Trifluoromethyl Fluoroformyl Trioxicarbonate, CF₃OC(O)OOOC(O)F: The First Nonsymmetric Acyl Trioxide

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This paper reports for the first time the synthesis and characterization of trifluoromethyl fluoroformyl trioxicarbonate, $CF_3OC(O)OOOC(O)F$. The new trioxide is obtained from the gas-phase photolytic reaction of $CF_3C(O)OC(O)CF_3$ and $FC(O)C(O)F$ at 223−228 K. It is a very thermally labile molecule that decomposes at room temperature by rupture of either of the $CF_3OC(O)O-O-OC(O)F$ bonds. These bonds are nonequivalent, and a branching ratio of 0.8 for fragmentation through the $CF_3OC(O)OO-OC(O)F$ bond was obtained. Unambiguous identification was possible through reaction of the trioxide with an excess of NO_2. Potential-energy surfaces (PES) of the different rotamers were studied by the B3LYP/6-311+G* method, and analysis of the IR frequency of the possible mixture of rotamers agrees excellently with the experimental IR spectrum. This molecule is the first nonsymmetric acyl trioxide reported in the literature.

Introduction

In recent years much work has been devoted to the study of the properties and reactions of many compounds and radicals containing only F, C, and O atoms that can be formed in the laboratory when fluorinated substances react in the presence of oxygen and relatively high concentrations of CO.[1−7] In the atmosphere the trifluoromethyl, CF_3, and fluoroformyl, FCO, radicals are formed through degradation processes of many chlorofluorocarbons (CFCs) and their replacements (HCFCs, HFCs, and HFEs). The reactions of these radicals with O_2 and CO lead to the family of radicals[8] CF_3O_x, CF_3CO_x, FCO_x, and CF_3OCO_x, from which it is possible to obtain new species. The study of these reactions afforded new compounds to be synthesized and used as precursors of atmospherically relevant radicals which were thus isolated.[9−15]

Particularly interesting are the trioxides, among which bis-(trifluoromethoxy) trioxodicarbonate, $CF_3OC(O)OOOC(O)$-OCF_3, the first open chain acyl trioxide that has been isolated and characterized,[12] appears potentially as the main product of the reaction involving the recombination of the radicals formed when CF_3 reacts with excess O_2 and CO at low temperatures. The molecule formed is unstable, and this may be the main reason for the limited number of trioxides known so far. The second, simpler example of an acyl trioxide is bis(fluoroformyl) trioxide, $FC(O)OOOC(O)F$, another molecule that we isolated, identified, and characterized, which is also short lived.[4,13] This molecule involves only FCO_x radicals.

Bis(trifluoromethyl) trioxide, CF_3OOOCF_3, is probably an exception since it is a stable trioxide which has been known for many years.[9,16,17] Its stability could be ascribed to lack of an acyl group.

All of these trioxides share a feature: they are symmetric in the sense that they are formed by the recombination of two similar fragments. In this work, we present the synthesis of a new and the first nonsymmetric acyl trioxide, the trifluoromethyl fluoroformyl trioxicarbonate, $CF_3OC(O)OOOC(O)F$, a species

that we synthesized and characterized based essentially on IR techniques and the invaluable help of high level ab-initio theoretical calculations. This paper also reports thermal decay for the trioxide at 273 K when it reacts in the presence of excess NO_2. This decomposition is essential in order to discern between the two possible reaction paths

$$CF_3OC(O)OOOC(O)F \rightarrow CF_3OC(O)OO + FOO_2 \quad (1)$$

$$CF_3OC(O)OOOC(O)F \rightarrow CF_3OCO_2 + FC(O)OO \quad (2)$$
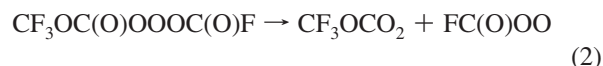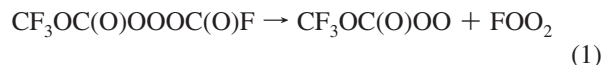
that can yield a nonsymmetric molecule. Since the peroxynitrates that form, $CF_3OC(O)OONO_2$ and $FC(O)OONO_2$, are known, measuring their amounts (by recording the course of the reaction as a function of time using FTIR spectroscopy) allowed determination of the branching ratio for the decomposition.

Experimental Section

Commercially available samples of perfluoroacetic anhydride $CF_3C(O)OC(O)CF_3$ (PCR), CO (PRAXAIR), N_2, and O_2 (AGA) were used. Oxygen was first condensed by making it flow at atmospheric pressure through a trap immersed in liquid air. It was then pumped under vacuum several times and transferred to a glass bulb while the trap was still immersed in liquid air. $FC(O)C(O)F$ was prepared by fluorination of oxalyl chloride.[18]

Volatile materials were manipulated in a glass vacuum line equipped with two capacitance pressure gauges (0−760 Torr, MKS Baratron; 0−70 mbar, Bell and Howell), three U traps, and valves with poly(tetrafluoroethylene) stems (Young,
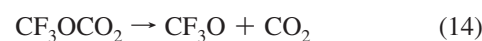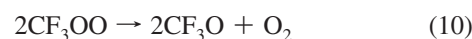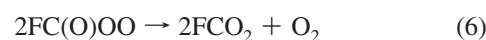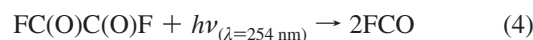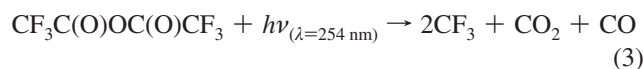
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London). The vacuum line was connected to the photoreactor and to an IR gas cell (double-walled quartz with Si windows, optical path length 210 mm) placed in the sample compartment of a Fourier transform infrared (FT-IR) spectrometer (Bruker IFS 66v). This arrangement made it possible to follow the course of both the synthesis and the thermal decomposition. The spectra were taken with a resolution of 2 cm^{-1} and with the addition of 4 interferometer scans, since the time spanned between successive spectra was of the order of 30 s and the trioxide is so labile that precluded a better averaging of scans. According to the results obtained, which showed a reasonably good S/N ratio, and for the sake of simplicity, we decided to record all spectra with the same settings.
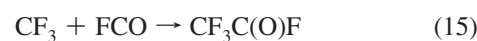
Photochemical Synthesis of CF₃OC(O)OOOC(O)F. The photoreactor consisted of a one-neck 12 L glass round-bottom flask with a 30 cm long double-walled water-jacketed quartz tube inside in which a low-pressure mercury lamp was placed. The reactor was immersed in an ethanol bath cooled to about 223−228 K and connected to a vacuum line via stainless-steel tubing. At this temperature, the trioxides formed in the gas phase stick to the surface of the photoreactor, and this allowed their isolation from the bulk of reaction.[12] In a typical experiment, the reactor was loaded with partial pressures of 6 mbar of perfluoroacetic anhydride, CF₃C(O)OC(O)CF₃, 15 mbar of oxalyl fluoride, FC(O)C(O)F, 50 mbar of CO, and 800 mbar of O₂. Every 60 min, a small amount of the gas mixture was expanded through the line into the gas cell in the spectrometer to check by FT-IR the advance of the reaction. IR signals at 1054 and 1861 cm^{-1} corresponding to CF₃C(O)OC(O)CF₃ and FC(O)C(O)F, respectively, were suitable to monitor their time evolution during the synthesis. Since FC(O)C(O)F disappeared faster than CF₃C(O)OC(O)CF₃, new injections of FC(O)C(O)F were needed every 120 min. The photolysis was stopped when the bands of CF₃C(O)OC(O)CF₃ had almost disappeared (about 8 h). After that, O₂ and CO were removed from the reaction mixture by slowly making flow the content of the photoreactor through three U traps kept at 77 K. To purify and identify the collected products, we transferred them to a glass trap which was connected before the U traps. The temperatures of the U traps were changed to 193, 153, and 77 K, and the sample was pumped through the traps. The most volatile products, retained in the 77 K trap, were identified as CF₂O, CO₂, and CF₃OOCF₃, and they were later discarded. The products found at 153 K were identified as CF₃C(O)F and peroxides FC(O)OOC(O)F, CF₃OC(O)OOC(O)OCF₃, CF₃OC(O)OOC(O)F, and CF₃OC(O)-OOCF₃. At 193 K we found mainly the trioxides, i.e., the two symmetric ones, CF₃OC(O)OOOC(O)OCF₃ and FC(O)OOO-C(O)F, reported elsewhere[12,13] and the new molecule CF₃-OC(O)OOOC(O)F. Due to the closeness in the vapor pressures of the trioxides, it was not possible to separate them by dynamic distillation, so we had to resort to a static method using only two traps. The temperatures were set to 233 and 173 K until FC(O)OOOC(O)F was completely separated from the remaining two trioxides. The resultant mixture, i.e., CF₃OC(O)OOOC-(O)OCF₃ and CF₃OC(O)OOOC(O)F, was left as it was because a further rise in temperature increased the thermal decomposition of the new trioxide. All the experiments were carried out with a known composition of the mixture given by the knowledge of the absorption cross sections of the symmetric trioxide.[12] The amount of CF₃OC(O)OOOC(O)OCF₃ was 10%. The experiments with pure samples of CF₃OC(O)OOOC(O)OCF₃ as control were carried out following procedures already reported.[12]
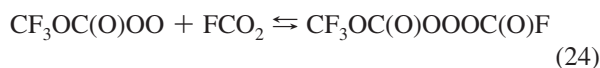
Results and Discussion

Mechanistics Aspects. The mechanism for the formation of this new species begins with the photolytic generation of CF₃ and FCO radicals via reactions 3 and 4, which in turn react with O₂ and CO. The catalytic oxidation of CO proceeds by the two chain reaction cycles given in eqs 5−8 and 9−14

$$CF_3C(O)OC(O)CF_3 + h\nu_{(\lambda=254\,nm)} \rightarrow 2CF_3 + CO_2 + CO \tag{3}$$

$$FC(O)C(O)F + h\nu_{(\lambda=254\,nm)} \rightarrow 2FCO \tag{4}$$

$$FCO + O_2 \rightarrow FC(O)OO \tag{5}$$

$$2FC(O)OO \rightarrow 2FCO_2 + O_2 \tag{6}$$

$$FCO_2 \rightarrow F + CO_2 \tag{7}$$

$$F + CO \rightarrow FCO \tag{8}$$

$$CF_3 + O_2 \rightarrow CF_3OO \tag{9}$$

$$2CF_3OO \rightarrow 2CF_3O + O_2 \tag{10}$$

$$CF_3O + CO \rightarrow CF_3OCO \tag{11}$$

$$CF_3OCO + O_2 \rightarrow CF_3OC(O)OO \tag{12}$$

$$2CF_3C(O)OO \rightarrow 2CF_3OCO_2 + O_2 \tag{13}$$

$$CF_3OCO_2 \rightarrow CF_3O + CO_2 \tag{14}$$

The electron-paired compounds are formed by the termination reactions, eqs 15−24

$$CF_3 + FCO \rightarrow CF_3C(O)F \tag{15}$$

$$2FCO_2 \rightarrow FC(O)OOC(O)F \quad (16)$$

$$2CF_3O \rightarrow CF_3OOCF_3 \quad (17)$$

$$2CF_3OCO_2 \rightarrow CF_3OC(O)OOC(O)OCF_3 \quad (18)$$

$$CF_3OCO_2 + FCO_2 \rightarrow CF_3OC(O)OOC(O)F \quad (19)$$

$$CF_3OCO_2 + CF_3O \rightarrow CFOC(O)OOCF_3 \quad (20)$$

$$CF_3OCO_2 + CF_3OC(O)OO \leftrightarrows CF_3OC(O)OOOC(O)OCF_3 \quad (21)$$

$$FCO_2 + FC(O)OO \leftrightarrows FC(O)OOOC(O)F \quad (22)$$

$$CF_3OCO_2 + FC(O)OO \leftrightarrows CF_3OC(O)OOOC(O)F \quad (23)$$

$$CF_3OC(O)OO + FCO_2 \leftrightarrows CF_3OC(O)OOOC(O)F \quad (24)$$
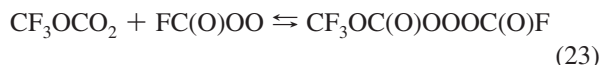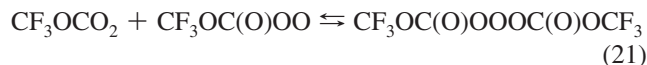
The outlined termination reactions account for the main products found in the synthesis. No attempts were made to explain in full detail neither the whole mechanism nor the products, and it is therefore possible that other compounds not discussed here could be formed, though their contribution, if any, has to be minor on account of the relative yields. The overall yield of the new trioxide is low, and many side products are obtained. Low temperature stabilizes both $FC(O)O_x$ and $CF_3OC(O)O_x$ ($x = 1, 2$) radicals, the precursors of the trioxide and other side products (16 and 18−24).

Kinetic Aspects. $CF_3OC(O)OOOC(O)F$ is unstable at room temperature, and it decomposes like all acyl trioxides to yield a peroxy and an oxy radical. Its thermal decomposition was studied following the disappearance of the characteristic band of the trioxide at 954 cm^{-1} ($\sigma_{954} = 8.1 \pm 0.3 \times 10^{-19}$ cm^2 molecules^{-1}) with the results shown in Figure 1. It can be observed that there is a good linear relationship for the logarithmic ratio of the absorbances with time, which yields an overall first-order rate constant of $(1.02 \pm 0.01) \times 10^{-3}$ s^{-1}; that is, a lifetime of around 10 min at 273 K.

In order to prove experimentally the feasibility of reactions 1 and 2, we studied the thermal decomposition in the presence
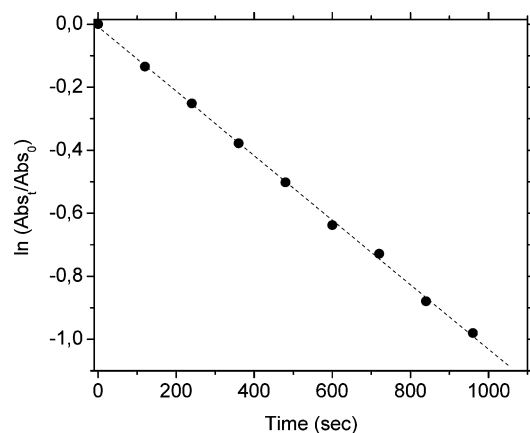

Figure 1. First-order decay of $CF_3OC(O)OOOC(O)F$ at 273 K.

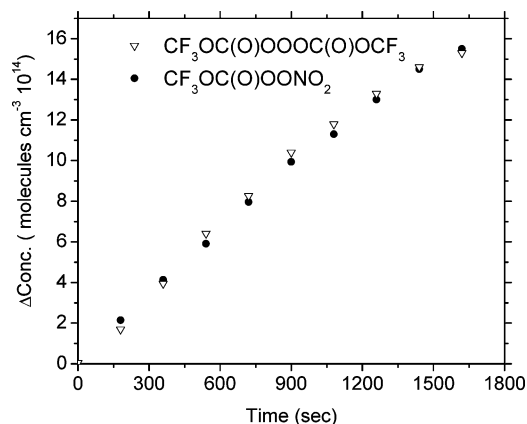**Figure 2.** Temporal progression of the decomposition of $CF_3OC(O)OOOC(O)OCF_3$ in the presence of excess NO_2: ($\triangledown$) molecules of $CF_3OC(O)OOOC(O)OCF_3$ decomposed; ($\bullet$) molecules of $CF_3OC(O)OONO_2$ formed.

of excess NO_2 at 273 K. Under these conditions, peroxy radicals should be efficiently trapped to form peroxynitrates (see below).

Nevertheless, we first had to study the decomposition of pure $CF_3OC(O)OOOC(O)OCF_3$ in excess of NO_2 to be able to subtract its contribution when dealing with the purest synthesized sample of $CF_3OC(O)OOOC(O)F$ (see Experimental Section). Figure 2 shows the temporal progression for decomposition of $CF_3OC(O)OOOC(O)OCF_3$ and the concomitant formation of $CF_3OC(O)OONO_2$; as can be seen, both process have the same slope, and this indicates that every molecule of $CF_3OC(O)OOOC(O)OCF_3$ decomposed gives rise to one peroxynitrate molecule. The dots in the figure correspond to absolute quantities measured using the IR absorption cross sections of the reagent (trioxide) and product (peroxynitrate) that have been taken from spectra reported in the literature. From its observation it is clear that the stoichiometry of the reaction is 1:1. This result clears the way to quantification of reactions 1 and 2 in the actual sample, which contains $CF_3OC(O)OOOC(O)OCF_3$ and $CF_3OC(O)OOOC(O)F$. It confirms, at the same time, the assumption that under these experimental conditions, $CF_3OC(O)OO$ radicals are effectively trapped.

The decomposition of $CF_3OC(O)OOOC(O)OCF_3$ following reaction 1 gives rise, in the presence of NO_2, to trifluoromethoxy carbonyl peroxynitrate[19]

$$CF_3OC(O)OO + NO_2 + M \leftrightarrows CF_3OC(O)OONO_2 + M \quad (25)$$
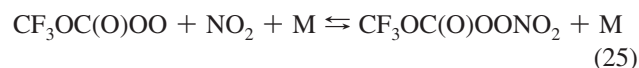
The reaction proceeds with a rate constant $k_{25} = 6.6 \times 10^{-12}$ cm^3 molecules^{-1} s^{-1}.[20] On the other hand, if decomposition followed path 2, $FC(O)OONO_2$ would be formed[21]

$$FC(O)OO + NO_2 + M \leftrightarrows FC(O)OONO_2 + M \quad (26)$$
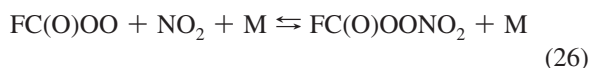
with a rate constant $k_{26} = 5.5 \times 10^{-12}$ cm^3 molecules^{-1} s^{-1}.[22]

The statement that $CF_3OC(O)OO$ radicals are efficiently trapped by NO_2 also applies to $FC(O)OO$ radicals on account of the given rate constants k_{25} and k_{26}.

The thermal decomposition of the actual sample ($CF_3OC(O)OOOC(O)F$ with around 10% $CF_3OC(O)OOOC(O)OCF_3$) was carried out at 273 K in excess (ratio 1:10) NO_2. Figure 3 depicts the temporal progression of both reagents and products. For the reagents (upward and downward triangles for
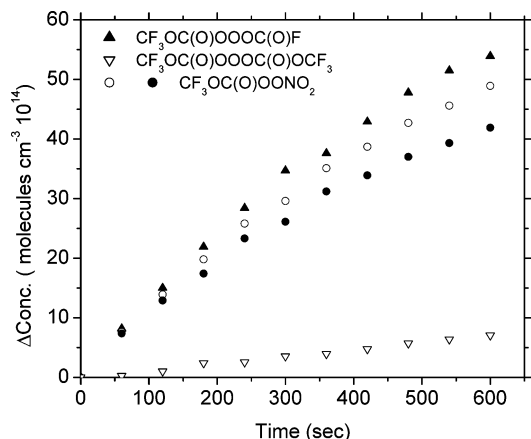
Figure 3. Temporal progression of the decomposition of CF$_3$-OC(O)OOOC(O)F (▲) and CF$_3$OC(O)OOOC(O)OCF$_3$ (▽) in the presence of excess NO$_2$: (○) total CF$_3$OC(O)OONO$_2$ formed; (●) peroxynitrate coming from CF$_3$OC(O)OOOC(O)F.
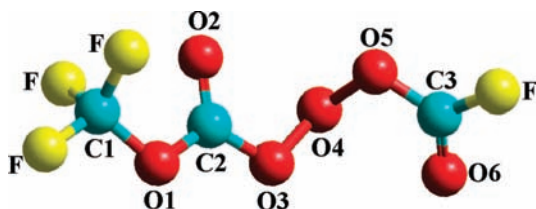
Figure 4. Most stable conformer at the B3LYP/6-311*G+ level.

CF$_3$OC(O)OOOC(O)F and CF$_3$OC(O)OOOC(O)OCF$_3$, respectively), the ordinate axis should be read as the number of molecules consumed and for products as the number of molecules formed. In this way, all the curves have a positive slope. The total amount of CF$_3$OC(O)OONO$_2$ (open circles) was again determined by its IR absorption cross section ($\sigma_{1760\ cm^{-1}}$ = 3.1 ± 0.1 × 10^{-18} cm^2 molecules^{-1}), and the amount of peroxynitrate coming from the symmetric impurity was subtracted in accordance with the results shown in Figure 2. In this way, the absolute concentration of CF$_3$OC(O)OONO$_2$ coming exclusively from CF$_3$OC(O)OOOC(O)F is indicated in the figure by the filled circles.

It is immediately clear that not all the CF$_3$OC(O)OOOC(O)F decomposes forming CF$_3$OC(O)OONO$_2$.

Since the two possible peroxynitrates that should form from the actual sample have been independently characterized[4,19,21,24] and as they are the only peroxy species formed, their quantification as the main products in the thermal decomposition of the trioxide is conclusive proof of the identity of trifluoromethyl fluoroformyl trioxicarbonate. The products obtained and the sum of the absolute quantities of FC(O)OONO$_2$ and CF$_3$OC-(O)OONO$_2$ account for only two possible precursor molecules:

TABLE 1: B3LYP/6-311+G* Absolute and Relative Energies Plus ZPE for the 18 Conformers Found for CF$_3$OC(O)OOOC(O)F

conformer	E+ZPE (H)	ΔE+ZPE (kcal mol^{-1})	Relative population (%)
s-s-(90.70)-(91.17)-s	−965.110573	0	68.1
s-s-(84.00)-(−136.0)-s	−965.107670	1.82	2.37
s-s-(130.7)-(−82.09)-s	−965.107170	2.13	1.33
s-s-(90.60)-(92.03)-a	−965.108822	1.10	8.99
s-s-(82.98)-(−126.62)-a	−965.107014	2.23	1.11
s-s-(132.08)-(90.47)-a	−965.104691	3.69	0.08
s-a-(91.34)-(90.92)-s	−965.109199	0.86	13.9
s-a-(125.42)-(−82.57)-s	−965.107081	2.19	1.20
s-a-(−90.49)-(140.04)-s	−965.105584	3.13	0.21
s-a-(90.96)-(91.15)-a	−965.107589	1.87	2.16
s-a-(89.459)-(−133.97)-a	−965.104339	3.91	0.03
s-a-(132.29)-(−88.96)-a	−965.103830	4.23	0.04
a-s-(90.60)-(90.63)-s	−965.106108	2.80	0.39
a-s-(83.08)-(−133.42)-s	−965.103176	4.64	0.01
a-s-(131.64)-(−82.91)-s	−965.102945	4.79	0.01
a-s-(90.61)-(91.50)-a	−965.104301	3.93	0.05
a-s-(82.28)-(−124.26)-a	−965.102630	4.98	0.01
a-s-(133.40)-(−89.89)-a	−965.100555	6.29	0.00
a-a-φ_3-φ_4-s → s-a-φ_3-φ_4-s			
a-a-φ_3-φ_4-a → s-a-φ_3-φ_4-a			

CF$_3$OC(O)OOOC(O)F and CF$_3$OC(O)OOOC(O)OCF$_3$. The calculated yield is 0.80 ± 0.05. We can thus postulate that the two O−O bonds are nonequivalent, though very similar in energy, and for this reason the yield for the formation of fluoroformyl peroxy nitrate is 0.2. The difficulty in measuring other physical properties of the new trioxide (because of its lability) to fully characterize it was overcome by focusing on chemical properties that leave no doubt about the nature of the constituents.

Calculations. CF$_3$OC(O)OOOC(O)F has 6 main torsion angles considering the skeleton F−C(F$_2$)−O−C(=O)−O−O−O−CF=O which can be conveniently reduced to five because φ_0(F−C(F$_2$)−O−C(O)) always adopts the anti configuration. Three of the remaining five torsion angles can adopt either anti (∼180.0°) or syn (∼0.0°) configurations: (i) the relative position of the CF$_3$− group to the C=O bond, φ_1(F$_3$C−O−C=O), (ii) the relative position of each C=O bond to the −O−O−O− fragment, φ_2(O=C−O−O−), and (iii) the relative position of the fluoroformyl group to the oxygen bridge, φ_5(−O−O−CF=O). The remaining two dihedral angles, related with the COOOC backbone, φ_3(C−O−O−O) and φ_4(O−O−O−C) usually adopt only gauche configurations (ca. ±90.0°). When both φ_3 and φ_4 are either positive or negative (i.e., $\varphi_3 \wedge \varphi_4 > 0°$, or $\varphi_3 \wedge \varphi_4 < 0°$) the C−OOO−C bonds are trans with regard to the plane formed by the OOO fragment, and when φ_3 and φ_4 have opposite signs (i.e., $\varphi_3 > 0°$ and $\varphi_4 < 0°$ or $\varphi_3 < 0°$ and $\varphi_4 > 0°$) the C−OOO−C bonds adopt the cis configuration in relation to the OOO plane. Enantiomeric forms are not taken into account in the present study since there is no
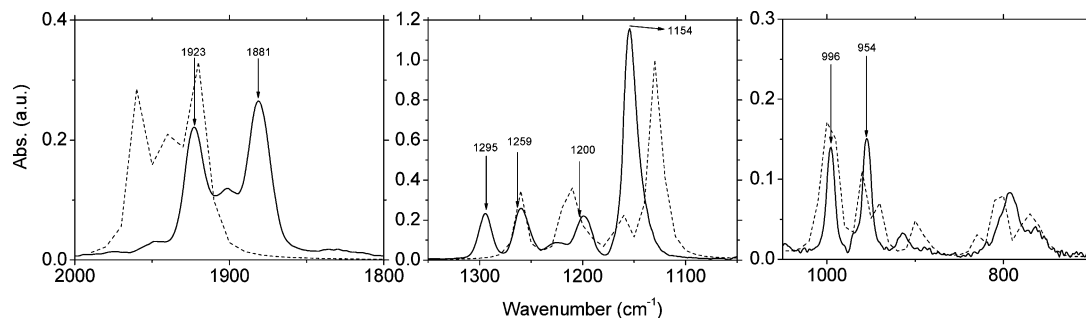

Figure 5. Experimental and calculated MIR spectrum of CF$_3$OC(O)OOOC(O)F.

TABLE 2: Geometrical Parameters for CF₃OC(O)OOOC(O)F (B3LYP/6-311+G*) and the Related Tryoxides FC(O)OOOC(O)F[13] and CF₃OOOCF₃[17a]

	CF₃OC(O)OOOC(O)F	FC(O)OOOC(O)F	CF₃OOOCF₃
		distances (Å)	
C−F	1.334	1.334	1.326
C1−O1	1.390		
O1−C2	1.359		
C2=O2	1.179	1.181	
C2−O3	1.385	1.376	1.378
O3−O4	1.424	1.430	1.452
O4−O5	1.430	1.430	
O5−C3	1.372		
C3=O6	1.173	1.181	
		angles (deg)	
F1−C1−F2	109.25		108.3
F1−C1−O1	106.06		
C1−O1−C2	118.52		
O1−C2=O2	129.37	129.9	
O1−C2−O3	102.53		
C2−O3−O4	109.45		
O3−O4−O5	106.69	106.4	106.7
O4−O5−C3	109.60		105.8
O5−C3−F	103.93	103.9	
O5−C3=O6	129.89		
F4−C3=O6	126.2	126.2	
		dihedrals (deg)	
φ_0	180.00		
φ_1	0.19		
φ_2	−2.97	2.9	
φ_3	90.70	−90.7	96.0
φ_4	91.17	−90.7	96.0
φ_5	−2.70	2.9	

[a] Numbering of atoms follows from Figure 4 and strictly applies only to CF₃OC(O)OOOC(O)F. The values informed for FC(O)OOOC(O)F and CF₃OOOCF₃ are associations for the same type of bond or angle.

energy differences with regard to the conformers analyzed. The different conformers are designated according to the letter code "a" (anti) or "s" (syn) for φ_1, φ_2, and φ_5 and the values of the angles φ_3 and φ_4 in the sequence $\varphi_1-\varphi_2-\varphi_3-\varphi_4-\varphi_5$. Eighteen minima were found in the B3LYP/6-311+G* PES with s-s-(90.7)-(91.2)-s being the most stable conformer. Table 1 gives the absolute (Hartree units) and relative plus ZP (kcal mol⁻¹) energies from the most stable conformer as well as the relative population at 273 K. According to the designation adopted, the conformers can be divided into eight groups in the x-x-φ_3-φ_4-x sequence, where x = a or s, but only six lead to minima in the PES. It was found that the groups a-a-φ_3-φ_4-a and a-a-φ_3-φ_4-s converge to the s-a-φ_3-φ_4-a and s-a-φ_3-φ_4-s forms, respectively. In the antianti forms the CF₃ and the −OOO− groups are quite

close and the electronic repulsion is so high that the rotation of φ_1 to adopt the syn−anti conformation is forced.

Three minima were found in each group according to the different values of φ_3 and φ_4. One of them corresponds to the trans configuration of the backbone C−OOO−C and is always the most stable, while the other two correspond to cis configurations. For these, φ_3 and φ_4 adopt quite different absolute values, around 85° and 130°. This interesting finding can be attributed to the relative distance of both C=O fragments, since at the hypothetical configuration where $\varphi_3 = 90°$ and $\varphi_4 = -90°$, the distance C=O···O=C is about 2.1 Å, which is even shorter than the distance of the outer oxygen atoms in the OOO fragment (∼2.3 Å), but when φ_3 and φ_4 turn to ∼85° and ∼−130°, respectively, the C=O···O=C distance increases to 3.3 Å, thus significantly reducing the electronic repulsion between the nonbonding electrons of both C=O groups.

Figure 4 shows the structure of the most stable calculated conformer. The theoretically postulated helical structure of the oxygen framework,[25] later confirmed for FC(O)OOOC(O)F,[13] is also observed. Bond lengths and angles are presented in Table 2 together with the gas-phase experimental parameters of the two related trioxides FC(O)OOOC(O)F[13] and CF₃OOOCF₃.[17] The geometrical parameters calculated agree with those observed in the related compounds. The most interesting features are the O−O bond distances, the O−O−O angle, and the dihedrals φ_3 and φ_4. The O−O bond distances calculated (1.430 and 1.424 Å) are very similar to that in the acyl trioxide FC(O)OOOC(O)F (1.430 Å), shorter than in CF₃OOOCF₃ (1.452 Å), and longer than in CF₃OOCF₃ (1.419 Å)[26] and ozone (1.272 Å). The O−O−O angle (106.69°) is very similar to those in FC(O)OOO-C(O)F and CF₃OOOCF₃ and considerably smaller that than in ozone (117.79°). The dihedral angles φ_3 and φ_4 for the most stable conformer (∼91°) are very similar to those in FC(O)OOO-C(O)F but smaller than that in CF₃OOOCF₃ (96°).

Infrared Analysis. CF₃OC(O)OOOC(O)F has 33 vibrational modes and belongs to the symmetry group C_1. Thus, all of them are IR active. It is not possible to record all the fundamental modes with conventional mid-IR equipment. Table 3 shows the experimental as well as calculated frequencies of the main bands together with their intensities and a comparison with the molecules FC(O)OOOC(O)F and CF₃OC(O)OOOC(O)OCF₃. A rough inspection of the table shows that the two frequencies of the two different carbonylic stretchings (1923 and 1881 cm⁻¹) correlate almost exactly with the unique carbonylic frequency of the symmetric trioxides FC(O)OOOC(O)F (1922 cm⁻¹) and

TABLE 3: Comparison of Experimental and Calculated (only most stable conformer) Vibrational Wavenumbers of CF₃OC(O)OOOC(O)F and Its Parent Symmetric Molecules[a]

CF₃OC(O)O₃C(O)F	FC(O)O₃C(O)F	CF₃OC(O)O₃C(O)OCF₃	calculated	assignment/approximate description of mode
1923 (19)	1922 (44)		1957 (28)	ν_1 ν_sC=O
1881 (28)		1878 (34)	1921 (31)	ν_2 ν_{as}C=O
1295 (27)		1293 (67)	1261 (20)	ν_3 ν_sCF₃
1259 (29)		1257 (92)	1214 (30)	ν_4 ν_{as}CF₃
1226			1204 (11)	ν_5 νF−C(O)
1200 (19)	1207 (18)	1185 (21)	1165 (16)	ν_6 νF₃C−O/F−C(O)
1154 (100)	1167 (100)	1138 (100)	1127 (100)	ν_7 ν_{as}O−O−O/O−C−O
996 (11)	1139		1003 (14)	ν_8 ν_sO−O−O/O−C−O
973	969	974 (28)	960 (12)	ν_9 ν_{as}O−O−O/O−C−O
954 (12)	945 (11)	899	942	ν_{10} ν_{as}O−O−O
			886	ν_{11}
793	797	795	804 (17)	ν_{12} ν_{sim}O−O−O

[a] Relative intensities higher than 10 are shown in parentheses. Description of selected modes are qualitative because of strong coupling. The following are the rest of the calculated frequencies that were not observed experimentally: ν_{13}, 768; ν_{14}, 767; ν_{15}, 750; ν_{16}, 694; ν_{17}, 673; ν_{18}, 605; ν_{19}, 591; ν_{20}, 552; ν_{21}, 483; ν_{22}, 426; ν_{23}, 385; ν_{24}, 375; ν_{25}, 293; ν_{26}, 235; ν_{27}, 151; ν_{28}, 137; ν_{29}, 97; ν_{30}, 74; ν_{31}, 51; ν_{32}, 398; ν_{33}, 30.

$CF_3OC(O)OOOC(O)OCF_3$ (1878 cm^{-1}), respectively. This can be rationalized assuming that there is no interaction between the two modes, that is, there is no coupling through the trioxide bridge, maintaining each fragment its identity. This effect is also seen in the geometric parameters of these molecules.

The comparison goes beyond with the analysis of the IR bands related with the CF_3 moieties, where it is clear that they are present in the title compound as well as in $CF_3OC(O)$-$OOOC(O)OCF_3$ but not in the fluoroformyl trioxide.

A complete mid-IR spectrum is shown in Figure 5 along with the calculated spectrum obtained accounting for the contribution of the three most stable conformers that together yield more than 90% of the populations at 273 K. The agreement of the spectra is encouraging not only because of the position of the bands but also because of their intensities, which are excellently reproduced.

Theoretical Calculations. All of the electronic structure calculations were carried out using the GAUSSIAN03 program package.[27] The geometries of all the conformers were optimized using the hybrid density functional B3LYP method with the 6-311+G* basis set. Additionally, harmonic vibrational frequencies and zero-point energies (ZPE) were calculated at the same level of theory to check whether the obtained stationary points were either isomers or first-order transition states; the calculated conformers possessed all real frequencies. The determination of the Hessian matrix also enabled calculation of the thermochemical quantities for the conformers at 298.15 K. The selected DFT method has been previously applied to the determination of geometric parameters of related fluoro-carbon-oxygenated compounds, yielding very accurate results, tested with gas electron diffraction experiments.[28−30] Since we are interested in the minima of the potential-energy surface, and DFT methods take into account the electron correlation energy in part,[31] we think that the B3LYP/6-311+G* method should be adequate to describe the relative energies for the isomers. All symmetry restrictions were turned off in the calculations.

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