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Gas-Phase Structure of 3,3,4,4-Tetrafluoro-1-oxa-2-thietane 2,2-Dioxide, $\overline{CF_2CF_2OSO_2}$

Gary L. Gard,[1a] Nick N. Hamel,[1a] and Heinz Oberhammer*,[1b]

Department of Chemistry, Portland State University, Portland, Oregon 97207, and Institut für Physikalische und Theoretische Chemie, Universität Tübingen, 72076 Tübingen, Germany

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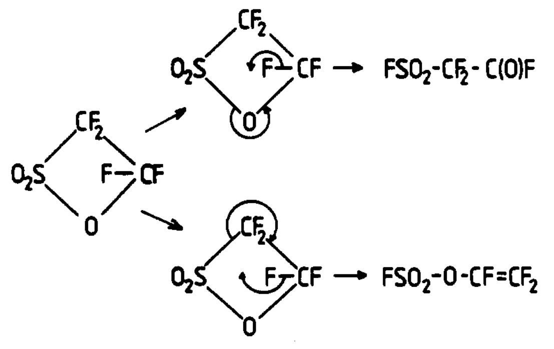
The first gas-phase structure of a sultone is reported. Surprisingly, the four-membered ring of $\overline{CF_2CF_2OSO_2}$ is planar. The following ring parameters (r_a distances and $\angle_\alpha$ angles with 3σ uncertainties) were derived in the electron diffraction analysis: C–O = 1.41(2) Å, C–C = 1.545(15) Å, S–O = 1.656(4) Å, S–C = 1.866(6) Å, S–C–C = 85.8(10)°, C–C–O = 97.4(24)°, C–O–S = 98.9(16)°, and O–C–S = 78.0(5)°. A comparison of these results with a previously estimated structural model will be discussed.

Introduction

The title compound is an example of a β-fluorosultone. β-Fluorosultones are cyclic compounds formed by the addition of monomeric sulfur trioxide to fluorinated olefins. Their extensive chemistry is due to the ease of forming reactive isomeric fluorosulfonyl fluorocarbonyl fluorides which leads to a large number of structurally modified fluorosulfonyl fluorides, amides, alkoxides, fluorosulfonic acids, and esters.[2] Tetrafluoroethylene-β-sultone, $\overline{CF_2CF_2OSO_2}$ (TFES), with the IUPAC name 3,3,4,4-trifluoro-1-oxa-2-thietane 2,2-dioxide, is easily prepared by reaction of gaseous C_2F_4 with monomeric SO_3.[3,4] Some progress has been made in structural elucidation of β-fluorosultones. A geometrical model for TFES was suggested on the basis of literature values for bond lengths.[5] The purpose of this study was to distinguish between an inter- or intramolecular rearrangement mechanism of this sultone. From the estimated contact between sulfur and the β-fluorines (2.8–3.2 Å), the authors concluded that the intramolecular pathways are favored.



In 1990, the X-ray crystal structure of the β-fluorosultone $SF_5\overline{CHCF_2OSO_2}$ was reported;[6] this sultone contains a four-membered nonplanar sultone ring. The packing appears to be dictated by relatively strong C–H···O hydrogen-bonding interactions and appears to be the reason for the crystalline phase at room temperature.[6] In the present paper we report an electron diffraction study of gaseous TFES.

Structure Analysis

The radial distribution function (RDF, Figure 1) was calculated by Fourier transform of the modified molecular intensities which were multiplied with an artificial damping function $\exp(-\gamma s^2)$ ($\gamma = 0.0019$ Å^2). The first peak near 1.40 Å with two shoulders at the long distance side corresponds to the various bonded distances in this compound. The endocyclic C–O bond length is expected to be very similar to the exocyclic S═O bond length. Since the contribution of the two S═O bonds is about five times as big as that of the C—O bond, this latter bond length cannot be determined accurately in the electron diffraction experiment. The C–O distance in the saturated four-membered ring of trimethylene oxide[7] is 1.448(5) Å. From this value and from the effect of fluorination in dimethylether (C–O = 1.415(1) Å in $(CH_3)_2O$[8] and C–O = 1.369(4) Å in $(CF_3)_2O$[9]), we estimate the C–O bond length in TFES to 1.41 Å with an uncertainty of ±0.02 Å. The peak in the RDF at ca. 2.6 Å with shoulders on either side determines the endo- and exocyclic bond angles. The RDF for $r > 3$ Å depends strongly on the conformation of the four-membered ring, i.e., on the degree of puckering. Analysis of this part of the radial distribution function reveals that the peak at ca. 3.3 Å is primarily due to the distances between sulfur and the β-fluorine atoms S···F2 and S···F2′, and that both distances are equal or nearly equal. This implies that the four-membered ring is planar or nearly planar.

The preliminary structural model which was derived from the RDF was refined by least-squares fitting of the molecular intensities. For this purpose, the intensities were modified with a diagonal weight matrix and scattering amplitudes and phases of Haase were used.[10] The geometry of the ring is described by the four bond lengths, the ring diagonal S···C2 and a puckering angle θ between the SCC and SOC planes. The exocyclic C–F bond lengths and the FCF angles at C1 and C2 carbon atoms were set equal. The assumption that the CF_2 and SO_2 groups lie exactly in the plane which bisects the adjacent endocyclic angles does not lead to a good fit of the RDF in the range $2.3 < r < 3$ Å. However, with the introduction of a wagging angle for the

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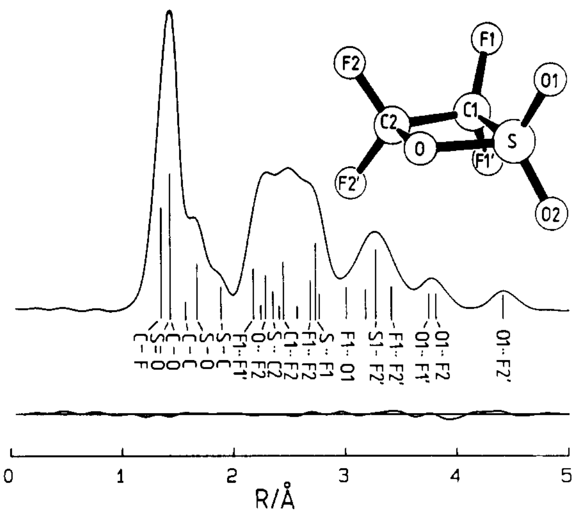

Figure 1. Experimental radial distribution function for TFES and difference curve. The positions of interatomic distances are indicated by vertical bars.

β-CF_2 group, a good fit was obtained. The wagging occurs away from the α-CF_2 group and toward the ring oxygen atom. Refinements of wagging angles for the α-CF_2 and SO_2 groups result in small values (<2°) with standard deviations which are larger than these refined angles. Therefore, these two wagging angles were set to zero in all further refinements.

The most interesting structural feature of this four-membered ring system is its degree of puckering. Least-squares refinements were performed for various fixed puckering angles θ. The agreement factors of the two camera distances which correspond to a planar ring with $\theta = 0°$ ($R_{50} = 0.037$ and $R_{25} = 0.073$) decrease very little for $\theta = 5°$ and increase sharply by 22% (R_{50}) and 14% (R_{25}) for $\theta = 10°$. The disagreement between calculated and experimental RDF occurs mainly in the region $3.0 < r < 3.5$ Å, where the S···F2 and S···F2′ distances make the strongest contributions. Refinement of the puckering angle in the least squares analysis results in $\theta = 4(3)°$. This small deviation from the exact planar structure has to be considered as a vibrational effect due to the out of plane vibration. The effective puckering angle of only 4° indicates a rather rigid ring structure. This conclusion is supported by the result for the vibrational amplitudes of the S···F2 distances (0.125(9) Å), which would be larger for a nonrigid ring structure with a low frequency puckering vibration.

In the final refinements the ring was constrained to planarity. Vibrational amplitudes were refined in groups according to their distances and further constraints are evident from Table 1. With these assumptions nine geometric parameters p_i and nine vibrational amplitudes a_k were refined simultaneously. Three correlation coefficients had values larger than $|0.6|$: $p_3/p_8 = -0.65$, $p_7/a_3 = 0.77$, and $a_3/a_4 = 0.66$. The full correlation matrix is available as supplementary material. Numbering of the geometric parameters p_i and vibrational amplitudes a_k and the final results are given in Table 1. Error limits are 3σ values and include possible systematic errors due to the constraints for the C—O bond distance and the vibrational amplitude for the short bond distances (C—F, S═O, and C—O). These systematic errors are estimated by varying the constrained parameters in the range given in square brackets.

Discussion

The surprising result of this structural study is the planarity of the sultone ring. The conformation of four-membered rings is a balance between angle strain, which favors a planar structure, and torsional strain, which favors a puckered conformation. The planarity of TFES implies that the C—F bonds at the α-carbon (C1) eclipse exactly the C—F bonds at the β-carbon (C2) and the S═O double bonds. In noncyclic compounds such bonds prefer staggered conformations, C—F/C—F bonds in CF_3CF_3 and C—F/S═O bonds in $(CF_3)_2SO_2$.[11] Inspection of gas-phase data for cyclobutane, perfluorocyclobutane, and four-membered rings which contain one sulfur or oxygen atom in the ring (Table 2) demonstrates that such rings have puckered conformations. The observed flattening of cyclobutane ($\theta = 27.9(16)°$) upon fluorination ($\theta = 17.4(3)°$ in C_4F_8) can be rationalized by increased angle strain in the fluorinated ring.[18] Because of the higher p-character of C–F bond orbitals relative to C–H bond orbitals, fluorination increases the s-character of the endocyclic

Table 1. Results of Electron Diffraction Analysis for TFES[a]

Geometric Parameters			
C—F	1.321(4) (p_1)	S—C—C	85.8 (10)
S═O	1.396(3) (p_2)	C—C—O	97.4 (24)
C—O	1.41[2][b]	C—O—S	98.9 (16)
C—C	1.545(15) (p_3)	O—S—C	78.0 (5)
S—O	1.656(4) (p_4)	F—C—F	108.7 (11) (p_7)
S—C	1.866(6) (p_5)	O═S═O	118.8 (10) (p_8)
S···C2	2.333(10) (p_6)	wag(C2)[c]	4.8 (11) (p_9)

Interatomic Distances and Vibrational Amplitudes

	distance	amplitude		distance	amplitude
C—F	1.32	0.050[5][b]	O···O1	2.55	0.073(6) (a_5)
S═O	1.40		S···F1	2.71	
C—O	1.41		C1···O1	2.74	
C—C	1.55	0.061(7) (a_1)	F1···F2	2.67	0.220(45) (a_6)
S—O	1.65		F1···O1	2.99	
S—C	1.87	0.042(8) (a_2)	O···F1	3.18	0.125(9) (a_7)
F1···F1′	2.15	0.057(10) (a_3)	C2···O1	3.27	
C1···O	2.22		S···F2	3.28	
O···F2	2.24		F1···F2′	3.42	
S···C	2.33	0.073(7) (a_4)	O1···F1′	3.75	0.151(11) (a_8)
O1···O1′	2.40		O1···F2	3.81	
C2···F1	2.42		O1···F2′	4.43	0.120(15) (a_9)
C1···F2	2.42				

[a] Geometric parameters are r_a distances in Å and $\angle_\alpha$ angles in deg. Error limits are 3σ values and include possible systematic errors due to the constrained parameters (see text). Atom numbering is given in Figure 1. [b] Value was not refined in the least squares analysis, but was varied within the given range. [c] Wagging angle at carbon at C2. wag(C2) = $^1/_2$(C1C2F2 + C1C2F2′ – OC2F2 – OC2F2′).

Table 2. Bond Lengths (Å) and Puckering Angle (deg) for Saturated Four-Membered Rings

compound	C–C	C–O	C–S	S–O	θ
$CH_2CH_2CH_2CH_2$[a]	1.552(1)				27.9(16)
$CF_2CF_2CF_2CF_2$[b]	1.566(8)				17.4(3)
$CH_2CH_2CH_2S$[c]	1.549(3)		1.847(2)		26.0(20)
$CH_2CH_2CH_2SO$[d]	1.542(6)		1.836(4)		34.9(7)
$CH_2CH_2CH_2SO_2$[e]					27.3
$CH_2CH_2CH_2O$[f]	1.546(5)	1.448(5)			7.3
$CF_2CF_2OSO_2$[g]	1.545(15)	1.41[2]	1.866(6)	1.654(4)	0
$SF_5CHCF_2OSO_2$[h]	1.508(8)	1.438(8)	1.792(6)	1.621(5)	14.0

[a] r_z values.[12] [b] r_a values.[13] [c] r_g values.[14] [d] r_s values.[15] [e] r_e value.[16] [f] r_0 values for bond lengths;[7] r_e value for puckering angle is calculated from geometric parameters of ref 7 and the separation of the potential minima (0.135 Å) of ref 17. [g] r_a value, this study. [h] X-ray structure.[6]

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carbon bond orbitals and leads to an increase of the endocyclic angles and to the observed flattening of the ring. Rings which contain one sulfur atom (S(II), S(IV), or S(VI)) have puckering angles similar to that found in cyclobutane or even greater as in the case of trimethylene sulfoxide. The effect of replacing one CH_2 group in cyclobutane by oxygen differs appreciably from that of replacement by sulfur. Trimethylene oxide (oxetane) possesses a highly nonrigid "pseudoplanar" ring structure. The puckering potential derived from the far infrared spectrum has minima at $\theta_e = \pm 7.3°$ and a potential barrier of 15.1(5) cm^{-1} at the planar configuration. The barrier lies below the vibrational ground state and this leads to a large amplitude puckering vibration. Thus, the presence of one oxygen atom in the four-membered ring leads to a nearly planar (pseudoplanar) structure. The electron diffraction analysis of TFES results in a planar four-membered CCOS ring with a potential minimum at $\theta = 0°$. This planarity can be rationalized as a combination of two effects, i.e. fluorination at the carbon atoms, which increases angle strain, and the presence of oxygen in the ring, which favors flattening of saturated four-membered rings. The torsional strain between the two eclipsed CF_2 groups is reduced by the wagging of the β-CF_2 group which increases the F1···F2 distance to 2.67 Å. This contact is only slightly shorter than the van der Waals distance of 2.70 Å.

The endocyclic C–C and C–O distances in TFES are determined only with low accuracy. The C–S bond length (1.886(6) Å) is typical for bonds between S(VI) and fluorine substituted sp^3-hybridized carbon atoms. Examples of compounds with such bonds are $(CF_3)_2SO_2$ (1.858(5) Å),[11] $CF_2(SO_2F)_2$ (1.848(4) Å),[19] or the 6-membered trithiane ring $(CF_2SO_2)_3$ (1.866(4) Å).[20] These bonds are much longer than those in analogous protonated systems, such as e.g. 1.771(4) Å in $(CH_3)_2SO_2$.[21] This effect of fluorination can be rationalized by strong electrostatic repulsion between the positive net charges on sulfur and carbon atoms.[22] A very limited number of compounds which contain a S(VI)–O single bond have been studied in the gas phase, and the lengths for such bonds vary over a wide range: 1.574(10) Å in sulfuric acid H_2SO_4,[23] 1.567(3) Å in dimethyl sulfate $(CH_3O)_2SO_2$,[24] 1.586(11) Å in bis(pentafluorosulfur) oxide $(SF_5)_2O$,[25] 1.653(6) Å in sulfur cyanate pentafluoride SF_5OCN,[26] and 1.671(7) Å in pentafluorosulfur hypofluorite, SF_5OF.[27] The S–O bond length in the sultone ring (1.654(4) Å) is considerably longer than that in dimethyl sulfate, but it is similar to those reported for SF_5OCN and SF_5OF. All these S–O bonds are shorter than the Schomaker–Stevenson value for an S–O single bond of 1.70 Å.[28]

Table 2 compares the gas-phase bond lengths of the TFES ring with the solid state values for $SF_5CHCF_2OSO_2$. In the latter sultone the two fluorines at the α-carbon atom are substituted by H and SF_5. These substituents have a large effect on the S–C bond, and the bond length decreases from 1.866(6) to 1.792(6) Å; this shortening is expected, because of the reduced positive net charge at the α-carbon atom which reduces the electrostatic repulsion in the S–C bond. If we consider the experimental uncertainties of both experiments and systematic differences between gas-phase and solid-state values due to vibrational effects, all other endocyclic bond distances are in reasonable agreement. Very close agreement exists for the ring bond angles in TFES and $SF_5CHCF_2OSO_2$: SCC = 85.8(10) vs 86.7(4)°, CCO = 97.4(24) vs 96.0(4)°, COS = 98.9(16) vs 96.3(4)°, and OSC = 78.0(5) vs 79.4(3)°. The four-membered ring of $SF_5CHCF_2OSO_2$ is slightly puckered in the crystal ($\theta = 14.0°$) and this distortion can be attributed to crystal effects which include an intermolecular C–H···O hydrogen bonding network.

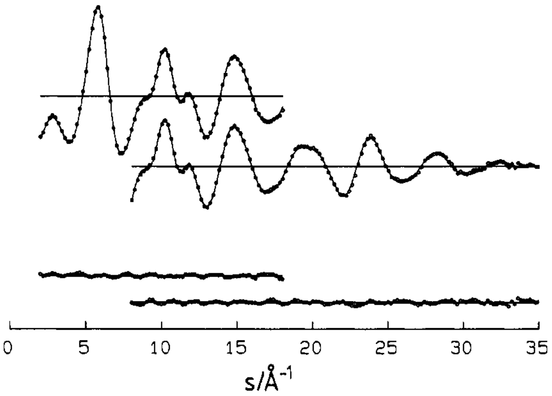

Figure 2. Experimental (points) and calculated (full line) molecular intensities and differences.

Some experimental bond lengths and angles for the four-membered ring of TFES differ considerably from the estimated parameters[5] discussed in the Introduction: C–O = 1.41[2] vs 1.42 Å, C–C = 1.545(15) vs 1.45 Å, S–O = 1.656(4) vs 1.60 Å, S–C = 1.866(6) vs 1.77 Å, COS = 98.9(16) vs 90°, CCO = 97.4(27) vs 104°, CCS = 85.8(10) vs 82°, and OSC = 78.0(5) vs 84°. The interatomic contact between sulfur and the β-CF_2 fluorine atoms (S···F2) which is derived from the electron diffraction analysis (3.28 Å) is greater than the estimated value (2.8–3.2 Å) and longer than the van der Waals distance (3.20 Å). Thus, the conclusion drawn by Sokol'skii and Knunyants[5] from their estimated molecular model, that isomerization occurs via an intramolecular mechanism, may have to be revised.

Experimental Section

TFES was prepared and purified by a modified procedure of England et al.[4] The boiling point and infrared and NMR spectra agreed with literature values.

The electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2[29] at two camera distances (25 and 50 cm) and with an accelerating voltage of ca. 60 kV. The electron wavelength was calibrated with ZnO diffraction patterns. The sample reservoir was kept at –45 °C and inlet system and nozzle were at room temperature. The camera pressure during the experiment was ca. 1.5×10^{-5} Torr. The purity of the sample was checked after the electron diffraction experiment by the gas infrared spectrum, which was recorded under the same conditions as the diffraction intensities. The photographic plates were analyzed by the usual procedures,[30] and averaged molecular intensities in the s-ranges 2–18 and 8–35 Å^{-1} are shown in Figure 2. Numerical values of the total scattering intensities are available as supplementary material.

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Supplementary Material Available: Tables with numerical values for total electron diffraction intensities and a full correlation matrix (3 pages). Ordering information is given on any current masthead page.

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