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Stucture and Conformational Properties of Bis(trifluoromethyl) Peroxydicarbonate, $CF_3OC(O)O{-}OC(O)OCF_3$

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The molecular structure of free bis(trifluoromethyl) peroxydicarbonate, $CF_3OC(O)O{-}OC(O)OCF_3$, was investigated by the concerted use of gas electron diffraction and theoretical calculations of various quantities (geometry, energy, vibrational frequencies, ^{13}C NMR chemical shifts). This combined approach justified the assumption that the syn−syn−syn−syn structure with C_2 overall symmetry (both CF_3 groups synperiplanar to the respective C═O bonds and both C═O bonds synperiplanar to the O−O bond) is the only observable conformer in the vapor of the title compound. The molecule possesses a skew structure with a dihedral angle of $\tau(C{-}O{-}O{-}C) = 87.1(21)°$. This narrow angle and the short O−O bond, 1.403(19) Å, are reproduced satisfactorily by a DFT method.

Introduction

Peroxides of the general formula XOOY have attracted considerable interest in chemistry for a long period of time. Some of them have been found to play an important role in the chemistry of the atmosphere, in particular those with X = FC(O), CF_3, $CH_3C(O)$, $CF_3C(O)$ and Y = NO_2. With respect to such importance of this class of compounds, their structural studies have been undertaken. Thus, the molecular structure of fluorocarbonyl peroxynitrate, $FC(O)O{-}ONO_2$ was determined by gas-phase electron diffraction (GED) and ab initio calculations.[1] The other components comprising photochemical smog, acetyl peroxynitrate, $CH_3C(O)O{-}ONO_2$, and trifluoroacetyl peroxynitrate $CF_3C(O)O{-}ONO_2$, were also investigated in the gaseous phase.[2] The most interesting feature in the structures of peroxides in general is the dihedral angle $\tau(XO{-}OY)$. Interestingly, this parameter was determined to be smaller than 90° for the above three peroxides [86.2(14)°, 84.7(13)°, and 85.8(29)°, respectively]. In contrast, τ (XO−OY) in a further atmospheric peroxide, $CF_3O{-}ONO_2$, is larger than 90°, i.e., 105.1(16)°, as determined by GED.[3] In summary, the torsional angle of interest in the four peroxynitrates tends to be smaller than the effective value for the parent compound HOOH [120.0(5)°].[4] However, in the majority of peroxides so far studied in which X = Y, the XO−OX dihedral angle exceeds the value reported for HOOH. For example, in the gas phase, this angle amounts to 123(4)° and 135(5)° for CF_3OOCF_3[5] and CH_3OOCH_3,[6] respectively. Some peroxides of the XOOX type, such as FOOF, do not meet these observations and exhibit quite unusual structures in the same manner as noticed in the above peroxynitrates that contain the carbonyl group, i.e., $\tau(XO{-}OX) \leq 90°$. For difluoroperoxide[7] a dihedral angle of 88.1(4)° was derived from a joint analysis of GED data and rotational constants. The gauche orientation of the fluorine atoms was qualitatively ascribed to the anomeric effect.[8] The molecular structures of bis(fluorocarbonyl) peroxide,[9] FC(O)OOC(O)F, and bis(trifluoroacetyl) peroxide,[10] $CF_3C(O)OOC(O)CF_3$, revealed the CO−OC dihedral angle to be 83.5(14)° and 86.5(32)°, respectively. For the last two compounds only the syn−syn conformation (both C═O bonds synperiplanar to the O−O bond) was observed.

In the context of computational examinations of peroxides, various types of calculations were applied to difluoroperoxide by Scuseria in order to reproduce the corresponding experimental data with high accuracy.[11] This system is small enough to utilize a coupled cluster or quadratic CI calculation and the efficacy of such extensive computations was unambiguously demonstrated. In contrast, the MP2 approximation with standard basis sets does not reproduce the experimental structure in this case. On the other hand, a three-hybrid functional, B3LYP, with 6-31+G* and 6-311+G* basis sets proved to perform as well as the CCSD calculations. Similarly, the MP2 calculations on $CH_3C(O)OONO_2$ and $CF_3C(O)OONO_2$ deviate from the corresponding electron diffraction and B3PW91/6-311+G* geometries, mainly by underestimating the CO−OC dihedral angle. The same trend was observed for $CF_3C(O)OOC(O)CF_3$ where the DFT calculations turned out to be superior to those carried out at a correlated level (MP2). Very recently, a further peroxide containing only O, C, and F, $CF_3OC(O)OOC(O)OCF_3$, was synthesized.[12] This novel peroxide promised to be an interesting target to be tackled. To get a deeper insight into the structural chemistry of peroxides, we have undertaken the structural study of the gaseous bis(trifluoromethyl) peroxydicarbonate, $CF_3OC(O)OOC(O)OCF_3$, **1**, taking into account previous results for

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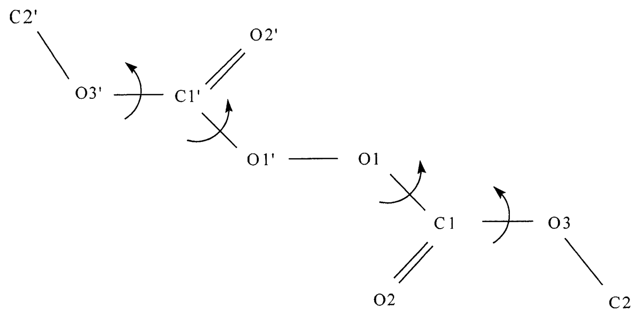
SCHEME 1



peroxides and carbonates. The combined method of GED together with ab initio and DFT calculations of geometries, vibrational frequencies, and ^{13}C NMR chemical shifts was employed.

Results and Discussion

Selection of the Conformers. For the purpose of the selection of the possible conformers that might constitute the vapor of **1**, quantum chemical calculations were performed using the Gaussian94[13] (in Prague) and Gaussian98[14] (in Tübingen) program packages. The C_2 symmetry derived for the syn−syn conformer of $CF_3C(O)OOC(O)CF_3$ prompted us to assume the same point group for **1**. Note that there are four O−C(O) bonds in **1** (Scheme 1, for atomic numbering see also Figure 3). The conformer shown in Scheme 1, in which both terminal O3−C2 and O3′-C2′ bonds are synperiplanar to the C═O bonds and both C═O bonds are synperiplanar to the central O−O bond and which possesses C_2-symmetry, is denoted as syn−syn−syn−syn, **1a**. At first, a *relaxed* potential-energy surface scan of the C1′−O1′−O1−C1 dihedral angle (Scheme 1) of this most probable form was performed in a region of dihedral angles 0−180° at the RHF/6-311+G* level, with an increment of 10°. These calculations revealed the minimum to be at an angle of 90° (Figure 1). Final optimizations included also this angle and were performed at various levels of theory (RHF, MP2, B3LYP) with different basis sets (6-31G*, 6-311+G*). Frequency calculations (RHF/6-311+G*, B3LYP/6-31G*) determined the nature of the stationary point. The form with an overall symmetry of C_2 was characterized by no imaginary frequency (NIMAG=0). As pointed out for FC(O)OOC(O)F and $CF_3C(O)OOC(O)CF_3$, the presence of two O−C(O) bonds in these compounds requires considering other conformers with lower symmetry. In **1**, the four torsional angles O2−C1−O3−C2, O1′−O1−C1−O2, O1−O1′−C1′−O2′, and O2′−C1′−O3′−C2′ (Scheme 1), each of which can assume synperiplanar (syn) or antiperiplanar (anti) orientations, result in 16 possible forms. As mentioned in the Introduction, only the syn orientation of the C═O bond with respect to O−O was observed in peroxides containing carbonyl groups.[1−3,9,10] Furthermore, gas-phase studies of compounds containing the $CF_3OC(O)$ moiety such as $CF_3OC(O)F$[15] and $(CF_3O)_2CO$[15] revealed that in these compounds the syn orientation of the CF_3 groups with respect to the C═O double bond is strongly favored. Consequently, these observations further support the idea that the all syn arrangements, **1a**, are preferred in **1**. Only such additional forms were examined that contain only one anti arrangement, i.e., syn−anti−syn−syn, **1b**, and anti−syn−syn−syn, **1c**, both of them having multiplicity 2. The optimizations of these two alternatives started again at RHF/6-311+G*, **1a** providing the starting value of 41 variables computed at the same level with the exception of the torsional angle which is responsible for reducing symmetry from C_2 to C_1. Hence, 180° instead of −4.6° [τ(O1′−O1−C1−O2)] and −2.2° [τ(O2−C1−O3−C2)] for **1b** and **1c**, respectively, served as an initial value in both optimizations. Similarly, a second derivative analysis at the same level revealed **1b** and **1c** to be minima on the respective potential energy hypersurface. Final optimizations of **1b** and **1c** were performed at B3LYP/6-31G* for the reasons outlined above. The dihedral angles of interest together with r(O1−O1′) and relative energies for **1a**, **1b**, and **1c** are summarized in Table 1.

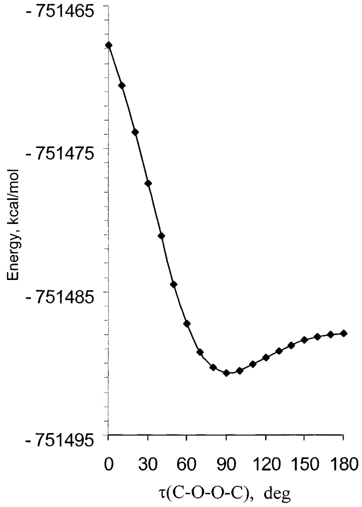


Figure 1. Results of the relaxed potential energy scan of the C1−O1−O1′−C1′ dihedral angle.

According to the IR Ar-matrix spectra of **1**, there are only two characteristic C═O stretching vibrations at 1884 and 1857 cm^{-1}.[12,16] The calculated values at B3LYP/6-31G* (after scaling by 0.9613)[17] for **1a**, 1869 and 1842 cm^{-1}, show good agreement with the experimental frequencies, and the experimental frequency difference of 27 cm^{-1} is reproduced exactly by the calculation. If the gas was heated to 450 K before deposition in the argon matrix, two additional ν(CO) bands were observed at 1895 and 1867 cm^{-1}.[16] These might be assigned to either of the two additional isomers considered. On the basis of the estimated ratio 8:1 (**1a**:**1b** or **1c**) for the high-temperature sample, the population of either **1b** or **1c** would be about 3% at room temperature. The calculated C═O-stretching frequencies (B3LYP/6-31G*, scale factor 0.9613) are 1850 and 1846 cm^{-1} for **1b** and 1879 and 1848 cm^{-1} for **1c**. The experimental frequency difference of 28 cm^{-1} is much closer to the corresponding theoretical value of the anti−syn−syn−syn conformer **1c** (31 cm^{-1}) than to that for the syn−anti−syn−syn conformer **1b** (4 cm^{-1}), but an unambiguous assignment of these two bands to either **1b** or **1c** is not possible based solely on the vibrational spectra. The predicted relative energy (B3LYP/6-31G*) of the **1c** form (2.78 kcal/mol) is higher than that of **1b** (1.45 kcal/mol). The ^{13}C NMR spectra of **1** were recorded at −30 °C and only two signals were detected and unambiguously assigned.[12] If the population of any C_1-symmetrical isomer were significant, this could only be observed at lower temperatures, since at −30 °C the exchange between these conformers (rotation around C−O bonds) is expected to occur at a rate that is fast on the NMR time scale. The computed ^{13}C NMR chemical spectra for **1b** and **1c** at a SCF level using the GIAO (gauge-invariant atomic orbitals) method incorporated in the Gaussian, with a II Huzinaga basis set[18] (well-designed for magnetic properties calculations), exhibit four signals although the splitting of the δ(C1,C1′) and δ(C2,C2′) doublets, measured and calculated for **1a**, into δ(C1), δ(C1′) and δ(C2), δ(C1′) are quite small (see

TABLE 1: Dihedral Angles (deg), *r*(O1−O1′) (Å), and Relative Energies Δ*E* (kcal/mol) for 1a, 1b, and 1c of $CF_3OC(O)OOC(O)OCF_3$[a]

1a

	syn						
	τ(O2C1O3C2)	τ(O1′O1C1O2)	τ(O1O1′C1′O2′)	τ(O2′C1′O3′C2′)	*r*(O1−O1′)	τ(C1O1O1′C1′)	Δ*E*
RHF/6-31G*	−2.2	−4.6	−4.6	−2.2	1.357	90.7	
MP2/6-31G*	−1.8	−3.9	−3.9	−1.8	1.446	82.5	
MP2/6-311+G*	−2.0	−4.0	−4.0	−2.0	1.427	83.5	
B3LYP/6-31G*	−2.0	−4.9	−4.9	−2.0	1.428	87.8	0.00

1b

	syn	anti	syn				
	τ(O2C1O3C2)	τ(O1′O1C1O2)	τ(O1O1′C1′O2′)	τ(O2′C1′O3′C2′)	*r*(O1−O1′)	τ(C1O1O1′C1′)	Δ*E*
B3LYP/6-31G*	0.8	176.3	−8.8	−3.1	1.443	89.5	1.45

1c

	anti	syn					
	τ(O2C1O3C2)	τ(O1′O1C1O2)	τ(O1O1′C1′O2′)	τ(O2′C1′O3′C2′)	*r*(O1−O1′)	τ(C1O1O1′C1′)	Δ*E*
B3LYP/6-31G*	174.4	−5.7	−4.0	−1.2	1.429	87.4	2.78

[a] For atom numbering see Scheme 1.

TABLE 2: GIAO-SCF Results for 1a, 1b, and 1c of $CF_3OC(O)OOC(O)OCF_3$

	δ(^{13}C),[a] ppm			
level of theory/basis set// geometry	C1	C1′	C2	C2′
1a				
GIAO-SCF/II//B3LYP/6-31G*	153.3	153.3	113.2	113.2
GIAO-SCF/II//B3LYP/6-311+G*	153.8	153.8	113.0	113.0
GIAO-SCF/II//MP2(fc)/6-31G*	155.6	155.6	113.6	113.6
GIAO-SCF/II//MP2(fc)/6-311+G*	152.8	152.8	112.0	112.0
GIAO-SCF/II//GED	149.7	149.7	119.9	199.9
1b				
GIAO-SCF/II//B3LYP/6-31G*	151.1	153.8	113.3	113.2
1c				
GIAO-SCF/II//B3LYP/6-31G*	149.5	152.9	112.9	113.2
exptl ($CDCl_3/CFCl_3$)[b]	145.7	145.7	119.9	119.9

[a] Relative to $Si(CH_3)_4$. [b] From ref 12.

Table 2). In conclusion, all theoretical calculations and the IR Ar-matrix spectra provide a good basis for assuming that in the gas phase of **1** the conformer **1a** is predominant with a possible very small contribution of **1b** or **1c**, which would not be observable in the GED experiment.

Molecular Model and Refinement of the Structure. The overall symmetry of the syn−syn−syn−syn form of bis(trifluoromethyl) peroxydicarbonate, $CF_3OC(O)OOC(O)OCF_3$, was thus adopted to be C_2, as revealed by the concerted use of several theoretical and experimental approaches given above. With this fact, the structure of **1** was described with 17 independent geometrical parameters p_1 to p_{17} (see Table 3). These included two mean bond lengths, two actual bond lengths, one mean bond angle, four actual bond angles, four dihedral angles, and three bond length differences. To complete the molecular description, the local C_3 axes of the CF_3 groups were allowed to deviate from the direction of the O3−C2 and O3′−C2′ bonds by a tilt angle. The parameters derived at various theoretical levels are also shown in Table 3 for comparison. Refinements were performed by least-squares fitting of the molecular intensities (Figure 2). The intensities were modified with a diagonal weight matrix, and known scattering factors were used.[19] The number of refined parameters was gradually increased, until eventually 11 geometrical parameters were included in the refinement scheme. Those parameters that could not be refined (e.g., p_{11} tends to be too large, 191.1°) were set

TABLE 3: Molecular Parameters (*r*/Å or ∠/deg) of $CF_3OC(O)OOC(O)OCF_3$ (Conformer 1a, C_2 Symmetry)

parameter	definition	GED[a]	RHF/X[h]	MP2/Y[i]	MP2/X[h]	B3LYP/Y[i]	B3LYP/X[h]
p_1	[*r*(C2−F1) + 2 × *r*(C2−F2)]/3	1.317(3)	1.299	1.331	1.324	1.329	1.329
p_2	[*r*(C2−O3) + *r*(C1−O3) + *r*(C1−O1)]/3	1.370(5)	1.345	1.380	1.374	1.380	1.376
p_3	*r*(C1−O2)	1.177(4)	1.160	1.197	1.188	1.187	1.181
p_4	*r*(O1−O1′)	1.403(19)	1.357	1.446	1.427	1.428	1.424
p_5	∠(O3−C2−F)$_{mean}$	109.3(4)	109.7	109.5	109.6	109.4	109.7
p_6	∠(C1−O3−C2)	117.3(14)	119.9	116.1	116.5	117.5	118.5
p_7	∠(O1−C1−O3)	102.2(5)	104.5	102.2	102.4	103.0	102.8
p_8	∠(O1−C1−O2)	127.4(22)	127.0	128.2	128.0	127.7	127.8
p_9	∠(O1′−O1−C1)	110.2(13)	111.4	107.6	108.2	108.8	109.3
p_{10}	∠(CF_3−O3 tilt)[c]	3.6[b]	3.4	3.7	3.7	3.7	3.6
p_{11}	τ(C1−O3−C2−F1)[d]	−179.5[b]	−179.5	−179.5	−179.3	−179.8	−179.5
p_{12}	τ(O2−C1−O3−C2)[e]	−3.0[b]	−2.2	−1.8	−2.0	−2.0	−3.0
p_{13}	τ(O1′−O1−C1−O2)[f]	−7.8(42)	−4.6	−3.9	−4.0	−4.9	−5.6
p_{14}	τ(C1−O1−O1′−C1′)[g]	87.1(27)	90.7	82.5	83.5	87.8	90.6
p_{15}	*r*(C2−F1) − *r*(C2−F2)	−0.005[b]	−0.003	−0.005	−0.006	−0.005	−0.005
p_{16}	*r*(C2−O3) − *r*(C1−O3)	0.031[b]	0.037	0.030	0.029	0.037	0.031
p_{17}	*r*(C2−O3) − *r*(C1−O1)	0.014[b]	0.002	0.012	0.012	0.017	0.014

[a] r_a values, uncertainties are 3σ values. For atom numbering see Scheme 1 and Figure 3. [b] Fixed at the B3LYP/6-311+G* value. [c] Tilt angle between the C_3 axes of the CF_3 groups and the direction of the O−C bonds away from the C=O bond. [d] Taken to be negative for counterclockwise rotations of the CF_3 group when viewing from O3 to C2. [e] Taken to be negative for counterclockwise rotations of the (O3)−C2F$_3$ group when viewing from C1 to O3. [f] Taken to be negative for counterclockwise rotations of the (O1)−O2C1O3C2F$_3$ fragment when viewing from O1 to C1. [g] Taken to be positive for counterclockwise rotations of the (O1′)−O1O2C1O3C2F$_3$ fragment when viewing from O1′ to O1. [h] 6-311+G*. [i] 6-31G*.

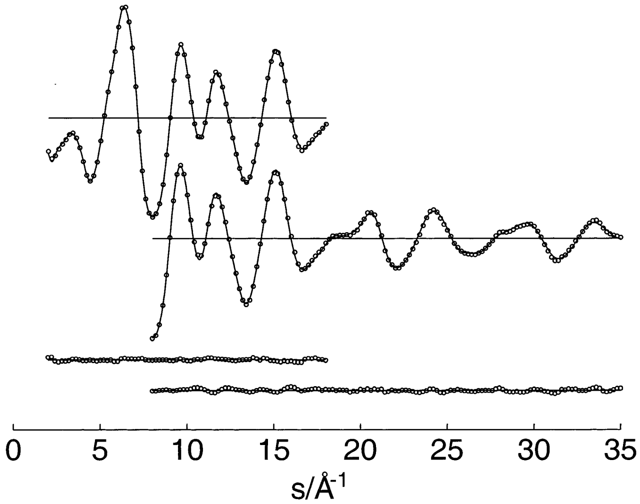


Figure 2. Experimental (dots) and calculated (full line) moloecular intensities and differences for **1**.

TABLE 4: Interatomic Distances and Experimental and Calculated (B3LYP/6-31G*) Vibrational Amplitudes for $CF_3OC(O)OOC(O)OCF_3$[a]

atom pair	distance	ampl (GED)		ampl (B3LYP)
C=O	1.177	0.037[b]		0.037
C2−F1	1.314	0.045[b]		0.045
C2−F2	1.319	0.045[b]		0.045
C1−O3	1.354	0.046[b]		0.046
C1−O1	1.372	0.048[b]		0.048
C2−O3	1.384	0.049[b]		0.049
O1−O1′	1.403	0.048[b]		0.048
O1···O3	2.122	0.057(4)	l_1	0.058
O3···F1	2.151	0.057(4)	l_1	0.058
F···F	2.152−2.156	0.057(4)	l_1	0.057[c]
C···C	2.338	0.063[b]		0.063
O···X[d]	2.229−2.299	0.057[b]		0.057[c]
O1′···O2	2.602	0.092[b]		0.092
C···Y[e]	2.767−2.944	0.115[b]		0.115[c]
O···Y[e]	2.851−3.331	0.150(27)	l_2	0.213[c]
O1···O3′	3.396	0.072(8)	l_3	0.062[c]
C···Z[f]	3.416−3.435	0.072(8)	l_3	0.063[c]
O···Y[e]	3.940−4.247	0.132(16)	l_4	0.156[c]
O···Y[e]	4.591−5.240	0.255(46)	l_5	0.277[c]
C···X[d]	5.126−5.220	0.255(46)	l_5	0.240[c]
O···F	5.546−6.000	0.302[b]		0.302[c]
F···Y[e]	6.040−7.352	0.249(8)	l_6	0.295[c]
F···X[d]	7.747−9.412	0.366[b]		0.366[c]

[a] Values in Å, uncertainties are 3σ values. For atom numbering see Scheme 1 or Figure 3. [b] Fixed at the B3LYP/6-31G* value. [c] Meam values are given for the amplitudes that are not unique. [d] X = F or C. [e] Y = F, C, or O. [f] Z = F or O.

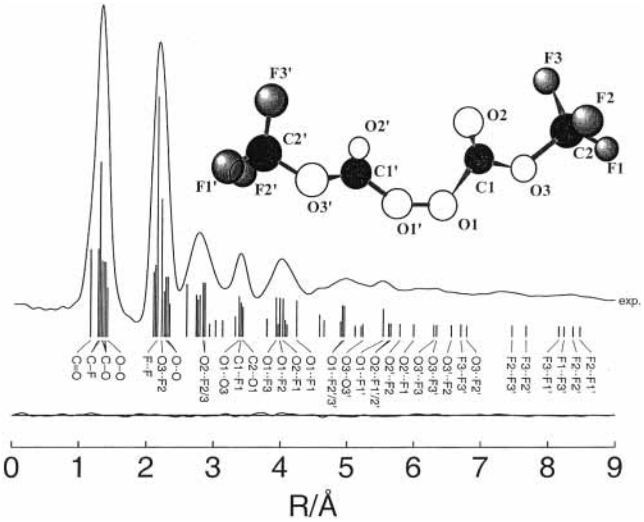


Figure 3. Experimental radial distribution function and difference curve for **1**. The positions of important interatomic distances are shown by vertical bars. Molecular model of **1** in the optimum refinement of the electron diffraction data constrained by some B3LYP/6-311+G* differences also showing the atomic numbering of the most predominant conformer **1a**.

to the corresponding B3LYP/6-311+G* values. In the final stage six amplitudes of vibrations or tied groups were refined simultaneously (Table 4) with these 11 geometrical parameters. Although l_2 is correlated with p_6 and p_8 rather strongly (correlation coefficients are 0.87 and 0.81, respectively), fixing this vibrational parameter leads to a small value of p_{14} (close to the two MP2 values that were shown to be too small in similar compounds) complemented by opening of p_6. The fit became worse under this refinement condition. Amplitudes that were not refined were fixed at values calculated with the program ASYM40,[20] using a B3LYP/6-31G* force field. The following additional correlation coefficients had values larger than |0.7|: $p_1/p_2 = -0.89$, $p_2/p_4 = -0.85$, $p_6/p_8 = -0.95$, $p_8/p_9 = -0.86$, and $p_1/l_1 = -0.79$. Radial distribution curves were obtained by Fourier transformation of the molecular intensities (Figure 3). The experimental radial distribution curve is relatively rich in structural information, each feature encompassing several contributions. No problems were encountered fitting the peaks due to nonbonded distances that depend on the C1−O1−O1′−C1′ dihedral angle, p_{14}. The success of the analysis may be gauged on the basis of the difference between the experimental and calculated radial distribution curve (Figure 3). Figure 2 offers a similar comparison between the experimental and calculated molecular scattering curves. The agreement factors for intensities of the long and short nozzle-to-plate distances were $R_{50} = 2.2\%$ and $R_{25} = 4.9\%$. The final results of the GED refinement are summarized together with the calculated values in Tables 3 and 4. If fixed geometric parameters were varied within the range of the various computational methods, refined parameters changed by less than the respective standard deviations. Thus, the uncertainties given in Tables 3 and 4, which are 3σ values are reasonable estimates of the error limits.

Conclusions

The most striking features in the structural chemistry of peroxides, XOOY, are the O−O bond length and the XO−OY dihedral angle. All other geometric parameters are of minor interest, and their values are close to those in related molecules. As mentioned in the Introduction, the experimentally established XO−OY dihedral angles are subject to a considerable variation, their effective values ranging from 81(1)°, determined for ClOOCl,[21] to 166(3)°, determined for $(CH_3)_3COOC(CH_3)_3$.[22] It has been shown how sensitive calculated values for these two parameters are toward the computational methods. On one hand, with the exceptions of these two parameters of interest, the structures **1a** obtained by the B3LYP and MP2 methods do not differ appreciably. On the other hand, inspection of Table 3 demonstrates that only the DFT method reproduces the O−O bond distance (p_4) and the CO−OC dihedral angle (p_{14}) correctly. **1** thus expands the family of peroxides in which the XO−OY dihedral angle is smaller than 90° (87.1(27)°), an inherent phenomenon noticed in peroxides with two sp^2-hybridized substituents.[1,2,9,10] In the present case, C1 and C1′ are $sp^{2.38}$-hybridized, as revealed by a natural bond orbital (NBO) analysis[23] carried out at B3LYP/6-311+G* with geometry optimized at the same level. Whereas the RHF/6-311+G* bond angles do not differ significantly from those computed at MP2 and DFT as well as from the GED values, the calculated bond lengths exhibit a much larger dependence on the computational method. For example, the O−O bond length at this level, 1.357 Å, is appreciably shorter than $r_a = 1.403(19)$ Å and r_e computed at the DFT level (1.424 Å, B3LYP/6-31G*). The O−O bond length in **1** is shorter than those in peroxides with electropositive substituents (1.464 Å in HOOH,[24] 1.457(12) Å in CH_3OOCH_3 [6]) and it is indistinguishable from those in peroxides with sp[2]-hybridized substituents, such as FC(O)O−OC(O)F (1.419(9) Å),[9] $CF_3C(O)O{-}OC(O)CF_3$ (1.426(10) Å),[10] $FC(O)O{-}ONO_2$ (1.420(6) Å),[1] or $CF_3C(O)O{-}ONO_2$ (1.408(8) Å).[2]

We have made an attempt to rationalize why τ(C(O)O−OC(O)) is about 90° or smaller on the basis of the NBO analysis. The weak stabilizing orbital interaction between the p-shaped lone pair on the peroxide oxygen with the σ^* orbital of the opposite O−C(O) bond (1.95 kcal/mol) as well as the much stronger interaction between this lone pair and the π^* orbital of the adjacent C═O bond (35.9 kcal/mol) possess their maxima at C(O)O−OC(O) dihedral angles of about 85°. This accounts for dihedral angles in peroxides with RC(O) or NO_2 smaller than 90°, steric repulsions undoubtedly playing an important role.

Finally, the GED geometry was computed to lie only 1.65 kcal/mol higher in energy (B3LYP/6-311+G* single point) than the B3LYP/6-311+G*optimized structure. Such a small "excess energy" indicates a very close agreement between calculated and experimental geometry of compound **1**.

A comparison between calculated (B3LYP/6-31G*) geometries of the nonfluorinated counterpart $CH_3OC(O)O{-}OC(O)OCH_3$ with those of **1** demonstrates that fluorination has a minor effect on the geometry of the peroxide skeleton. The central O−O bond is predicted to be equal (1.428 Å) in both compounds and the O1−C1 bond length (1.381 Å vs 1.384 Å), O1′−O1−C1 angle (109.2° vs 108.8°), and C−O−O−C dihedral angle (85.5° vs 87.8°) change only slightly upon fluorination. A similar result has been observed for acetylperoxynitrate, $CH_3C(O)O{-}ONO_2$, and the fluorinated species $CF_3C(O)O{-}ONO_2$. In these compounds the experimental O−O bond lengths (1.418(12) Å vs 1.408(8) Å) and dihedral angles (84.7(13)° vs 85.8(29)°) are equal within their experimental uncertainties.[2]

Experimental Section

The compound was synthesized and purified as described in ref 12. A sample was transported to Tübingen at liquid nitrogen temperature. Electron scattering intensities for $CF_3OC(O)O{-}OC(O)OCF_3$ were recorded on Kodak electron image plates using the KDG2-Diffraktograph[25] at the University of Tübingen, operating at approximately 60 kV, at two nozzle-to-plate distances (25 and 50 cm). The sample was kept at −8 °C, and the inlet nozzle was at room temperature during the experiments. Scattering data for ZnO were recorded simultaneously and used to calibrate the electron wavelength (0.04878(1) Å for long and 0.04886(1) Å for short nozzle to plate distances). Data were obtained in digital form using a modified ELSCAN E−2500 microdensitometer.[26] Two photographic plates for each nozzle-to-plate distance were analyzed by the usual procedures.[27] Averaged molecular intensities in the s-ranges 2−18 and 8−35 A^{-1} [$s = (4\pi/\lambda)\sin\theta/2$, λ = electron wavelength, θ = scattering angle] are shown in Figure 2.

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