for σ are Å for distances and amplitudes, degrees for angles. R is dimensionless. Matrix elements are given by $\rho_{ij} = (M_x)_{ij}/[(M_x)_{ii} \cdot (M_x)_{jj}]^{1/2}$, where M_x is the zeroth-order error matrix. Only the upper half of the matrix is given. All entries, except for the standard deviations, have been multiplied by 100. The numbering of the parameters follows from Table III, except where indicated. [b] Angle between the threefold axis of the CF_3 group and a C-F bond.

bond length is similar to that in CF_3OOH, although the $C–O_1$ bond is somewhat shorter and the $O_2–F_4$ distance is less than that in OF_2.[30] Minimum I was stable, all parameters converging successfully, whereas minimum II could be made to converge only if one parameter, such as the $O_2–F_4$ bond length or the $F_4–O_2–O_1$ bond angle, were fixed. The precise position of the minimun was located by determining that fixed value of the nonvaried parameter leading to the converged solution with the lowest residuals.

We think that minimum I is the real solution and that II arises simply from the severe parameter correlation. The fractional standard deviations of the diffraction intensity data are 8.41×10^{-4} for I and 9.14×10^{-4} for II. Since the residuals in our data are far from randomly distributed, it is difficult to apply objective criteria as to the significance of the better fit achieved by minimum I than by II. It is our intuitive feeling that the difference in fit is sufficiently large that II can be regarded as an artifact, a consequence of the limited resolution of overlapping distances obtainable by electron diffraction. In addition to its unstable behavior in the least-squares refinements, and its poorer fit, we note that the values of several parameters in minimum II agree less well with those found for CF_3OOH and CF_3OOCl than do those for minimum I. Parameters such as the C–F bond length, the $O_2–O_1–C$ bond angle, and the CF_3 tilt angle might reasonably be expected to be very similar in all three CF_3OOX molecules studied, although in view of the fairly large uncertainties involved, such considerations do not furnish strong additional evidence for rejecting minimum II. Also consistent with the selection of minimum I is the compatibility between the O–O bond length and the C–O–O–F torsional force constant as outlined in the Discussion.

In the final least-squares cycles for minimum I, six amplitudes of vibration were allowed to vary. Converged values

Table VI. Structural Parameters for CF_3OOF^a

	Minimum I, preferred			Minimum II		
Parameter description and no.	r_g, Å, or $\angle_\alpha$, deg	l_α, Å	Calcd amplitude, Å	r_g, Å, or $\angle_\alpha$, deg	l_α, Å	Calcd amplitude, Å
$r(O_2-F_4)\ r_1$	1.449 (15)	0.051^b	0.051	1.385 (15)	0.051^b	0.051
$r(O_1-O_2)\ r_2$	1.366 (33)	0.054^b	0.054	1.454 (18)	0.054^b	0.054
$r(C-O_1)\ r_3$	1.419 (24)	0.048^b	0.048	1.415 (15)	0.048^b	0.048
$r(C-F)\ r_4$	1.322 (9)	0.046 (8)	0.044	1.318 (3)	0.045 (4)	0.044
$\angle(O_2-O_1-C)\ \angle_1$	108.2 (1.2)			105.7 (1.5)		
$\angle(F_1-C-F_2)\ \angle_2$	109.0 (1.0)			110.6 (0.6)		
$\angle$tilt $\angle_3$	3.9 (1.8)			6.7 (1.2)		
$\angle(F_4-O_2-O_1)\ \angle_4$	104.5 (4.5)			105.0^b		
$\angle\tau(F_4-O_2-O_1-C)\ \angle_5$	97.1 (6.0)			99.9 (3.0)		
$\angle$twist $\angle_6$	−2.2 (5.0)			0.0^b		
$r(F_1\cdots F_2)\ l_3$	2.153	0.057 (7)	0.054	2.165	0.054 (6)	0.054
$r(O_1\cdots F_1)$	2.191	0.061^b	0.061	2.122	0.061^b	0.061
$r(O_1\cdots F_2)$	2.269	0.059^b	0.059	2.258	0.059^b	0.059
$r(O_1\cdots F_3)$	2.267	0.059^b	0.059	2.258	0.059^b	0.059
$r(O_2\cdots C)$	2.250	0.065^b	0.065	2.280	0.065^b	0.065
$r(O_2\cdots F_2)\ l_4$	2.634	0.120 (24)	0.127	2.660	0.121 (16)	0.127
$r(O_2\cdots F_3)\ l_4$	2.689	0.120 (24)	0.127	2.660	0.121 (16)	0.127
$r(O_2\cdots F_1)\ l_5$	3.375	0.062 (16)	0.066	3.386	0.059 (18)	0.066
$r(F_4\cdots O_1)$	2.215	0.066^b	0.066	2.241	0.066^b	0.066
$r(F_4\cdots C)$	2.974	0.11^b	0.11	2.993	0.11^b	0.11
$r(F_4\cdots F_1)\ l_7$	4.032	0.12 (4)	0.13	4.010	0.13^b	0.13
$r(F_4\cdots F_2)\ l_8$	3.662	0.16 (6)	0.17	3.682	0.17^b	0.17
$r(F_4\cdots F_3)\ l_9$	2.827	0.18^b	0.18	2.836	0.18^b	0.18
$\sigma(I)/\bar{I}^c$	8.41×10^{-4}			9.14×10^{-4}		

[a] Uncertainties in parentheses, in units of least significant digit quoted, are 3σ. σ includes random errors and our estimates of possible systematic errors and of the effects of correlation between neighboring data points ($\gamma \approx 1$ Å). [b] Parameter not varied in least-squares refinements. [c] Mean fractional standard deviation of diffraction intensity points.

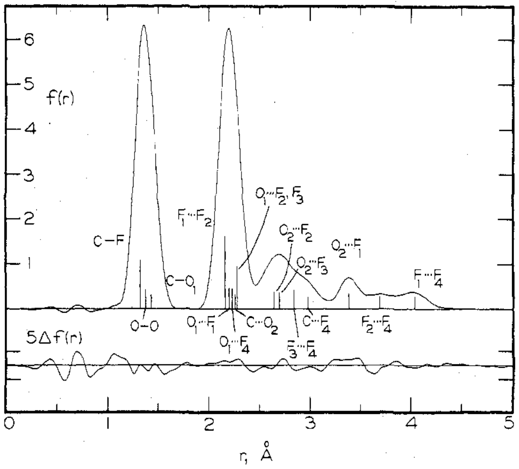

Figure 5. Experimental radial distribution function for CF_3OOF. $\Delta = f(r)_{exptl} - f(r)_{calcd}$ (model used was minimum I).

for all six are acceptably close to those calculated spectroscopically, confirming the frequency assignment for the torsional motions in CF_3OOF. That assignment requires a barrier to rotation about the O–O bond several times higher in CF_3OOF than in CF_3OOH, although the C–O barriers in the two molecules are not distinguishable. Final parameter values for both minima are presented in Table VI. The large uncertainties quoted are simply a reflection of the extreme parameter correlation encountered and do not indicate that our model provides a poor fit to the diffraction data. In the correlation matrix for minimum I, displayed in Table VII, there are 24 elements numerically greater than 0.7. It can be seen that several amplitudes of vibration are strongly correlated with certain geometrical parameters, emphasizing the importance of assigning correct values to these amplitudes and of the calculation of amplitudes spectroscopically whenever possible.

C. CF_3OOCl. Experimental and final calculated molecular intensities are shown in Figure 6, and the radial distribution

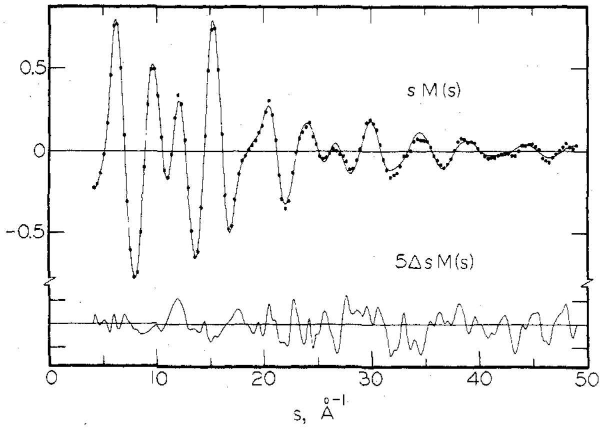

Figure 6. Observed and calculated molecular intensity function $sM(s)$ for CF_3OOCl: filled circles are experimental points; smooth line is theoretical curve. $\Delta = sM(s)_{exptl} - sM(s)_{calcd}$.

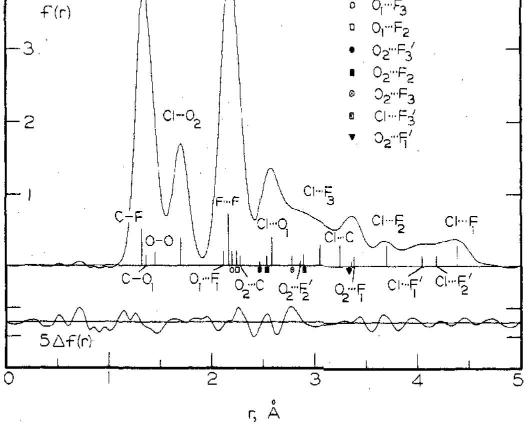

Figure 7. Experimental radial distribution function for CF_3OOCl. $\Delta = f(r)_{exptl} - f(r)_{calcd}$.

Table VII. Matrix of Correlation Coefficients[a] for CF_3OOF

	r_1	r_2	r_3	r_4	$\angle_1$	$\angle_2^{\,b}$	$\angle_3$	$\angle_4$	$\angle_5$	$\angle_6$	l_2	l_3	l_4	l_5	l_7	l_8	R
σ	0.0033	0.0084	0.0062	0.0020	0.31	0.24	0.47	1.2	1.7	1.1	0.0014	0.0017	0.0065	0.0042	0.011	0.015	0.0046
r_1	100	18	−66	−5	30	23	17	39	−42	30	3	−29	31	3	1	<1	21
r_2		100	−75	−95	38	−75	74	84	−82	68	−87	−48	64	<−1	−2	−1	−35
r_3			100	64	−56	30	−58	−90	88	−72	48	59	−67	−1	1	<1	26
r_4				100	−42	82	71	−82	80	−66	85	46	−62	1	2	1	35
$\angle_1$					100	−27	24	51	−59	47	−25	−39	42	−2	4	10	−28
$\angle_2$						100	−79	−51	56	−31	76	5	−36	1	5	11	35
$\angle_3$							100	69	−74	35	−62	−16	42	<1	−7	−19	−20
$\angle_4$								100	−94	77	−63	−69	67	<1	−2	−3	−35
$\angle_5$									100	−70	62	58	−72	−2	<−1	−3	32
$\angle_6$										100	−52	−64	74	−1	2	9	−32
l_2											100	36	−49	1	2	1	42
l_3												100	−47	1	−2	−9	35
l_4													100	1	1	9	−29
l_5														100	14	35	4
l_7															100	45	2
l_8																100	−2
R																	100

[a] Units for σ are Å for distances and amplitudes, degrees for angles. R is dimensionless. Matrix elements are given by $\rho_{ij} = (M_x)_{ij}/[(M_x)_{ii} \cdot (M_x)_{jj}]^{1/2}$, where M_x is the zeroth-order error matrix. Only the upper half of the matrix is given. All entries, except for the standard deviations, have been multiplied by 100. The numbering of the parameters follows from Table IV, except where indicated. [b] Angle between the threefold axis of the CF_3 group and a C–F bond.

Table VIII. Matrix of Correlation Coefficients[a] for CF_3OOCl

	r_1	r_2	r_3	r_4	$\angle_1$	$\angle_2^{\,b}$	$\angle_3$	$\angle_4$	$\angle_5$	$\angle_6$	$\angle_7$	l_1	l_2	l_3	l_5	l_6	l_7	l_8	l_9	R
σ	0.0016	0.0038	0.0055	0.0014	1.0	0.39	0.70	0.34	1.9	1.1	2.3	0.0015	0.0014	0.0033	0.0064	0.0041	0.011	0.015	0.017	0.011
r_1	100	31	−10	13	−1	3	10	−46	3	−9	−5	4	13	−4	4	5	−1	−2	10	25
r_2		100	−57	55	15	−7	37	−69	2	26	−5	1	50	−13	10	22	1	−7	32	61
r_3			100	−87	−41	4	−10	41	19	12	−17	<−1	−80	−14	−2	−23	−2	20	−41	−32
r_4				100	17	25	18	−41	−7	−15	8	−2	68	−1	3	19	1	−12	36	23
$\angle_1$					100	−67	27	−7	−51	−25	17	11	45	−21	4	48	5	−28	49	47
$\angle_2$						100	−39	<−1	18	36	12	−8	−14	26	−9	−24	−3	−1	−12	−37
$\angle_3$							100	−23	12	−76	−38	7	21	−86	20	34	3	23	30	54
$\angle_4$								100	−12	9	17	−1	−37	7	−9	−18	5	3	−20	−43
$\angle_5$									100	4	−63	−5	−19	−7	24	−16	−20	45	−44	−13
$\angle_6$										100	34	−6	−20	62	−12	−14	−9	−21	−23	−40
$\angle_7$											100	−1	9	30	−26	−4	14	−48	43	−11
l_1												100	5	−5	2	6	1	−1	4	14
l_2													100	3	5	28	3	−16	39	51
l_3														100	−15	−31	−1	−19	−28	−27
l_5															100	10	−3	22	4	15
l_6																100	−2	−11	42	39
l_7																	100	16	6	5
l_8																		100	−32	−5
l_9																			100	35
R																				100

[a] Units for σ are Å for distances and amplitudes, degrees for angles. R is dimensionless. Matrix elements are given by $\rho_{ij} = (M_x)_{ij}/[(M_x)_{ii} \cdot (M_x)_{jj}]^{1/2}$, where M_x is the zeroth-order error matrix. Only the upper half of the matrix is given. All entries, except for the standard deviations, have been multiplied by 100. The numbering of the parameters follows from Table V, except where indicated. [b] Angle between the threefold axis of the CF_3 group and a C–F bond.

function is shown in Figure 7. The problems posed by parameter correlation are not as severe as in CF_3OOF, since the O_2–Cl distance is well separated from the other bonded distances, and the Cl···F distances are better resolved than are the $F_1 \cdots F_{2,3,4}$ distances in CF_3OOF. The radial distribution function contains seven distinct peaks and two additional poorly defined features. Starting from CF_3OO parameters similar to those found for CF_3OOH, it was not possible to obtain an acceptable fit to the longer distances in the radial distribution function. Reliable low-frequency vibrational spectra of CF_3OOCl are not yet available, due to its low thermal and photolytic stability. Amplitudes of vibration for torsion-dependent distances were thus unknown. The shape of the longest Cl···F distance in the radial distribution function indicated that its amplitude was close to 0.12 Å, yet the area of the peak was smaller than that calculated, and the experimental curve contained additional features not present in the theoretical model. This problem was solved by the introduction of a second isomer, differing from the first only in the angle of twist of the CF_3 group. A series of refinements was performed assuming various proportions of the two conformers but applying the same amplitude constraints in each case. A plot of the fractional standard deviation of the diffraction intensity data as a function of conformer compostion is shown in Figure 8. The best fit was found for a model with 66% isomer A, whose twist angle is −15.5°, and 34% isomer B, for which the twist angle is +23.6°. Our best estimate is that ±10% represents 3σ limits of the uncertainty in conformer composition; the nonrandom distribution of least-squares residuals renders the application of statistical tests somewhat doubtful. Refinements were carried out in which isomers A and B were allowed different $Cl–O_2–O_1–C$ dihedral angles; since their converged values differed by only a few tenths of one degree, while their uncertainties were several degrees, a common dihedral angle was assumed in subsequent cycles.

Eight amplitudes of vibration were free to vary in the final refinements. Their converged values are in acceptable agreement with those calculated spectroscopically, if the force constants for torsional motion about the C–O and O–O bonds

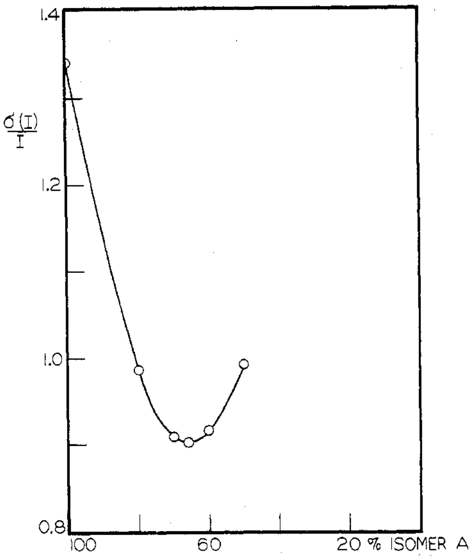

Figure 8. A plot of the mean fractional standard deviation of diffraction intensity points as a function of conformer composition for CF_3OOCl. See text. Ordinate: × 10^{-3}.

in the CF_3OOCl are assumed equal or similar to those in CF_3OOF. Final parameter values are given in Table IV. The correlation matrix, in Table VIII, has four elements numerically greater than 0.7.

Discussion

The principal motive for this research was to ascertain the extent of variation in O–O bond lengths of CF_3-substituted peroxides induced by changes of the other substitutent. H_2O_2[31] has O–H and O–O bond lengths of approximately 0.97 and 1.46 (1) Å, respectively; interpretational difficulties obscure a finer determination of the internuclear distances. These distances are consistent with expectations for normal single bonds. In striking contrast, the O–F distance in O_2F_2[32] of 1.579 Å is much greater than that of 1.409 Å in OF_2,[30] while the O–O distance of 1.219 Å is virtually as short as that of the double bond in the O_2 molecule.

We have found that the O–O distances in CF_3OOH and CF_3OOCl are scarcely distinguishable from that in H_2O_2.[31] Likewise, the O–Cl bond length in CF_3OOCl of 1.699 (2) Å is not significantly different from that in Cl_2O,[33] which is 1.695 (3) Å. Although the C–O distances of 1.376 (3) and 1.372 (7) Å in CF_3OOH and CF_3OOCl are less than the r_g value of 1.428 (3) reported for CH_3OH,[34] a shortening of this magnitude is to be expected, as it has been observed[35] that $(F_3)C–X$ bonds are in general shorter than $(H_3)C–X$ if X is highly electronegative. Thus all the evidence indicates that the bond lengths in CF_3OOH and CF_3OOCl are entirely normal. However, the O–O distance in CF_3OOF is 0.09 Å shorter than that in H_2O_2,[31] while the O–F distance is 0.040 Å greater than that in OF_2,[30] and the C–O bond length is 0.045 Å longer than the average of the values for CF_3OOH and CF_3OOCl. These observations show that CF_3OOF has some of the character of O_2F_2, although it is more like H_2O_2 or CF_3OOH than like O_2F_2. Subdividing trends in peroxides more finely, it would be reasonable to suppose that CF_3OOCF_3 is intermediate between CF_3OOF and CF_3OOH. Available evidence[5] (1.419 (20) Å for O–O) tends to support this idea but is insufficiently precise to establish it.

Extensive studies have been made of the torsional potential function for H_2O_2;[36] the cis and trans barriers are 7.0 and 1.1 kcal/mol, respectively. The data for other peroxides are more meager. All that is available is the harmonic force constant which reproduces the observed torsional frequency. For the three molecules CF_3OOH, CF_3OOF, and O_2F_2, the torsional force constants are 0.034, 0.25,[29] and 0.91[21] mdyn Å/rad^2, respectively. It is not possible to extract the magnitudes of the cis and trans barriers from this one datum, and the example of H_2O_2 shows that they may be considerably different. For purposes of approximate comparisons, we note that if a simple twofold potential is assumed, a force constant of 0.034 mdyn Å/rad^2 corresponds to a barrier of 2.4 kcal/mol. Thus it appears that the barriers to rotation about the O–O bonds in H_2O_2 and CF_3OOH are comparable. This result agrees with elementary expectations, since the O–O distances in the two molecules are similar, and the shortest H···F distance in CF_3OOH involved in torsional motion about the O–O bond, which would be about 2.08 Å in an unrelaxed conformation, appears sufficiently great to preclude any appreciable intramolecular hydrogen bonding.

The high barriers in O_2F_2 inferred from the large torsional force constant may naturally be ascribed to the extensive p_π–p_π overlap. It appears that the barrier in CF_3OOF is several times greater than in CF_3OOH but only a fraction that of O_2F_2. Variations in the barriers, as reflected in the torsional force constants, correlate strikingly with variations in the O–O bond lengths. Indeed, if Pauling's formula[38]

$$r(1) - r(n) = 0.71 \log n$$

relating bond length $r(n)$ to bond order n is adopted for sake of argument, if $r(1)$ is taken to be 1.46 Å, and if it is assumed that $(n - 1)$ represents a π bond order associated with a π bond requiring an energy of 55 kcal/mol to break if $(n - 1)$ is unity, it is straightforward to calculate twofold barriers about the O–O bonds from the O–O bond lengths. Resultant values are 2.4, 20, and 65 kcal/mol for CF_3OOH, CF_3OOF, and FOOF, respectively. For comparison, values of 2.4, 18, and 65 kcal/mol are obtained from the torsional force constants, k_τ, listed above by conversion to the barriers $k_\tau/2$, assuming that the barrier functions are twofold. Although this comparison is suggestive, it does not preclude a significant steric contribution to the barrier in the cases of CF_3OOF and CF_3OOCl and, in the latter case, evidence was found for appreciable F···Cl interactions as discussed below. No simple assessment of the steric barrier in CF_3OOF is available but the extremely close F···F approach of about 2.0 Å would occur at a dihedral angle of 40° if all molecular parameters were frozen (at Table VI values) except for the C–O_1–O_2–F dihedral angle. Such an unfavorable contact is undoubtedly relieved greatly by relaxation of bond angles and the CF_3 torsion but it cannot be avoided altogether. Similar conclusions apply to CF_3OOCl. Torsional frequencies have not yet been observed for CF_3OOCl; from the measured amplitudes of vibration the O–O barrier in this molecule cannot be differentiated from that in CF_3OOF.

It is noteworthy that whereas the CF_3 groups in CF_3OOH and CF_3OOF either are in or are very close to a staggered conformation, evidence was found for two conformations of CF_3OOCl in which angles of twist differ in sign. We believe that these observations can be rationalized by steric considerations. In molecular fragments $BCDE_3$ linked by single bonds, it is generally found that the E_3 group is staggered with respect to the B–C bond, and this conformation is to be expected if the B···E interactions are repulsive, the repulsion decreasing sharply as the separation increases. If an atom A is bonded to B, then A···E interactions must also be considered. The F_3···F_4 separation in CF_3OOF is 2.83 Å, slightly greater than the sum of the van der Waals radii of 2.70 Å, so no energetic advantages accrue from twisting the CF_3 group away from the staggered conformation. In CF_3OOCl, however, if the CF_3 group were staggered but all other parameters maintained their values listed in Table IV, the Cl···F_3 distance would be 2.94 Å, whereas the sum of the van der Waals radii is 3.15 Å. Twisting the CF_3 group in a negative direction (isomer A) steadily increases the Cl···F_3 distance, whereas when a positive twist is applied (isomer B), that distance initially decreases slowly and then increases once the twist angle exceeds 20°. A twist in either direction decreases the O_2···F_2 distance for conformer A or the O_2···F_3' separation for conformer B, and so an energy balance must be struck between a decrease of unfavorable Cl···F interactions and an increase of unfavorable O···F interactions. At the experimental twist angles of −15.5° (conformer A, 66%) and +23.6° (conformer B, 34%), the internuclear separations are Cl···F_3 3.06 Å and O_2···F_2 2.54 Å for A but Cl···F_3 2.90 Å and O_2···F_3' 2.49 Å for B. The greater concentration determined for A than B is in accord with the less unfavorable nonbonded interactions involved for A.

Although the present study of members of the series CF_3OOX has revealed worthwhile details about CF_3 conformations, tilts, and structures, the most noteworthy results are those concerned with the OOX linkages. In a comparison including XOOX molecules a highly significant trend of peroxide bond lengths was found which correlated strikingly with the torsional freedom about the O–O bond. Measured O–O and O–X distances proved to be more illuminating than the vibrational frequencies (Table I). They reinforced chemical evidence that CF_3OOF departs significantly from the other, more typical, peroxides in the direction of the anomalous compound O_2F_2.

Acknowledgment. This research was supported by grants from the National Science Foundation (D.D.D. and L.S.B.). We are deeply grateful to Dr. R. L. Hilderbrandt for his normal-coordinate computer programs MSAV. We thank the University of Michigan Computing Center for a generous allocation of computer time.

Registry No. CF_3OOH, 16156-36-8; CF_3OOCl, 32755-26-3; CF_3OOF, 34511-13-2.

Supplementary Material Available: Tables of molecular intensities and force constants (34 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Alfred P. Sloan Foundation Fellow, 1975-1977.
(2) R. A. DeMarco and J. M. Shreeve, *Adv. Inorg. Chem. Radiochem.*, **16**, 110 (1974).
(3) F. Swartz, *Bull. Soc. Chim. Belg.*, **42**, 102 (1933).
(4) O. Ruff and W. Menzel, *Z. Anorg. Allg. Chem.*, **211**, 204 (1933).
(5) C. J. Marsden, L. S. Bartell, and F. P. Diodati, *J. Mol. Struct.*, in press.
(6) R. H. Jackson, *J. Chem. Soc.*, 4585 (1962).
(7) See, for example, L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 345; J. W. Linnett, "The Electronic Structure of Molecules", Methuen, London, 1964; and R. D. Spratley and G. C. Pimentel, *J. Am. Chem. Soc.*, **88**, 2394 (1966).
(8) R. L. Talbott, *J. Org. Chem.*, **33**, 2095 (1968).
(9) P. A. Bernstein, F. A. Hohorst, and D. D. DesMarteau, *J. Am. Chem. Soc.*, **93**, 3882 (1971).
(10) C. T. Ratcliffe, C. V. Hardin, L. R. Anderson, W. B. Fox, *J. Am. Chem. Soc.*, **93**, 3886 (1971).
(11) N. Walker and D. D. DesMarteau, *J. Am. Chem. Soc.*, **97**, 13 (1975).
(12) D. D. DesMarteau, *Inorg. Chem.*, **11**, 193 (1972).
(13) I. J. Solomon, A. J. Kacmarek, W. K. Sumida, and J. K. Raney, *Inorg. Chem.*, **11**, 195 (1972).
(14) F. A. Hohorst and D. D. DesMarteau, *J. Inorg. Nucl. Chem.*, supplement 1976, 63 (1976).
(15) R. R. Smardzewski and W. B. Fox, *J. Fluorine Chem.*, **16**, 417 (1975).
(16) R. A. DeMarco and W. B. Fox, *Inorg. Nucl. Chem. Lett.*, **10**, 965 (1974).
(17) R. M. Hammaker and D. D. DesMarteau, to be submitted for publication.
(18) R. M. Smardzewski, R. A. DeMarco, and W. B. Fox, *J. Chem. Phys.*, **63**, 1083 (1975).
(19) P. G. Thompson, *J. Am. Chem. Soc.*, **89**, 4316 (1967).
(20) C. T. Ratcliffe, A. J. Melveger, L. R. Anderson, and W. B. Fox, *Appl. Spectrosc.*, **26**, 381 (1972).
(21) K. R. Loos, C. T. Goetschel, and V. A. Campanile, *J. Chem. Phys.*, **52**, 4418 (1970).
(22) N. J. Lawrence, J. S. Ogden, and J. J. Turner, *J. Chem. Soc. A*, 3100 (1968).
(23) R. L. Redington, W. B. Olson, and P. C. Cross, *J. Chem. Phys.*, **36**, 1311 (1962).
(24) L. S. Bartell in "Physical Methods in Chemistry", 4th ed, A. Weissberger and B. W. Rossiter, Ed., Interscience, New York, N.Y., 1973, pp 125–158.
(25) W. J. Adams, private communication. Method identical with that described by F. P. Diodati and L. S. Bartell, *J. Mol. Struct.*, **8**, 395 (1971), but with $A_0 = 4.31$.
(26) L. Schafer, A. C. Yates, and R. A. Bonham, *J. Chem. Phys.*, **55**, 3055 (1971).
(27) H. L. Cox and R. A. Bonham, *J. Chem. Phys.*, **47**, 2599 (1967).
(28) L. S. Bartell, *J. Chem. Phys.*, **23**, 1219 (1955).
(29) R. Hammaker and C. J. Marsden, unpublished research.
(30) L. Pierce, R. Jackson, and N. DiCianni, *J. Chem. Phys.*, **35**, 2240 (1961).
(31) R. L. Redington, W. B. Olson, and P. C. Cross, *J. Chem. Phys.*, **36**, 1311 (1962); W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **42**, 3054 (1965); G. A. Khachkuruzov and I. N. Przhevalskii, *Opt. Spectrosc. (USSR)*, **36**, 172 (1974).
(32) R. H. Jackson, *J. Chem. Soc.*, 4585 (1962).
(33) B. Beagley, A. H. Clark, and T. G. Hewitt, *J. Chem. Soc. A*, 658 (1968).
(34) K. Kimura and M. Kubo, *J. Chem. Phys.*, **30**, 151 (1959).
(35) C. J. Marsden and G. M. Sheldrick, *J. Mol. Struct.*, **10**, 419 (1971).
(36) R. H. Hunt, R. A. Leacock, C. W. Peters, and K. T. Hecht, *J. Chem. Phys.*, **45**, 3141 (1966).
(37) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., p 239.