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Synthesis and Characterization of Trifluoromethyl Fluoroformyl Peroxycarbonate, $CF_3OC(O)OOC(O)F$

Maximiliano A. Burgos Paci, Plácido García,[†] Fabio E. Malanca, and Gustavo A. Argüello*

INFIQC, Departamento de Físico Química, Facultad de Ciencias Químicas,
Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina

Helge Willner*

Fakultät 4, Anorganische Chemie, Gerhard-Mercator-Universität Duisburg,
Lotharstrasse 1, D-47048 Duisburg, Germany

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The synthesis of $CF_3OC(O)OOC(O)F$ is accomplished by the photolysis of a mixture of $(CF_3CO)_2O$, FC(O)C(O)F, CO, and O_2 at –15 °C using a low-pressure mercury lamp. The new peroxide is obtained in pure form in low yield after repeated trap-to-trap condensation and is characterized by NMR, IR, Raman, and UV spectroscopy. Geometrical parameters were studied by ab initio methods [B3LYP/6-311+G(d)]. At room temperature, $CF_3OC(O)OOC(O)F$ is stable for many days in the liquid or gaseous state. The melting point is –87 °C, and the boiling point is extrapolated to 45 °C from the vapor pressure curve $\log p = 8.384 - 1715/T$ (p/mbar, T/K). A possible mechanism for the formation of $CF_3OC(O)OOC(O)F$ is discussed, and its properties are compared with those of related compounds.

Introduction

The interest in the study of the chemistry of compounds and species containing only F, O, and C atoms has increased in the last years because of their involvement in atmospheric chemistry. Many $C_xF_yO_z$ species are formed as products in the atmospheric degradation process of chlorofluorocarbons (CFCs) or their replacements. Hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs), and partially fluorinated ethers are being used as CFC replacements because they have very similar thermodynamical and physical properties but are degraded in the troposphere.[1−3] Their environmental acceptability depends on the role that their degradation products play in the chemistry of the atmosphere. HFCs lead in their degradation path mainly to radicals, which react with atmospheric gases to form molecules such as CF_2O, CFClO, CFHO, and $CF_3C(O)X$ (X = Cl, F).[4] In the degradation path, CF_3O_x and $FC(O)O_x$ ($x = 1, 2$) radicals are involved. The participation of these radicals in catalytic cycles that could eventually destroy O_3 has already been studied,[5−7] and it is generally accepted that they have no impact on stratospheric ozone. Nevertheless, these species, in particular the CF_3O radical, are effective catalysts in the oxidation of atmospheric carbon monoxide, and this cycle has been extensively investigated.[8−10] Laboratory studies on the mechanism of the reaction of CF_3O_x ($x = 1, 2$) radicals in the presence of O_2 and CO (at much higher concentrations than those found in the natural atmosphere) demonstrated the formation of new molecules such as the peroxide $CF_3OC(O)OOC(O)OCF_3$ and the trioxide $CF_3OC(O)OOOC(O)OCF_3$.[11]

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* Authors to whom correspondence should be addressed. E-mail: gaac@fisquim.fcq.unc.edu.ar (G.A.A.); willner@uni-duisburg.de (H.W.).

[†] Permanent address: Fakultät 4, Anorganische Chemie, Gerhard-Mercator-Universität Duisburg, Lotharstrasse 1, D-47048 Duisburg, Germany.

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On the other hand, it is known that FCO_x ($x = 1, 2$) radicals form, in the presence of O_2 and CO, mainly FC(O)OOC(O)F as the stable product.[12] Recently, these observations encouraged us to study systems where CF_3O_x and FCO_x radicals react simultaneously in the presence of O_2 and CO. In this system, some evidence for $CF_3OC(O)OOC(O)F$ was found by infrared spectroscopy in the reaction products.[13] The aim of the present work is to isolate $CF_3OC(O)OOC(O)F$ on a preparative scale and to characterize this molecule by physical and chemical techniques unambiguously.

Experimental Section

Caution! Although this study was conducted without mishap, it is important to take appropriate safety precautions when oxidizing fluorinated compounds are handled in the liquid or solid state because many peroxides are explosive. Reactions involving these compounds should be carried out only in millimolar quantities.

General Procedures and Reagents. 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, London). The vacuum line was connected to the photoreactor and to an IR gas cell (optical path length 200 mm, KBr windows) placed in the sample compartment of a Fourier transform infrared (FTIR) instrument. This arrangement made it possible to follow the course of the reaction during the synthesis and to monitor, at a later stage, the improvement in the purification process. The products were stored in flame-sealed glass ampules in liquid nitrogen. The ampules were opened and resealed by use of an ampule key.[14]

Photochemical Synthesis of $CF_3OC(O)OOC(O)F$. 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 40-W low-pressure mercury lamp (Heraeus, Hanau) was placed. The reactor was immersed in an ethanol bath cooled to about −15 °C and connected to a vacuum line via flexible stainless-steel tubing. After evacuation of the photoreactor, the inner surface was conditioned with perfluoroacetic anhydride $(CF_3CO)_2O$ vapor (100 mbar) for a couple of hours to remove residual water from the surface. In a typical experiment, the reactor was loaded with partial pressures of 2.5 mbar of $(CF_3CO)_2O$, 4 mbar of FC(O)C(O)F, 50 mbar of CO, and 500 mbar of O_2. Every 30 min, a small amount of the gas mixture (0.8% of the reactor content) was analyzed by IR spectroscopy. In particular, the band at 1320 cm^{-1} that belongs to $(CF_3CO)_2O$, that at 1100 cm^{-1} to FC(O)C(O)F, and that at 2150 cm^{-1} to CO were suitable to monitor their disappearance. Because CO disappeared faster than the other reagents, a new injection of CO was needed after 90 min. The photolysis was stopped when the bands of $(CF_3CO)_2O$ and FC(O)C(O)F had almost disappeared (about 3 h). A previous work[13] reported a strong IR absorption band at 1152 cm^{-1} for $CF_3OC(O)OOC(O)F$, and this band was used to follow the formation of the product. The contents of several batches were collected by slowly passing the content of the photoreactor in a vacuum through three U traps kept at −196 °C to remove O_2 and CO from the reaction mixture. To purify the collected raw products, they were kept at −120 °C and small batches were pumped out. In this manner, the more volatile products (CF_2O, CO_2, and CF_3OOOCF_3) were first monitored by their IR bands (2350 cm^{-1} for CO_2, 1947 cm^{-1} for CF_2O, and 1170 cm^{-1} for CF_3OOOCF_3) and then discarded. The prepurified sample was afterward repeatedly fractionated through three U traps held at −80, −120, and −196 °C in a dynamic vacuum until almost pure (>99%) $CF_3OC(O)OOC(O)F$ was obtained. In the final batch, a small amount (less than 0.8%) of $(CF_3CO)_2O$ is still present, as revealed by the 1052 cm^{-1} band in the IR spectrum (see Results and Discussion). The product found at −196 °C was identified as FC(O)OOC(O)F, the one at −120 °C as $CF_3OC(O)OOC(O)F$, and the one at −80 °C as $CF_3OC(O)OOC(O)OCF_3$. $CF_3OC(O)OOC(O)F$ was obtained in an overall yield of around 8% with respect to $(CF_3CO)_2O$.

Chemicals. Perfluoroacetic anhydride was obtained from the dehydration of trifluoroacetic acid with phosphorus pentoxide, and FC(O)C(O)F was prepared by the mild fluorination of oxalyl chloride.[15] Oxygen (99.9%, Air Liquide) and CO (95.5%, Praxair) were obtained from commercial sources and used without further purification.

Instrumentation. (a) Vibrational Spectroscopy. Gas-phase infrared spectra in the range of 4000−400 cm^{-1} were recorded with a resolution of 2 cm^{-1} from 32 co-added interferograms using a FTIR instrument (Bruker IFS 28), whose cell was coupled to the vacuum line to enable direct measurements of the gas mixture.

FT-Raman spectra of a liquid (room temperature) sample were recorded with a Bruker RFS-106 FT-Raman spectrometer using the 1064-nm exciting line of a Nd:yttrium aluminum garnet laser (Adlas DPY30, Lübeck, Germany). A total of 256 spectra were co-added with a resolution of 4 cm^{-1} in the spectral region between 4000 and 80 cm^{-1}.

(b) NMR Spectroscopy. For the NMR measurements, neat samples were flame-sealed in thin-walled 3-mm-o.d. glass tubes and placed into 5-mm NMR tubes. The spectra were recorded with a Brucker Avance DRX-300 spectrometer with a multinuclear probe head with a deuterium lock, operating at 75.74 and 282.41 MHz for ^{13}C and ^{19}F, respectively. The sample was measured at 250 K using a mixture of CD_3CN and $CFCl_3$ as an external lock and reference.

(c) UV Spectroscopy. UV spectra of gaseous samples were recorded using a glass cell (optical path length of 10 cm) equipped with quartz windows placed in the sample compartment of a UV spectrometer (Agilent 8453E). The measurements were carried out in the spectral range of 200−400 nm.

(d) Molecular Weight. The molecular weight of the compound was calculated from the vapor density assuming ideal gas behavior. The vapor density was determined using a thin-walled round-bottom flask of 456.2 mL volume with a 6-mm glass valve with a PTFE stopcock.

Results and Discussion

The new compound is a colorless liquid and stable at room temperature for days in the liquid or gaseous state. The molecular weight was determined from the gas density to be 191 ± 3 g mol^{-1} (calcd 192 g mol^{-1} for $C_3F_4O_5$). The vapor pressure of $CF_3OC(O)OOC(O)F$ follows, in the temperature range between 249 and 292 K, the equation $\log p = 8.384 - 1715/T$ (p/mbar, T/K), and the extrapolated

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Table 1. NMR Data of $CF_3OC(O)OOC(O)F$ and Related Compounds

compound	$\delta_F(CF_3)$, ppm	$\delta_F(COF)$, ppm	$\delta_C(CF_3)$, ppm	$\delta_C(COF)$, ppm	$\delta_C(OCO)$, ppm	$^1J_{CF}(CF_3)$, Hz	$^1J_{CF}(COF)$, Hz
$CF_3OC(O)OOC(O)OCF_3$[a]	−61.3		119.9		145.5	269	
$CF_3OC(O)OOC(O)F$[b]	−59.7	−34.9	119.2	142.5	144.8	268	302
$FC(O)OOC(O)F$[c]		−37.9		142.3			302

[a] Reference 11. [b] This work. [c] Reference 24.

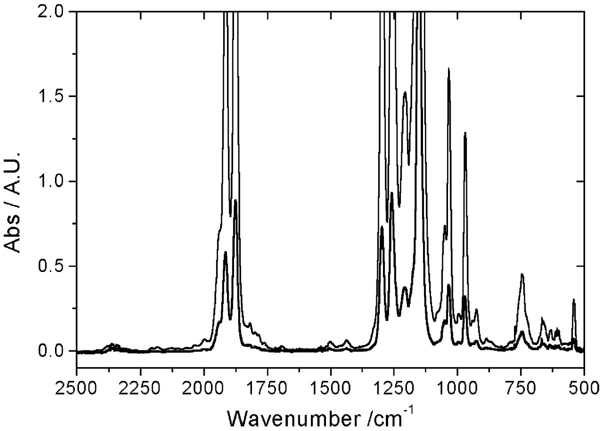

Figure 1. IR spectra of $CF_3OC(O)OOC(O)F$ in the gas phase. Pressures are 2 and 8 mbar.

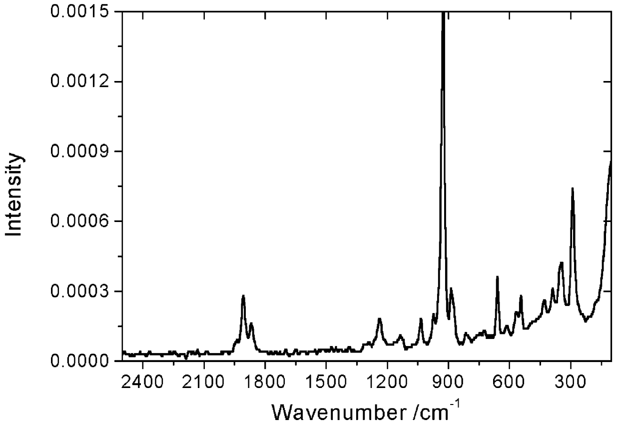

Figure 2. Room-temperature Raman spectrum of liquid $CF_3OC(O)OOC(O)F$.

Table 2. Observed and Calculated Vibrational Wavenumbers

experimental		calculated[c]	assignment/approximate description of mode
IR gas[a]	Raman[b]	syn−syn−syn	
1913 (17)	1906 m	1959 (24)	$\nu_1/\nu(C{=}O)$
1875 (25)	1866 m	1909 (27)	$\nu_2/\nu(C{=}O)$
1297 (21)	1289 vw	1264 (17)	$\nu_3/\nu(CF_3)$
1257 (27)	1235 w	1218 (8)	$\nu_4/\nu(CF_3)$
1203 (11)	n	1216 (25)	$\nu_5/\nu(CF_3)$
1152 (100)		1184 (10)	$\nu_6/\nu(F{-}C(O))$
	1137 vw	1126 (100)	$\nu_7/\nu(F_3C{-}O)$
1034 (11)	1033 w	1046 (16)	$\nu_8/\nu(OC{-}O)$
970 (9)	971 vw	973 (11)	$\nu_9/\nu(OC{-}O)$
924 (2)	924 vs	944 (2)	$\nu_{10}/\nu(O{-}O)$
	885 m	884 (<1)	$\nu_{11}/\nu(F_3C{-}O)$
		771 (<1)	ν_{12}
		759 (1)	ν_{13}
744 (3)		746 (2)	ν_{14}
	722 vw	722 (1)	ν_{15}
	658 m	659 (<1)	ν_{16}
		605 (<1)	ν_{17}
	564 w	554 (<1)	ν_{18}
542 (<1)	543 w	541 (1)	ν_{19}
	427 vw	425 (<1)	ν_{20}
	387 w	381 (<1)	ν_{21}
	344 m	350 (<1)	ν_{22}
		335 (<1)	ν_{23}
	288 s	281 (<1)	ν_{24}
		163 (<1)	ν_{25}
	94 s	109 (<1)	ν_{26}
		83 (<1)	ν_{27}
		68 (<1)	ν_{28}
		50 (<1)	ν_{29}
		40 (<1)	ν_{30}

[a] Relative absorbance at band maximum in parentheses. [b] Liquid, room temperature. Band intensities: vs = very strong; s = strong; m = medium; w = weak; and vw = very weak. [c] B3LYP/6-311+G(d). Relative IR band intensities in parentheses.

boiling point reaches 45 °C. This value is between the boiling points of the respective symmetrical peroxides, that is, 73 °C for $CF_3OC(O)OOC(O)OCF_3$[11] and 16 °C for $FC(O)OOC(O)F$.[12] The white solid melts at −87 °C. In contrast, the melting points of the symmetrical peroxides are −38 °C for $CF_3OC(O)OOC(O)OCF_3$[11] and −43.2 °C for $FC(O)OOC(O)F$.[12] Because the dipole moment (calculated using the quantum chemical method discussed as follows) for the new compound, 1.24 D, is higher than those for $CF_3OC(O)OOC(O)OCF_3$ (0.74 D) and $FC(O)OOC(O)F$ (1.0 D), we could expect a higher melting point, but this contrasts with the experimental finding. Thus, we believe that the interactions in the solid should be less efficient than those in the symmetrical peroxides, and this fact could be due to the packing.

The NMR spectra of the new compound are in perfect agreement with that of the anticipated peroxide $CF_3OC(O)OOC(O)F$. In the ^{19}F NMR spectrum, two signals with an intensity ratio of 1:3 are observed, and the ^{13}C NMR spectrum exhibits one doublet, one quartet, and one broad (15 Hz) singlet. The NMR data are compared in Table 1 with those of the respective symmetrical peroxides, and the data of the same groups show very similar values of chemical shifts and coupling constants.

Additional evidence for the identity of $CF_3OC(O)OOC(O)F$ comes from the analysis of the vibrational spectra. The IR and Raman spectra are shown in Figures 1 and 2, and all vibrational data are gathered in Table 2.

The IR spectrum shows characteristic bands corresponding to the C=O stretching vibrations at 1913 and 1875 cm^{-1}; to the C−F vibrations at 1297, 1257, and 1203 cm^{-1}; and to the C−O bands at 1034 and 970 cm^{-1}. These features agree with the bands reported for $CF_3OC(O)OOC(O)F$ in our earlier study.[13] The Raman spectrum shows a strong band at 924 cm^{-1}, characteristic for a peroxide stretching mode. Table 2 also contains vibrational data of the 30 fundamentals obtained by density functional theory (DFT) calculations at the B3LYP/6-311+G(d) level of theory (discussed as follows).

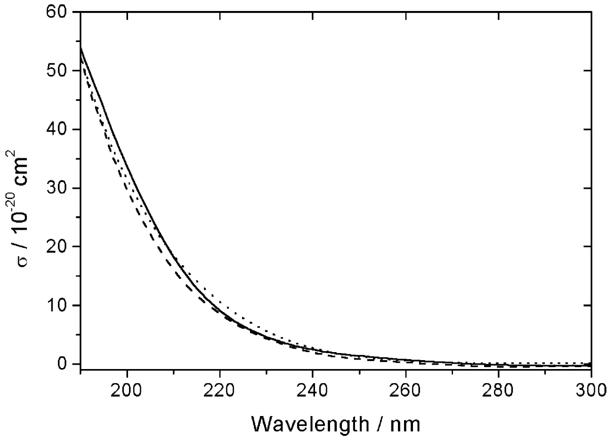

Figure 3. Absorption cross sections for gaseous $CF_3OC(O)OOC(O)F$ (solid line), $FC(O)OOC(O)F$ (dashed line), and $CF_3OC(O)OOC(O)OCF_3$ (dotted line).

The UV spectrum of $CF_3OC(O)OOC(O)F$ shows, as usual for organic peroxides, no structured features and relatively small absorption cross sections that grow toward shorter wavelengths. The calculated cross sections of the title compound have been represented in Figure 3 along with those of the symmetric peroxides $CF_3OC(O)OOC(O)OCF_3$ and $FC(O)OOC(O)F$. A remarkable coincidence can be seen among them. This is somewhat predicted because the electron withdrawal ability of the F atom or the CF_3O group are very similar, and we should not expect shifts in the energy gap between the ground and excited states.

The mechanism for the formation of this new species involves the generation of FCO and CF_3 radicals, which in turn react with O_2 and CO. Some of the reactions involved in the mechanism are

Initiation Steps

$$(CF_3CO)_2O + h\nu \Rightarrow CF_3 + CO + CO_2 \qquad (1)$$

$$FC(O)C(O)F + h\nu \Rightarrow FCO \qquad (2)$$

It is known that CO, in the presence of either CF_3 or FCO radicals and O_2, is converted catalytically to CO_2 by the decomposition of the intermediate radicals XCO_2[9,13,16−18] (X = F in eqs 3−6; X = CF_3O in eqs 7−12). To slow these two fast reactions, the synthesis was carried out at low temperature. In this manner, the rate constants (k_5 and k_{12}) are lowered and the radicals stabilized.

Radical Reactions

$$FCO + O_2 \Rightarrow FC(O)OO \qquad (3)$$

$$2FC(O)OO \Rightarrow 2FCO_2 + O_2 \qquad (4)$$

$$FCO_2 \Rightarrow F + CO_2 \qquad (5)$$

$$F + CO \Rightarrow FCO \qquad (6)$$

$$CF_3 + O_2 \Rightarrow CF_3OO \qquad (7)$$

$$2CF_3OO \Rightarrow 2CF_3O + O_2 \qquad (8)$$

$$CF_3O + CO \Rightarrow CF_3OCO \qquad (9)$$

$$CF_3OCO + O_2 \Rightarrow CF_3OC(O)OO \qquad (10)$$

$$2CF_3OC(O)OO \Rightarrow 2CF_3OCO_2 + O_2 \qquad (11)$$

$$CF_3OCO_2 \Rightarrow CF_3O + CO_2 \qquad (12)$$

$$CF_3O \Rightarrow CF_2O + F \qquad (13)$$

Some Termination Reactions

$$2CF_3O \Rightarrow CF_3OOCF_3 \qquad (14)$$

$$2FCO_2 \Rightarrow FC(O)OOC(O)F \qquad (15)$$

$$2CF_3OCO_2 \Rightarrow CF_3OC(O)OOC(O)OCF_3 \qquad (16)$$

$$FCO_2 + CF_3OCO_2 \Rightarrow CF_3OC(O)OOC(O)F \qquad (17)$$

$$FC(O)OO + CF_3OC(O) \Rightarrow CF_3OC(O)OOC(O)F \qquad (18)$$

The outlined termination reactions account for the main products found in the synthesis. No attempts were made to explain in full detail the whole mechanism or the products, and it is also possible that other species not discussed could be formed.

Although further investigations for the thermal stability of this molecule will be accomplished, we observed that $CF_3OC(O)OOC(O)F$ is quite stable at room temperature. For this reason, as with other fluorocarboxygenated peroxides and trioxides (i.e., $CF_3OC(O)OOC(O)OCF_3$, $CF_3OC(O)OOCF_3$, and $CF_3OC(O)OOOC(O)OCF_3$), the title compound can be used as a reservoir for CF_3O_x and FCO_x radicals in laboratory experiments. The formation of these types of molecules in a clean atmosphere is not expected because of the low concentration of CF_3O_x and FCO_x radicals. Nevertheless, we believe that their formation could be possible in highly contaminated atmospheres (like halon-extinguished fires).

Quantum Chemical Calculations. Ab initio calculations were performed with the Gaussian 98 program suite.[19] DFT, with the Becke's Three Parameter Hybrid Functional method using the Lee−Yang−Parr Correlation Functional (B3LYP) method with 6-311+G(d) basis sets, was used in all cases. The superiority of DFT methods over conventional Hartree−Fock methods for the study of fluorooxygenated systems has been demonstrated.[20−22] The geometries of the eight con-

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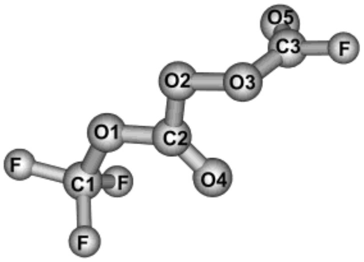

Figure 4. Calculated structure for the most stable syn−syn−syn $CF_3OC(O)OOC(O)F$ conformer.

formers, syn−syn−syn, syn−syn−anti, anti−syn−syn, anti−syn−anti, syn−anti−syn, syn−anti−anti, anti−anti−syn, and anti−anti−anti, were fully optimized without symmetry restrictions. The conformers were named according to the following criteria: (a) the position of the CF_3−O bond with respect to the C═O bond defines the first syn−anti term, (b) the position of the C═O bond with respect to the O−O bond defines the second syn−anti term, and (c) the position of the latter with respect to the fluoroformyl C═O defines the last syn−anti term. For all conformers, the C−O−O−C skeleton has a gauche configuration. At this level of theory, the syn−syn−syn conformer, depicted in Figure 4, is predicted to be the most stable by 1.7 kcal mol^{-1} with respect to the syn−syn−anti conformer and by 2.8 kcal mol^{-1} with respect to the anti−syn−syn conformer, which are next in increasing energy.

Vibrational frequencies were also obtained without using any scaling factors. The calculated and experimental wavenumbers agree quite well (cf. Table 2) within the errors expected for the calculated band positions. The assignment of the normal modes is based on a comparison between calculated and observed band positions and their relative intensities. As can be seen from the table, only a qualitative description of the stretching modes is presented; the others are not described because the coupling between different bendings and torsions is very strong, and the description could have little significance. In Table 3, the geometrical parameters found for the most stable conformer are listed. It can be seen that there is only one C−F distance listed, which means that the F atom bonded to the sp^2 carbon has the same length as the F atom bonded to the sp^3 carbon. Nevertheless, the most interesting features in the structure of peroxides are the dihedral angle around the O−O bond δ(X−O−O−X) and the O−O distance. The dihedral angles δ(X−O−O−X) are around 90° for peroxides with two strongly electron-withdrawing substituents (e.g., X = F, Cl) or with sp^2-hybridized substituents [RC(O), NO_2]. In this respect, the value calculated for δ(C−O−O−C) (91.7°) agrees in general with this tendency. It is yet higher than the experimental values reported for the related compounds $CF_3C(O)OOC(O)CF_3$[23] (86.5°) and FC(O)OOC(O)F[24] (85.5°), although the difference may be attributed to the basis set because the same discrepancy was observed with the theoretical value (94.6°) of FC(O)OOC(O)F at the same level of theory.[25] The O−O atomic distance (1.43 Å) should be compared with those of other fluorinated peroxides such as $CF_3C(O)OOC(O)CF_3$ (1.426 Å exptl, 1.427 Å B3LYP/631G*),[23] FC(O)OOC(O)F (1.419 Å exptl, 1.436 Å B3LYP/631+G*),[24] CF_3OOCF_3 (1.42 Å exptl),[26] and $CF_3C(O)OONO_2$ (1.408 Å exptl, 1.393 Å B3PW91/6-311+G*).[27] It is clear that there are no significant differences between experiment and theory for the O−O bond lengths.

Table 3. Calculated Geometrical Parameters of the Most Stable Conformer

distances (Å)		angles (deg)	
C−F	1.33	F−C−O	111.5
C1−O1	1.39	C1−O1−C2	119.0
O1−C2	1.36	O1−C2−O2	102.7
C2−O2	1.38	C2−O2−O3	109.2
O2−O3	1.43	O2−O3−C3	109.6
O3−C3	1.37	δ(C−O−O−C)	91.7
C═O	1.18	δ(O−C−O−O)	174.5
		δ(O═CO−O)	−5.5

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