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Bis(trifluoroacetyl) Peroxide, $CF_3C(O)OOC(O)CF_3$

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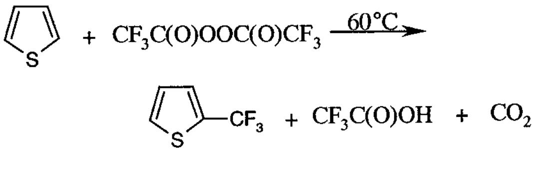
Pure, highly explosive $CF_3C(O)OOC(O)CF_3$ is prepared for the first time by low-temperature reaction between $CF_3C(O)Cl$ and Na_2O_2. At room temperature $CF_3C(O)OOC(O)CF_3$ is stable for days in the liquid or gaseous state. The melting point is −37.5 °C, and the boiling point is extrapolated to 44 °C from the vapor pressure curve $\log p = -1875/T + 8.92$ (p/mbar, T/K). Above room temperature the first-order unimolecular decay into $C_2F_6 + CO_2$ occurs with an activation energy of 129 kJ mol^{-1}. $CF_3C(O)OOC(O)CF_3$ is a clean source for CF_3 radicals as demonstrated by matrix-isolation experiments. The pure compound is characterized by NMR, vibrational, and UV spectroscopy. The geometric structure is determined by gas electron diffraction and quantum chemical calculations (HF, B3PW91, B3LYP, and MP2 with 6-31G* basis sets). The molecule possesses syn−syn conformation (both C═O bonds synperiplanar to the O−O bond) with O−O = 1.426(10) Å and dihedral angle ϕ(C−O−O−C) = 86.5(32)°. The density functional calculations reproduce the experimental structure very well.

Introduction

Bis(trifluoroacetyl) peroxide, $CF_3C(O)OOC(O)CF_3$, was first synthezised in 1951 by Miller and Dittman, and its explosive nature has been recognized.[1] Subsequently, in all further reports on $CF_3C(O)OOC(O)CF_3$ it was synthezised in two liquid phase systems from trifluoroacetyl anhydride in Freon 113 ($CFCl_2$-CF_2Cl) and aqueous $NaOH/H_2O_2$ solutions below 0 °C in 20−30% yield.[2,3] Determination of the content in the Freon solution was achieved by iodometry. In general perfluoroalkanoyl peroxides $R_FC(O)OOC(O)R_F$ can be prepared in a similar way from the respective acyl halides.[4] Because perfluoroalkanoyl peroxides decompose in solution thermally under mild conditions (<80 °C) in perfluoroalkyl radicals and CO_2, they can be used in the synthesis of fluoroalkyl end-capped oligomers and polymers of olefins,[5] in the synthesis of perhalogenated olefins,[1] and for telomerizations.[2] In addition, $CF_3C(O)OOC(O)CF_3$ is used as a trifluoromethylation reagent of aromatic compounds,[3] e.g.,



(1)

Only perhalogenated solvents can be used for such reactions, because otherwise hydrogen atoms are abstracted from C−H bonds of the solvent.[6,7] A recent review article deals with the interesting chemistry of fluorinated peroxides.[4] Even though $CF_3C(O)OOC(O)CF_3$ has been known for 50 years as a very useful reagent, the pure compound has never been isolated and many of its properties are still unknown. Only the chemical shift in the ^{19}F NMR spectrum at −61.9 ppm[6] and in the ^{17}O NMR spectrum of the peroxy group at 317 ppm[8] as well as the two CO-stretching wavenumbers 1860/1840 cm^{-1} in the IR spectrum[3] are mentioned in the literature. However, the thermal decomposition in different solvents has been studied in some detail.[3,6]

We became interested in $CF_3C(O)OOC(O)CF_3$ because this compound was detected as an impurity during our synthesis of $CF_3C(O)OONO_2$[9] and we wanted to know more about its spectroscopic properties. In addition, investigation of the thermal decomposition mechanism in the gas phase, with the CF_3CO_2 radical as a possible intermediate—in analogy to our earlier FCO_2 matrix study[10]—as well as study of its structural properties by electron-diffraction and theoretical methods in comparison to $FC(O)OOC(O)F$[11] and $CF_3C(O)OONO_2$[12] seemed to be worthwhile aims. Therefore we developed a synthesis of pure $CF_3C(O)OOC(O)CF_3$, and the results of its extensive characterization are reported in this paper.

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(1) Miller, W. T.; Dittman, A. L.; Reed, S. K. U.S. Patent **1951**, 2,580,358.
(2) Gumprecht, W. H.; Dettre, R. H. *J. Fluorine Chem.* **1975**, *5*, 245.
(3) Sawada, H.; Nakayama, M.; Yoshida, M.; Yoshida, T.; Kamigata, N. *J. Fluorine Chem.* **1990**, *46*, 423.
(4) Sawada, H. *Chem. Rev.* **1996**, *96*, 1779.
(5) Sawada, H. *J. Fluorine Chem.* **2000**, *101*, 315.
(6) Serov, S. I.; Zhurarlev, M. V.; Sass, V. P.; Sokolov, S. V. *J. Org. Chem. USSR (Engl. Transl.)* **1980**, 1360.
(7) Zhao, C.-X.; Chen, G.-F.; Qu, Y.-L.; Jiang, X.-K. *J. Fluorine Chem.* **1987**, *37*, 215.
(8) Barieux, J. J.; Schirmann, J. P. *Tetrahedron Lett.* **1987**, *28*, 6443.
(9) Kopitzky, R.; Bauleke, M.; Balzer, G.; Willner, H. *Inorg. Chem.* **1997**, *36*, 1994.
(10) Argüello, G. A.; Grothe, H.; Kronberg, M.; Willner, H.; Mack, H.-G. *J. Phys. Chem.* **1995**, *99*, 17525.
(11) Mack, H.-G.; Della Védova, C. O.; Oberhammer, H. *Angew. Chem.* **1991**, *103*, 1166; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1145.
(12) Hermann, A.; Niemeyer, J.; Mack, H.-G.; Kopitzky, R.; Beuleke, M.; Willner, H.; Christen, D.; Schäfer, M.; Bauder, A.; Oberhammer, H. *Inorg. Chem.* **2001**, *40*, 1672.

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Experimental Section

CAUTION! *During this study some violent explosions of bis(trifluoroacetyl) peroxide occurred. Especially the phase transition from the liquid to the solid state and vice versa can be accompanied by unpredictable explosions. Therefore it is important to take appropriate safety precautions when this compound is handled in the condensed state. Reactions involving this compound should be carried out only with submillimolar quantities.*

General Procedures and Reagents. Volatile materials were manipulated in a glass vacuum line equipped with two capacitance pressure gauges (221 AHS-1000 and 221 AHS-10, MKS Baratron, Burlington, MA), three U-traps, and valves with PTFE stems (Young, London). The vacuum line was connected to an IR cell (optical path length 200 mm, Si windows 0.5 mm thick) in the sample compartment of the FTIR instrument (Nicolet, Impact 400 D). This arrangement made it possible to follow the purification process. The product was stored in flame-sealed glass ampules (o.d. 12 mm) in liquid nitrogen. The ampules were opened and resealed by use of an ampule key.[13] Solid materials were handled in a drybox (Braun, Unilab) filled with nitrogen containing less than 1 ppm H_2O and O_2. Glass ampules (o.d. 20 mm, V = 33 mL) connected with a 6 mm o.d. glass tube were used as reaction vessels. Typically the dry ampule was charged with 0.5 g (6 mmol) of fine ground sodium peroxide (p.a. Merck, Darmstadt) inside the drybox. By using the ampule key[13] the ampule was connected to the vacuum line, filled with 3 mmol of $CF_3C(O)Cl$ (Solvay, Hannover), and flame sealed. The ampule was then placed in a 2 L metal Dewar vessel covered at the bottom with a 5 cm layer of cold (−65 °C) ethanol. After warming up to −10 °C (about 2 h) the volatile products were separated by fractional condensation in vacuo in a series of traps held at −65, −93, and −196 °C. The trap at −93 °C retained mainly $CF_3C(O)OOC(O)CF_3$, which was purified by repeated trap-to-trap condensation. The yield amounted about 50% based on $CF_3C(O)Cl$. In a few cases the glass ampules exploded or contained only the decomposition products CO_2 and C_2F_6.

The melting point of pure $CF_3C(O)OOC(O)CF_3$ was determined with a small pure sample (∼50 mg) placed inside a 6 mm o.d. glass tube, using a stirred cold ethanol bath in a transparent Dewar glass vessel. The temperature was measured with a small (5 × 1 mm) Pt-100 resistance sensor (Heraeus) attached to the sample tube.

Vapor pressures were measured with a small container connected with the capacitance manometer (1000 mbar absolute) of the vacuum line (total volume ∼20 mL) in a temperature range between −35 and 15 °C.

To determine the thermal decay of $CF_3C(O)OOC(O)CF_3$, 10 mbar of the gaseous compound was diluted with about 50 mbar of dry nitrogen in a 300 mL glass bulb equipped with a PTFE valve. Then the bulb was kept several times in a temperature-controlled water/ethylenglykol bath at $T = 60$, 70, 80, or 90 °C ($\Delta T = \pm 0.2$ °C) for about 1800, 900, 300, or 150 s, respectively, and immediately quenched with ice water to stop the decay. For each measurement the same pressure was adjusted inside the IR gas cell of the FTIR instrument (IFS 66v, Bruker).The decay was then monitored by measuring the absorbance of the 1048 cm^{-1} band. The first-order unimolecular rate constants are $k_{60°C} = (1.57 \pm 0.01)\ 10^{-5}\ s^{-1}$, $k_{70°C} = (5.93 \pm 0.08)\ 10^{-5}\ s^{-1}$, $k_{80°C} = (19.9 \pm 0.2)\ 10^{-5}\ s^{-1}$, and $k_{90°C} = (69.6 \pm 0.7)\ 10^{-5}\ s^{-1}$.

Instrumentation. (a) Vibrational Spectroscopy. Gas phase infrared spectra were recorded with a resolution of 2 cm^{-1} in the range 4000−50 cm^{-1} on the FTIR instrument Bruker IFS 66v. For recording matrix infrared spectra in the range 4000−400 cm^{-1} the Bruker IFS 66v spectrometer with a resolution of 1 cm^{-1} was used. Details of the matrix-isolation apparatus and of the pyrolysis device have been given elsewhere.[10]

FT-Raman spectra of liquid $CF_3C(O)OOC(O)CF_3$ were recorded with a Bruker RFS 100/S FT Raman spectrometer. The sample in a 2 mm o.d. glass capillary was excited with 500 mW of a 1064 nm Nd:YAG laser (ADLAS, DPY 301, Lübeck, Germany).

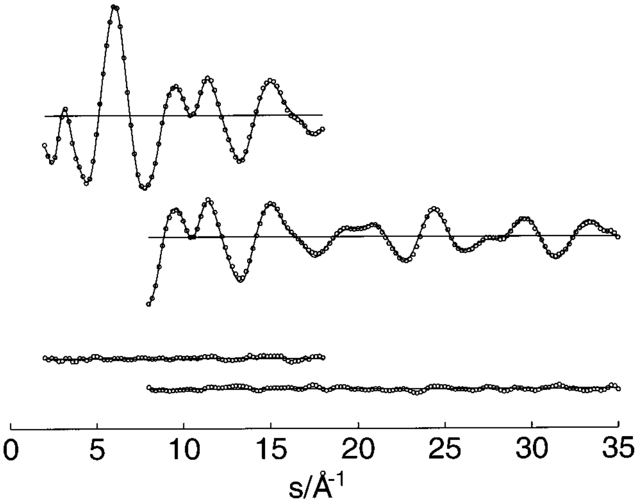

Figure 1. Experimental (points) and calculated (full line) molecular intensities and differences for $CF_3C(O)OOC(O)CF_3$.

(b) UV Spectroscopy. The gas phase UV spectrum of $CF_3C(O)OOC(O)CF_3$ was recorded in a glass cell (100 mm optical path length, quartz windows, Suprasil, Heraeus) on the UV/vis/near-IR Lambda 900 spectrometer (Perkin-Elmer). In the spectral region 190−400 nm, every 0.5 nm a data point was recorded with an integration time of 0.12 s and a resolution of 1 nm. To eliminate absorptions from atmospheric oxygen, the whole spectrometer was flushed with nitrogen.

(c) NMR Spectroscopy. The ^{19}F and ^{13}C NMR spectra of a sample, dissolved in trifluoroacetic anhydride, were recorded at −30 °C on a Bruker MSL 200 spectrometer with a $^{19}F/^{1}H$ dual or a multinuclear probe head operating at 188.31 or 50.33 MHz, respectively. The flame-sealed 5 mm o.d. sample tube was centered in a 10 mm o.d. tube containing $CDCl_3$ and $CFCl_3$ (Merck) as external lock and reference. For the ^{19}F NMR spectrum 50 scans were accumulated in a 64 k memory, with a delay time of 2.2 s between scans. For the ^{13}C NMR spectrum, 132 scans of the sample were recorded with a delay time of 60 s.

(d) Gas Electron Diffraction. The electron diffraction intensities were recorded with a Gasdiffractograph KD-62[14] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of ca. 60 kV. The gaseous sample at room temperature in a 200 mL glass container at 50 mbar was passed through a needle valve and the gas nozzle. The photographic plates (Kodak electron image plates, 13 × 18 cm) were analyzed by the usual methods.[15] Average molecular intensities in the *s* ranges of 2−18 and 8−35 $Å^{-1}$ (in steps of $\Delta s = 0.2\ Å^{-1}$) are shown in Figure 1.

Results and Discussion

Synthesis and General Properties of $CF_3C(O)OOC(O)CF_3$. The synthesis of solvent-free $CF_3C(O)OOC(O)CF_3$ is possible by a simple nucleophilic displacement reaction between solid Na_2O_2 and gaseous/liquid $CF_3C(O)Cl$ at −20 °C in a sealed glass tube.

$$Na_2O_2 + 2CF_3C(O)Cl \rightarrow CF_3C(O)OOC(O)CF_3 + 2NaCl \tag{2}$$

However, the synthetic and purification process is dangerous because a violent explosion may be occur in the liquid or solid phase. Small amounts of the product can be handled quite safely if $CF_3C(O)OOC(O)CF_3$ covers the inner surface of the reaction vessels or U-traps as a thin solid film at low temperatures.

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(13) Gombler, W.; Willner, H. *J. Phys. E: Sci. Instrum.* **1987**, *20*, 1286.

(14) Oberhammer, H. The Chemical Society: London, 1976; Vol. 4, p 24.

(15) Oberhammer, H.; Gombler, W.; Willner, H. *J. Mol. Struct.* **1981**, *70*, 273.

Table 1. Vibrational Wavenumbers (cm^{-1}) of the Thermolysis and Photolysis Products of $CF_3C(O)OOC(O)CF_3$ Isolated in an Argon Matrix[a]

thermolysis 150−300 °C		photolysis $\lambda < 225$ nm		reference $2CO_2 + C_2F_6$		
cm^{-1}	rel int	cm^{-1}	rel int	cm^{-1}	rel int	assignment
2345	100	2342	100	2346	100	CO_2
1250	95[c]	1251	65[c]			CF_3
~1242[b]		1242	70	1244	81	C_2F_6
1213	4[c]	1208	7[c]			CF_3
1111	4	1110	3	1111	18	C_2F_6
1086	7[c]	1083	10			CF_3
712	0.5	712	0.4	712	3	C_2F_6
703	3	700	3			CF_3
663	13	662	16	663	11	CO_2
		521	<0.1	521	1	C_2F_6
511	0.8	510	0.8			CF_3

[a] Most intensive matrix site. [b] The resolution of the recorded spectra do not allow the separation of the CF_3 vibrations of $CF_3C(O)OOC(O)CF_3$ and C_2F_6, and the difference spectra of pyrolyzed and nonpyrolyzed sample do not allow integrations. [c] Due to errors in the electronic subtraction process these values are uncertain by ±30%.

Pure $CF_3C(O)OOC(O)CF_3$ is a colorless liquid which freezes at -37.5 ± 1 °C, and the boiling point, extrapolated from the vapor pressures measured in the temperature range −35 to

$$\log p = -1875/T + 8.92 \qquad (p \text{ in mbar, } T \text{ in K})$$

15 °C, is 44 °C (for comparison, the bp of $CF_3C(O)OC(O)CF_3$ is 39 °C). The peroxide hydrolyzes slowly into $CF_3C(O)OH$ and $CF_3C(O)OOH$ and decomposes in the gas phase above room temperature in a first-order unimolecular decay according to

$$CF_3C(O)OOC(O)CF_3 \rightarrow C_2F_6 + 2CO_2 \qquad (3)$$

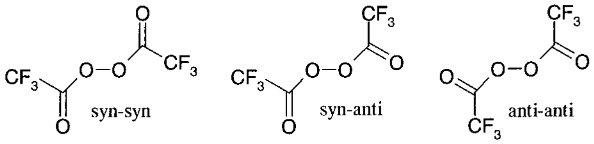
Never was $CF_3C(O)OCF_3$[16] as a possible product from the reaction of CF_3 and CF_3CO_2 radicals detected. From the measured rate constants the Arrhenius type temperature dependence is

$$\ln k = -15500(\pm 200)/T + 35.3(\pm 0.5) \qquad (k \text{ in } s^{-1}, T \text{ in K})$$

with an activation energy of 129(±2) kJ mol^{-1} and half-life times at 25 or 100 °C of 200 days or 6 min, respectively. The rate constants mentioned in the literature for the decay in solution (Freon 113, hexane) are 1−2 orders of magnitude higher[3,6] ($\ln k = -13359/T + 30.9$ or $\ln k = -13590/T + 34.7$; k in s^{-1}, T in K). The reason for this discrepancy is not obvious. It is interesting to note that we observed no decay of $CF_3C(O)OOC(O)CF_3$ at 80 °C in supercritical CO_2 solution ($\rho = 0.3$ g mL^{-1}) within 10 minutes.

In order to evaluate the thermal decomposition mechanism in detail and to detect the possible CF_3CO_2 radical, matrix-isolation experiments were performed. For this purpose highly diluted $CF_3C(O)OOC(O)CF_3$ in argon was pyrolyzed at low pressure with subsequent quenching of the product mixture at 13 K as a matrix. The observed IR bands and their assignments are presented in Table 1. In the temperature range 150−300 °C of the spray on nozzle the IR bands of the products CF_3, C_2F_6, and CO_2 were observed in a nearly constant intensity ratio and the band positions for CF_3 radicals are in agreement with the literature values.[17] By comparison with the measured reference spectrum of a $C_2F_6 + 2CO_2$ mixture a molar ratio of CF_3 to C_2F_6 of about 4:1 is estimated. In a separate photolysis experiment ($\lambda < 225$ nm) of matrix-isolated $CF_3C(O)OOC(O)CF_3$ the same decomposition products were detected, where the amount of CF_3 radicals was a little higher than in the pyrolysis experiments. The small deviations in the band position in both experiments are due to the different environments. In the photolysis experiment the produced molecules are interacting in one matrix cage, and in the pyrolysis experiment they are isolated from each other. No bands belonging to the CF_3CO_2[18] radical or to $CF_3C(O)OCF_3$[16] could be detected. Hence CF_3CO_2 is not involved in the thermal decay of $CF_3C(O)OOC(O)CF_3$ under our experimental conditions, and its activation energy for the $CF_3{-}CO_2$ bond fission is expected to be much smaller than the activation energy for the O−O bond fission (129 kJ mol^{-1} see above) of the peroxide. This finding is in accordance with theoretical calculations, where an activation energy of about 20 kJ mol^{-1} for the exothermal dissociation of CF_3CO_2 into $CF_3 + CO_2$ is predicted.[18] From kinetic measurements an atmospheric lifetime of ca. 15 μs for CF_3CO_2 is estimated,[19] much shorter than the residence time (~1 ms) of the $CF_3C(O)OOC(O)CF_3$ molecules and their fragments in the hot spray on nozzle of the matrix-isolation apparatus.

Spectroscopic Properties and Molecular Structure. (a) Vibrational Spectra. Besides the gauche configuration of the COOC skeleton in $CF_3C(O)OOC(O)CF_3$ there are three different conformers possible, depending on the orientation of the $CF_3C(O)$ groups:



Because in the IR matrix spectrum of $CF_3C(O)OOC(O)CF_3$ no more than two CO stretching modes at 1868/1838 cm^{-1} are observed, the presence of only one conformer is concluded. This is in agreement with the results of the electron diffraction experiment and theoretical calculations where the syn−syn species possessing C_2 symmetry is the most stable conformer (see below). All 36 fundamentals are active in the IR and Raman spectrum,

$$\Gamma_{vib} = 19 \text{ A (IR, Raman p)} + 17 \text{ B (IR, Raman dp)}$$

and they can be subdivided into 13 stretching, 18 deformation, and 5 torsional modes. As can be seen from the calculated IR spectrum in the Supporting Information (Table S1), many in-phase (A) and out-of-phase (B) modes are very similar in energy, and all those modes which differ by less than 3 cm^{-1} are collected together as one band in Table 2. Figure 2 shows the gas phase infrared and liquid phase Raman spectrum of $CF_3C(O)OOC(O)CF_3$. Due to the small rotational constants and the many low-frequency motions of the $CF_3C(O)OOC(O)CF_3$ molecule, the infrared bands show no distinct contours. For quantitative analysis the absorption cross sections at all band maxima, determined according to

$$\sigma = 31.79T \log(I_o/I)p^{-1}d^{-1}/10^{-20} \text{ cm}^2$$

$$(T \text{ in K, } p \text{ in mbar, optical path length } d \text{ in cm})$$

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(16) Varetti, E. L.; Aymonino, P. J. *J. Mol. Struct.* **1971**, *7*, 155.
(17) Jacox, M. E. *J. Phys. Chem. Ref. Data* **1998**, *27*, 261 and references therein.
(18) Francisco, J. S. *Chem. Phys. Lett.* **1992**, *191*, 7.
(19) Maricq, M. M.; Szente, J. J.; Khitrov, G. A.; Francisco, J. J. *J. Phys. Chem.* **1996**, *100*, 4514.

Table 2. Vibrational Wavenumbers (cm^{-1}) of $CF_3C(O)OOC(O)CF_3$ and Their Assignments

IR						
gas	σ[a]	Ar matrix[b]	*I*[c]	Raman[d]	calcd[e]	assignment according to C_2 sym ca. descr of mode[f]
3731	0.6	3727	0.2			$2\nu_1$
3691	2.3	3687	0.6			$\nu_1 + \nu_{20}$
3675sh	1.5	3667	0.2			$2\nu_{20}$
2542	1.0	2539	0.3			$\nu_3\,(\nu_{21}) + \nu_3\,(\nu_{22})$
2444	1.3	2432	0.5			$\nu_3\,(\nu_{22}) + \nu_4\,(\nu_{23})$
2394	1.2	2383	0.3			$2\nu_4\,(2\nu_{23})$
2129	1.8	2125	0.4			$\nu_5 + \nu_{24}$
2094	1.3	2087	0.2			$2\nu_{24}$
1956br	2.0	1963	0.2			$\nu_5 + \nu_{25}$; $\nu_4\,(\nu_{23}) + \nu_8\,(\nu_{26})$
1913	6.0	1921	0.9			$\nu_{24} + \nu_{25}$
1869	92	1868	28	1867 (s)	1855 (161)	A ν_1 $\nu_s(C{=}O)$
1843	154	1838	31	1839 (w)	1826 (211)	B ν_{20} $\nu_{as}(C{=}O)$
1500	2.6	1499	0.3			$\nu_3\,(\nu_{22}) + \nu_{33}$
1304	108	1306	13	1299 (w)	1260 (130)	A ν_2, B ν_{21} $\nu_s(CF_3)$
1243	397	1241	100	1239 (w)	1220 (570)	A ν_3, B ν_{22} $\nu_{as}(CF_3)$
1206	364	1198	69	1198 (w)	1186 (450)	A ν_4, B ν_{23} $\nu_{as}(CF_3)$
1087	38	1087	8.8	1088 (m)	1063 (35)	A ν_5, $\nu(C{-}O + C{-}C)$
1048	765	1044	88	(vw)	1034 (730)	B ν_{24}, $\nu(C{-}C + C{-}O)$
892sh	5	891	0.5	887 (vs)	899 (6)	A ν_6, $\nu(O{-}O)$
873	9	879	2.5	863 (s)	853 (14)	B ν_{25}, $\nu(C{-}O) + \delta(CO_2)$
		859	0.7		840 (3)	A ν_7, $\nu(C{-}O) + \delta(CO_2)$
754	77	756	11	757 (w)	760 (70)	A ν_8, B ν_{26}
		729	0.1	732 (s)	748 (17)	B ν_{27}
583br	2	586	0.2		584 (1)	B ν_{28}
571br	3	570	0.6		565 (3)	A ν_{10}
523	8	523	2.8		517 (13)	A ν_{11}, B ν_{29}
443	14	443	1.9	443 (w)	445 (13)	B ν_{30}
411	2.8	410	0.7	415 (m)	408 (3)	A ν_{12}, B ν_{31}
344	6.9			350 (w)	346 (8)	A ν_{13}, B ν_{32}
305	2.2			308 (m)	309 (3)	A ν_{14}
258	11.0			260 (vw)	250 (9)	B ν_{33}
228	1.4			232 (s)	217 (2)	A ν_{15}
202	0.2			201 (vw)	188 (<1)	B ν_{34}
158	0.1			159 (m)	145 (<1)	A ν_{16}
				~90	72 (<1)	A ν_{17}

[a] Absorption cross section in 10^{-20} cm^2. [b] Most intensive matrix site. [c] Relative integrated intensities $I(\nu_4) \equiv 100$. [d] Liquid. [e] B3PW91/6-31G*, wavenumbers of the stretching modes are scaled by a factor of 0.95, values in parentheses are IR intensities in km mol^{-1}. [f] The analysis of the displacement vectors shows that all vibrations excluding $\nu(C{=}O)$ and $\nu(O{-}O)$ are strongly mixed.

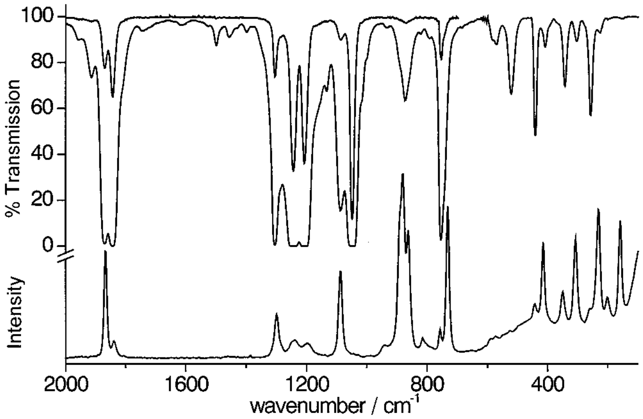

Figure 2. Upper trace: IR spectra of gaseous $CF_3C(O)OOC(O)CF_3$ (0.59 and 10.2 mbar at 20 cm optical path length and 300 K). Lower trace: Raman spectrum of liquid $CF_3C(O)OOC(O)CF_3$.

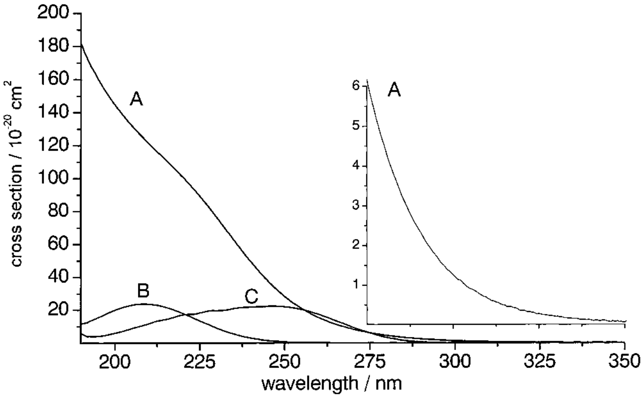

Figure 3. Gas phase UV spectra of $CF_3C(O)OOC(O)CF_3$ (A), $CF_3C(O)OH$ (B), and $CF_3C(O)OC(O)CF_3$ (C).

are collected in Table 2. In addition all vibrational data observed in the gas phase, in an argon matrix, and for the pure liquid are listed together with the calculated wavenumbers (DFT) and a tentative assignment in Table 2. The assignment is based on a comparison between calculated and observed band positions/intensities, and the descriptions of modes are based on the calculated displacement vectors.

(b) UV Spectrum. In Figure 3 the UV spectrum of $CF_3C(O)OOC(O)CF_3$ is compared with those of $CF_3C(O)OC(O)CF_3$ and $CF_3C(O)OH$. It ranges from 350 nm with increasing intensity toward 190 nm, and a shoulder appears at 220 nm. In steps of 5 nm the absorption cross sections are gathered in Table S2 of the Supporting Information. By comparison with the spectra of the other $CF_3C(O)$ compounds it can be concluded that the shoulder at 220 nm is due to the $n \rightarrow \pi^*$ transition of the $CF_3C(O)$ chromophore and the high-frequency absorption is caused by the peroxide group.

(c) NMR Spectra. In the ^{19}F NMR spectrum of a $CF_3C(O)OOC(O)CF_3$ sample dissolved in $CF_3C(O)OC(O)CF_3$ at -30 °C only one new signal at -73.2 ppm relative to $CFCl_3$ is

Table 3. NMR Data for $CF_3C(O)OOC(O)CF_3$ and Related Compounds

δ/ppm or J/Hz[a]	$[CF_3C(O)]O_x$		$CF_3C(O)O_xH$		
	$x = 1$[b]	$x = 2$[c]	$x = 1$[d]	$x = 2$[d]	$CF_3C(O)OONO_2$[b]
δ_F	−78.0	−73.2	−78.7	−74.9	−73.9
δ_c (CF_3)	113.8	114.4	115.2	115.0	115.0
δ_c (CO)	150.4	153.8	163.1	159.0	155.4
$^1J_{CF}$	284.0	286.2	282.9	285.2	286.0
$^2J_{CF}$	48.4	46.5	43.6	43.9	45.8

[a] All samples at −30 °C; external $CDCl_3/CFCl_3$ as reference and/or lock. [b] Neat compound. [c] Solution in $[CF_3C(O)]_2O$. [d] Mixture of neat compounds.

observed, which disagrees with the literature value of −61.9 ppm.[17] The coupling constants $^1J_{CF}$ or $^2J_{CF}$ are determined from the ^{13}C satellites to be 286.2 or 46.5 Hz, respectively. The ^{13}C NMR spectrum of the same sample at −30 °C shows two quartets at 114.4 (CF_3) and 153.8 (CO) ppm relative to TMS with the same $^1J_{CF}$ and $^2J_{CF}$ coupling constants as in the ^{19}F NMR spectrum. All NMR data are compared in Table 3 with those of some similar compounds containing the $CF_3C(O)$ group.

(d) Quantum Chemical Calculations. The geometries of syn−syn and syn−anti conformers were optimized with HF, MP2, B3PW91, and B3LYP methods using 6-31G* basis sets. The syn−anti form is predicted to be higher in energy than the syn−syn conformer by 3.6 (B3PW91) to 5.3 kcal/mol (HF). Vibrational frequencies were obtained with the HF, B3PW91, and B3LYP methods (see Supporting Information, Table S1). HF symmetry force constants were used to derive vibrational amplitudes after scaling all stretching and bending constants with a factor of 0.81. The quantum chemical calculations were performed with the GAUSSIAN98 program suite,[20] and vibrational amplitudes were derived with the program ASYM40.[21]

(e) Gas Phase Structure. The experimental radial distribution curve (Figure 4) which was derived by Fourier transformation of the molecular intensities is reproduced very well with a molecular structure possessing syn−syn conformation. The geometric parameters were refined by least-squares fitting of the molecular intensities. In this analysis C_2 overall symmetry, local C_{3v} symmetry for the CF_3 groups, and planarity of the carbonyl groups were assumed. The tilt angle between the C_3 axis of the CF_3 group and the C−C bond direction was constrained to the calculated (MP2) value. Vibrational amplitudes which either cause large correlations between geometric parameters or are poorly determined in the experiment were set to the theoretical values. With these assumptions 12 geometric parameters (p1 to p12) and eight vibrational amplitudes were refined simultaneously. The following correlation coefficients had values larger than |0.7|: p2/p5 = −0.90, p2/p9 = −0.87, p5/p9 = 0.92. Geometric parameters are listed in Table 4 together with the calculated values, and vibrational amplitudes are included as Supporting Information (Table S3).

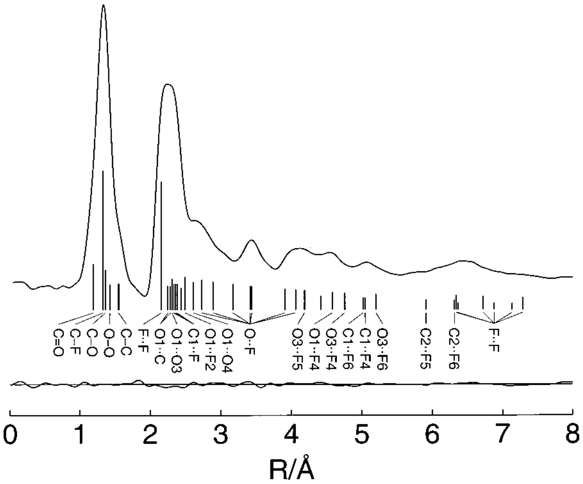

Figure 4. Experimental radial distribution function and difference curve of $CF_3C(O)OOC(O)CF_3$. The positions of interatomic distances are shown by vertical bars.

Table 4. Experimental and Calculated Geometric Parameters

	GED[a]		MP2/6-31G*	B3LYP/6-31G*
O−O	1.426(10)	p1	1.454	1.427
O−C	1.361(12)	p2	1.378	1.366
C=O	1.190(4)	p3	1.201	1.190
C−C	1.547(6)	p4	1.539	1.550
$(C-F)_{mean}$	1.326(3)	p5	1.340	1.333
O−O−C	107.5(11)	p6	109.0	110.5
O−C=O	130.3(12)	p7	127.4	127.2
O−C−C	104.5(12)	p8	106.6	107.1
F−C−F	108.7(4)	p9	109.1	109.1
tilt (CF_3)[b]	0.5[e]		0.5	0.8
$\tau(CF_3)$[c]	−22.8(29)	p10	−4.2	−4.1
ϕ(O−O−C=O)[d]	−11.5(30)	p11	−4.5	−2.0
ϕ(C−O−O−C)	86.5(32)	p12	81.0	86.3

[a] r_a values in angstroms and degrees with 3σ uncertainties. [b] Tilt angle of CF_3 group toward C=O bond. [c] Torsional angle of CF_3 groups around C−C bonds. For τ = 0° one C−F bond eclipses the C=O bond. The negative sign of τ implies that the shortest distances between a fluorine and opposite carbonyl oxygen atoms (F2···O4 and F5···O3) become longer. [d] Torsional angle around O−C bonds. Negative sign of ϕ implies that the O3···O4 distance becomes shorter. [e] Not refined.

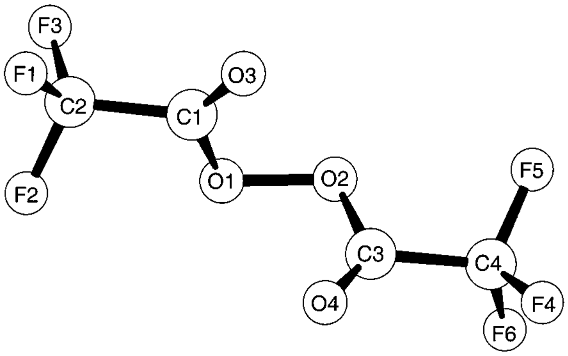

Figure 5. Syn−syn structure of $CF_3C(O)OOC(O)CF_3$ derived from the gas electron diffraction analysis.

The electron diffraction analysis results in a single conformer with a syn−syn structure (Figure 5). This is in agreement with the quantum chemical calculations which predict the syn−anti form to be higher in energy by 3.6 kcal/mol or more. If systematic differences between vibrationally averaged experimental r_a parameters and calculated equilibrium values r_e are neglected, the B3LYP method reproduces all bond distances very well. The MP2 approximation predicts the O−O bond too long by about 0.03 Å and the HF approximation too short by

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(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratman, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Menucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslovski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzales, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzales, C.; Head-Gordon M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN98*, version A6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(21) Hedberg, L.; Mills. I. M. *J. Mol. Spectrosc.* **1993**, *160*, 117.

ca. 0.05 Å. The experimental bond angles are reproduced by all methods to within ±3°. The experimental torsional angles around the O−C bond (ϕ(O−O−C═O)) and around the C−C bond (τ(CF_3)) differ appreciably from the predicted values. These differences, especially in the case of τ(CF_3), are due to large-amplitude torsional vibrations. The frequencies for the two CF_3 torsions are predicted to be 21 and 36 cm^{-1} (HF), 16 and 22 cm^{-1} (B3LYP), or 12 and 12 cm^{-1} (B3PW91). The dihedral angle around the O−O bond (86.5(32)°) is slightly smaller than 90°. Similar values have been observed in bis(fluorocarbonyl) peroxide, FC(O)OOC(O)F, (85.5(14)°)[11] and in the peroxynitrates $FC(O)OONO_2$ (86.2(14)°),[22] $CH_3C(O)OONO_2$ (84.7(13)°),[12] and $CF_3C(O)OONO_2$ (85.8(29)°).[12]

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Supporting Information Available: Tables listing calculated (HF/6-31G*, B3LYP/6-31G*, B3PW91/6-31G*) IR band positions (cm^{-1}) and band intensities (km mol^{-1}) of $CF_3C(O)OOC(O)CF_3$ (S1), UV absorption cross sections of gaseous $CF_3C(O)OOC(O)CF_3$ (S2), and interatomic distances and experimental and calculated vibrational amplitudes of $CF_3C(O)OOC(O)CF_3$ (S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Scheffler, D.; Schaper, I.; Willner, H.; Mack, H.-G.; Oberhammer, H. *Inorg. Chem.* **1997**, *36*, 339.