Gas-Phase Structures of Acetyl Peroxynitrate and Trifluoroacetyl Peroxynitrate

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The molecular structures and conformational properties of acetyl peroxynitrate (PAN, $CH_3C(O)OONO_2$) and trifluoroacetyl peroxynitrate (FPAN, $CF_3C(O)OONO_2$) were investigated in the gas phase by electron diffraction (GED), microwave spectroscopy (MW), and quantum chemical methods (HF/3-21G, HF/6-31G*, MP2/6-31G*, B3PW91/6-31G*, and B3PW91/6-311+G*). All experimental and theoretical methods show the syn conformer (C═O bond of acetyl group syn to O−O bond) to be strongly predominant relative to the anti conformer. The $O-NO_2$ bonds are extremely long, 1.492(7) Å in PAN and 1.526(10) Å in FPAN, which correlates with their low bond energy and the easy formation of $CX_3C(O)OO^•$ and $^•NO_2$ radicals in the atmosphere. The O−O bonds (1.418(12) Å in PAN and 1.408(8) Å in FPAN) are shorter than that in hydrogen peroxide (1.464 Å). In both compounds the C−O−O−N dihedral angle is close to 85°.

Introduction

Besides ozone, acetyl peroxynitrate, $CH_3C(O)OONO_2$ (peroxyacetyl nitrate, PAN), is the most abundant photooxidant component in the atmosphere, especially in summer smog. It is formed in oxidative degradation of many organic compounds. It can cause eye and throat irritation and plant damages and reacts with biologically important substances, such as enzymes.[1] Extensive field measurements have shown that PAN is ubiquitious in the atmosphere and that its concentrations can exceed those of NO_x in clean tropospheric conditions.[2] Halogenated acetyl peroxynitrates, such as trifluoroacetyl peroxynitrate ($CF_3C(O)OONO_2$, FPAN), have been detected in the atmosphere only in recent years. It is formed from chlorofluorocarbon (CFC) replacements, such as HFC-143 (CH_3CF_3), which contain a CF_3C moiety that may convert into $CF_3C(O)OO^•$ radicals.[3,4] This peroxyradical can react with NO_2 to form FPAN.[3,5] Both peroxynitrates, PAN and FPAN, are important reservoir species for $CX_3C(O)OO^•$ radicals and provide a mechanism for NO_2 transport.[2] Because of the importance of these substances in atmospheric chemistry, properties such as chemical stability, UV absorption cross sections,[6,7] IR,[7,8] and NMR spectra[7] have been reported. The chemical stability is characterized by the low $CX_3C(O)OO-NO_2$ bond energies of 28(1) kcal mol^{-1}.[3,9] In the present study we report a structure investigation of PAN and FPAN by gas electron diffraction (GED), microwave spectroscopy, and quantum chemical calculations.

Chart 1

PAN and FPAN can exist in two conformeric forms, with the acetyl C═O bond syn or anti with respect to the peroxide O−O bond (Chart 1). Spectroscopic investigations of PAN (IR (gas), Raman (liquid), IR (matrix), and ^1H NMR) demonstrated the presence of essentially a single conformer, with a contribution of about 1% of a second form, according to NMR data.[7] However, for FPAN there was no indication of a second conformer.[7] Also, in GED experiments it is difficult to detect small contributions of a second conformer. Various quantum chemical calculations (see below) predict energy differences larger than 2.7 kcal mol^{-1} between syn and anti forms for both PAN and FPAN and thus are in agreement with the spectroscopic observations.[7,8] To obtain additional spectroscopic data for air monitoring and unambiguous information about the conformational properties, an (unsuccessful) effort was made to record the microwave spectrum of FPAN at ambient temperatures. Subsequently, only the most stable syn conformer was detected in a supersonic jet using a pulsed nozzle Fourier transform microwave (FTMW) spectrometer.

Experiment

Caution! FPAN and especially PAN are potentially explosive.

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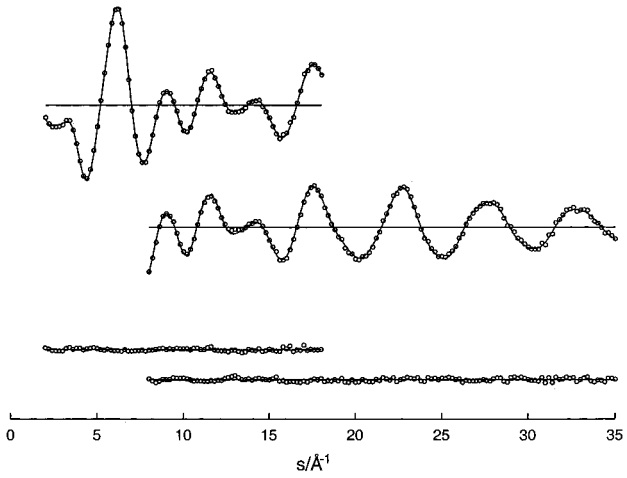

Figure 1. Experimental (dots) and calculated (full line) molecular intensities and differences for PAN.

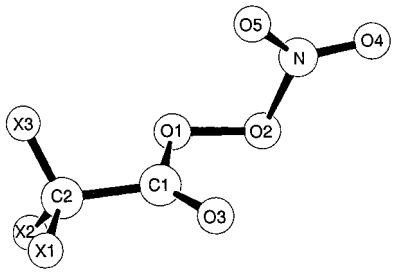

Figure 2. Molecular model for PAN (X = H) and FPAN (X = F) with atom numbering.

PAN and FPAN were synthesized and purified according to the methods described in ref 8. Electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2[10] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of about 60 kV. The sample reservoirs were kept at +8 °C (PAN) and −33 °C (FPAN), and the inlet system and nozzle were at room temperature. The photographic plates were analyzed with the usual methods.[11] Averaged molecular intensities for PAN 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 ($s = (4\pi/\lambda) \sin\theta/2$, λ = electron wavelength, θ = scattering angle). The intensities for FPAN are very similar and are not shown.

The observation of the microwave spectrum of $CF_3C(O)OONO_2$ was first attempted with a Stark spectrometer in Tübingen at ambient temperature. Only transitions due to OCF_2 and NO_2 were detected, however, and flowing the sample through the aluminum waveguide cell or using a glass cell only reduced the intensity of these decomposition products but did not show any new transitions. It was realized that the partition function even in the ground vibrational state was too unfavorable to allow a detection because of the existence of four possible internal rotations around single bonds in $CF_3C(O)OONO_2$.

The rotational spectrum of $CF_3C(O)OONO_2$ was recorded between 8 and 12 GHz with a pulsed nozzle Fourier transform microwave spectrometer in Zürich. The design of the spectrometer, which is similar to that described first by Balle and Flygare,[12] was reported previously.[13] For the initial broadband scans, the gas mixture of approximately 1% $CF_3C(O)OONO_2$ in argon at a pressure of 0.8 bar was introduced via an electromechanical valve perpendicular to the Fabry-Pérot resonator.

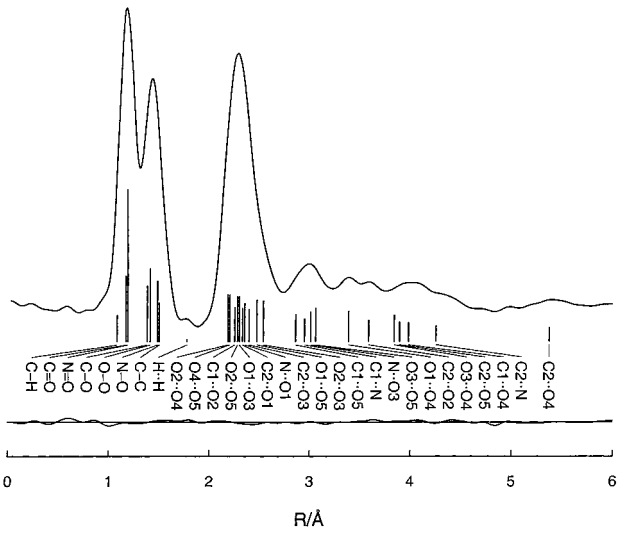

Figure 3. Experimental radial distribution function and difference curve for PAN. The positions of important interatomic distances are shown by vertical bars.

Table 1. Experimental and Calculated Geometric Parameters for $CH_3C(O)OONO_2$ (PAN)

	GED[a]		MP2/ 6-31G*[f]	B3PW91/ 6-311+G*[f]	HF/ 3-21G[f]
	Distances (Å)				
C═O	1.184[b]		1.205	1.188	1.183
$(N═O)_{mean}$	1.193(2)	p_1	1.205	1.184	1.212
C−C	1.505[10][c]		1.499	1.496	1.495
O−C	1.395(12)	p_2	1.402	1.402	1.423
O−N	1.492(7)	p_3	1.543	1.504	1.472
O−O	1.418(12)	p_4	1.424	1.390	1.436
$(C−H)_{mean}$	1.090[b]		1.091	1.091	1.081
	Angles (deg)				
O−C═O	125.7(25)	p_5	123.7	123.2	122.1
O−C−C	107.7(16)	p_6	107.4	107.8	106.4
O═N═O	135.1(56)	p_7	135.1	133.8	132.0
ΔONO[d]	7.2[b]		7.5	7.2	6.3
O−O−C	107.3(13)	p_8	110.1	111.9	111.2
O−O−N	108.6(20)	p_9	107.4	109.8	107.4
H−C−H	109.4[b]		109.4	109.1	109.5
ϕ(O−O−C═O)[e]	−3.0[b]		−3.7	−2.9	−0.6
ϕ(O−O−N═O5)[e]	2.0[b]		0.4	2.0	7.4
ϕ(C−O−O−N)	84.7(13)	p_{10}	80.2	85.7	84.7

[a] r_a values, uncertainties in parentheses are 3σ values and include systematic errors due to constraints (see text). [b] Not refined. [c] Assumed value with estimated uncertainty in brackets. [d] ΔONO = ∠O−N═O5 − ∠O−N═O4. For atom numbering, see Figure 2. [e] Torsion of the $CH_3C(O)$ and NO_2 groups around the O−C and O−N bonds, respectively. Both torsions lead to a decrease of the O3···O5 distance. [f] Mean values are given for parameters that are not unique.

Two separate microwave pulses of 1 μs duration with a peak power of 1 mW were applied to each gas pulse. The polarization decays of the sample molecules were digitized at a rate of 10 MHz for 1024 channels. The data of 600−6000 gas pulses were added in the time domain in order to improve the signal-to-noise ratio. The conventional amplitude spectrum was obtained from the fast Fourier transform of the time domain data. Accurate peak frequencies of selected transitions were determined from the time domain data when the gas was introduced along the resonator axis through one of the mirrors. Higher resolution was achieved with this arrangement.

Structure Analyses

Radial distribution curves (RDF's) were obtained by Fourier transformation of the molecular intensities. Analysis of the RDF's demonstrated that both compounds exist in the syn

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Table 2. Interatomic Distances and Experimental and Calculated (B3PW91/6-31G*) Vibrational Amplitudes for $CH_3C(O)OONO_2$ without Nonbonded Distances Involving Hydrogens[a]

	distance	amplitude (GED)		amplitude (B3PW91)[b]
C−H	1.09	0.076[c]		0.076
C═O	1.18	0.037(2)	l_1	0.036
N═O	1.19	0.037(2)	l_1	0.039
C−O	1.40	0.050[c]		0.00
O−O	1.42	0.045[c]		0.045
N−O	1.49	0.054(10)	l_2	0.049
C−C	1.51	0.052[c]		0.052
O···O	2.21−2.30	0.054(10)	l_2	0.059
O3···C2	2.41	0.054(10)	l_2	0.061
O2···X[d]	2.19−2.28	0.063(12)	l_3	0.061
O1···Y[e]	2.34−2.36	0.063(12)	l_3	0.066
O···O	2.49−2.54	0.093(16)	l_4	0.092
O5···C1	2.89	0.183(22)	l_5	0.178
C1···N	2.96	0.124[c]		0.124
O3··Z[f]	3.00−3.08	0.183(22)	l_5	0.225
O···X[d]	3.40−3.60	0.066(12)	l_6	0.064
O···X[d]	3.80−3.92	0.243[c]		0.243
O4···C1	3.97	0.149(44)	l_7	0.135
C2···Z[f]	4.27−5.37	0.149(44)	l_7	0.135

[a] Values in Å; error limits are 3σ values. For atom numbering, see Figure 2. [b] Mean values are given for amplitudes that are not unique. [c] Not refined. [d] X = C or O. [e] Y = C or N. [f] Z = O or N.

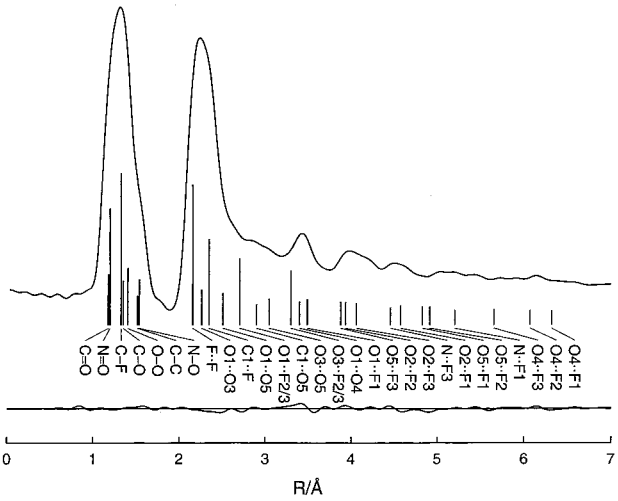

Figure 4. Experimental radial distribution function and difference curve for FPAN. The positions of important interatomic distances are shown by vertical bars.

conformation. Geometric parameters were refined by least-squares fitting of the molecular intensities. The intensities were modified with a diagonal weight matrix. The CH_3 and CF_3 groups were constrained to C_{3v} symmetry and assumed to eclipse the C═O double bond. Because of high correlations between closely spaced bond lengths, it was not possible to refine all of them in the least-squares analyses. In both compounds the C═O and C−C bond lengths were constrained to values in similar compounds, such as $CH_3C(O)F$,[14] $CH_3C(O)Cl$,[15] $CF_3C(O)Cl$,[16] $CF_3C(O)F$,[17] $CF_3C(O)CF_3$,[18] and $CF_3C(O)OH$.[19] Furthermore, the difference between the two O−N═O angles, ΔONO = ∠O−N═O5 − ∠O−N═O4, and the torsional angles for the $CX_3C(O)$, NO_2, and CF_3 groups, ϕ(O−O−C═O), ϕ(O−O−N═O5), and ϕ(O═C−C−F1), were set to an average of theoretical values (see below; for atom numbering see Figure 2). Vibrational amplitudes were set to the calculated values, and only a small number of amplitudes were refined.

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Table 3. Experimental and Calculated Geometric Parameters for $CF_3C(O)OONO_2$ (FPAN)

	GED[a]		MP2/ 6-31G*[f]	B3PW91/ 6-311+G*[f]	HF/ 3-21G[f]
	Distances (Å)				
C═O	1.180[b]		1.201	1.182	1.178
$(N═O)_{mean}$	1.199(3)	p_1	1.201	1.180	1.207
C−C	1.535[10][c]		1.535	1.554	1.516
O−C	1.360[10][c]		1.376	1.370	1.385
O−N	1.526(10)	p_2	1.587	1.529	1.491
O−O	1.408(8)	p_3	1.427	1.393	1.434
$(C−F)_{mean}$	1.328(3)	p_4	1.339	1.332	1.338
O−C═O	126.7(18)	p_5	127.4	127.1	126.0
O−C−C	106.5(18)	p_6	106.8	107.4	106.7
O═N═O	136.0[b]		136.6	135.1	133.4
	Angles (deg)				
ΔONO[d]	7.2[b]		7.1	7.2	6.3
O−O−C	107.6(20)	p_7	109.7	111.6	111.2
O−O−N	109.9(15)	p_8	106.7	109.5	107.1
F−C−F	108.0(3)	p_9	109.0	108.8	109.1
ϕ(O−O−C═O)[e]	−5.2[b]		−5.1	−5.4	−3.7
ϕ(O−O−N═O5)[e]	2.3[b]		1.9	3.6	10.1
ϕ(O═C−C−F1)	179.0[b]		179.0	178.7	177.2
ϕ(C−O−O−N)	85.8(29)	p_{10}	81.0	87.5	86.5

[a] r_a values, uncertainties in parentheses are 3σ values and include systematic errors due to constraints (see text). [b] Not refined. [c] Assumed value with estimated uncertainty in brackets. [d] ΔONO = ∠O−N═O5 − ∠O−N═O4. For atom numbering, see Figure 2. [e] Torsion of the $CF_3C(O)$ and NO_2 groups around the O−C and O−N bonds, respectively. Both torsions lead to a decrease of the O3···O5 distance. [f] Mean values are given for parameters that are not unique.

Table 4. Interatomic Distances and Experimental and Calculated (B3PW91/6-31G*) Vibrational Amplitudes for $CF_3C(O)OONO_2$[a]

	distance	amplitude (GED)		amplitude (B3PW91)[b]
C═O	1.18	0.036[c]		0.036
N═O	1.20	0.037[c]		0.037
C−F	1.33	0.044[c]		0.044
C−O	1.36	0.051(6)	l_1	0.048
O−O	1.41	0.048[c]		0.048
N−O	1.53	0.063		0.063
C−C	1.54	0.051(6)	l_1	0.051
F···F	2.15	0.056[c]		0.056
O···O	2.22−2.31	0.052[c]		0.052
O···X[d]	2.22−2.43	0. 065[c]		0.065
C1···F	2.36	0.073[c]		0.073
O···O	2.52−2.54	0.094[c]		0.094
O3···F1	2.73	0.106[c]		0.106
O1···F	2.71	0.175(73)	l_2	0.227
O···X[d]	2.94−3.11	0.148(67)	l_3	0.225
C1···N	2.99	0.126[c]		0.126
O3···F	3.31	0.281[c]		0.281
O···Y[e]	3.43−3.58	0.092(23)	l_4	0.067
O···Y[e]	3.83−4.02	0.246(72)	l_5	0.249
O··Z[f]	3.98−4.04	0.161(38)	l_6	0.184
C2···N	4.33	0.161(38)	l_6	0.143
N···F3	4.48	0.161(38)	l_6	0.156
O2···F1	4.59	0.076[c]		0.076
O5···F	4.85−4.93	0.399[c]		0.399
N···F	5.05−5.22	0.259[c]		0.259
O4···C2	5.43	0.126[c]		0.126
O4···F	5.67−6.27	0.226[c]		0.226

[a] Values in Å; error limits are 3σ values. For atom numbering see Figure 2. [b] Mean values are given for amplitudes that are not unique. [c] Not refined. [d] X = O, C, or N. [e] Y = O, F, or C. [f] Z = F or C.

Table 5. Observed Rotational Transitions (MHz) in $CF_3C(O)OONO_2$

$J'_{K-K+} \leftarrow$	J''_{K-K+}	F′ ← F″	exptl frequency	exptl − calcd
$2_{2\,0}$	$1_{1\,0}$	2 1	8637.387	0.008
		3 2	8637.400	−0.014
		1 0	8637.424	0.002
$2_{2\,1}$	$1_{1\,1}$	1 0	8638.609	−0.004
		2 1	8638.621	0.002
		3 2	8638.638	0.002
$3_{2\,1}$	$2_{1\,1}$	3 2	9855.648	0.004
		2 1	9855.698	0.000
		4 3	9855.698	0.020
$3_{2\,2}$	$2_{1\,2}$	3 2	9859.334	0.023
		4 3	9859.334	−0.010
		2 1	9859.356	0.003
$4_{2\,2}$	$3_{1\,2}$	4 3	11073.292	−0.006
		5 4	11073.324	−0.002
		3 2	11073.333	−0.005
$4_{2\,3}$	$3_{1\,3}$	3 3	11080.635	0.006
		4 3	11080.651	−0.003
		5 4	11080.668	0.006
		3 2	11080.668	0.002
		4 4	11080.668	−0.013
$5_{1\,4}$	$4_{0\,4}$	6 5	8172.978	−0.001
		4 3	8172.974	0.001
		5 4	8172.978	0.000
$5_{2\,3}$	$4_{1\,3}$	4 3	12290.365	−0.003
		6 5	12290.365	0.004
		5 4	12290.340	0.002
$5_{2\,4}$	$4_{1\,4}$	5 4	12302.576	−0.005
		6 5	12302.576	−0.007
		4 3	12302.587	0.001
$6_{1\,5}$	$5_{0\,5}$	5 4	9396.118	−0.001
		7 6	9396.122	0.002
		6 5	9396.127	−0.000
$7_{1\,6}$	$6_{0\,6}$	6 5	10619.875	−0.000
		8 7	10619.879	0.003
		7 6	10619.885	0.000
$8_{1\,7}$	$7_{0\,7}$	7 6	11844.236	−0.002
		9 8	11844.241	0.002
		8 7	11844.247	−0.001
$9_{0\,9}$	$8_{1\,7}$	9 8	8886.729	−0.000
		10 9	8886.736	−0.002
		8 7	8886.741	0.000
$10_{0\,10}$	$9_{1\,8}$	10 9	10100.574	0.002
		11 10	10100.579	−0.001
		9 8	10100.583	0.000

PAN. The RDF is shown in Figure 3. In addition to the assumptions described above, the C−H bond length and the H−C−H angle were set to the theoretical values. Ten geometric parameters p and seven vibrational amplitudes l (see Tables 1 and 2 for numbering) were refined simultaneously, and the following correlation coefficients had values larger than |0.7|: $p_2/p_4 = -0.79$, $p_5/p_7 = 0.83$, $p_7/p_9 = 0.89$, $p_4/l_2 = 0.73$, and $p_5/l_4 = -0.74$. The final results are listed together with calculated values in Table 1 (geometric parameters) and Table 2 (vibrational amplitudes).

FPAN. For the RDF see Figure 4. In addition to the assumptions described above, the O−C bond length was constrained to 1.360 Å with an estimated uncertainty of ±0.01 Å. This value was chosen on the basis of the theoretical calculations and the experimental value for PAN. The calculations predict this bond in FPAN to be shorter by about 0.03 Å than that in PAN (see Tables 1 and 3). Furthermore, the O═N═O angle was set to a mean theoretical value. Ten geometric parameters p and six vibrational amplitudes l were refined simultaneously, and the following correlation coefficients had values larger than |0.7|: $p_4/p_9 = 0.74$, $p_8/p_{10} = -0.70$, $p_{10}/l_2 = -0.80$, and $l_2/l_3 = 0.83$. The final results are listed together with the calculated values in Table 3 (geometric parameters) and Table 4 (vibrational amplitudes).

Table 6. Rotational, Centrifugal Distortion, and ^{14}N Nuclear Quadrupole Coupling Constants (MHz) and Dipole Moments (D) of $CF_3C(O)OONO_2$

parameter	MW spectra[a]	GED	B3PW91/6-31G*
A	2676.0918(3)	2680.9	2679.9
B	610.3603(1)	596.8	600.2
C	609.1355(1)	592.7	597.3
$\Delta_J \times 10^3$	0.0686(6)		
$\Delta_{JK} \times 10^3$	0.1694(107)		
$\Delta_K \times 10^3$	0.0009(3)		
χ_{aa}	0.151(7)		
χ_{bb}	−0.108(7)		
χ_{cc}	−0.044(7)		

[a] In parentheses is σ in units of the last decimal place.

Table 7. Calculated Energy Differences $\Delta E = E(\text{anti}) - E(\text{syn})$ (kcal mol^{-1}) of the Conformers of the Investigated Peroxynitrates

method	HF/ 3-21G	HF/ 6-31G*	MP2/ 6-31G*	B3PW91/ 6-31G*	B3PW91/ 6-311+G*
PAN	4.8	5.2	3.9	3.2	3.5
FPAN	4.7	5.2	2.7	3.3	4.1

Assignments and Analysis of the Rotational Spectrum. The frequencies of rotational transitions of FPAN were predicted from the moments of inertia that were calculated for the GED structure. The components of the permanent electric dipole moment were expected to have appreciable values mainly in the direction of the c principal axis of the nearly prolate symmetric top. Because of the large moment of inertia of the CF_3 group and the relatively high predicted barrier (1.1 kcal mol^{-1}; see below), internal rotation splittings are neither expected nor observed in the high-resolution spectrum. The first μ_c-type R-branch transitions were readily identified near the predicted positions of the syn conformer. They showed the typical hyperfine splittings from the ^{14}N quadrupole nucleus in FPAN. Finally, 14 transitions were assigned with angular momentum quantum numbers J between 1 and 10. The frequencies of their hyperfine components are listed in Table 5. No transitions were observed near the predicted frequencies of the anti conformer.

Rotational constants, three quartic centrifugal distortion constants and the diagonal quadrupole coupling constants were fitted to the measured transition frequencies using Pickett's program.[20] The results are collected in Table 6. The centrifugal distortion constants are defined in Watson's asymmetric reduction in the prolate I^r representation. The asymmetry parameter κ turned out to be −0.9988, very near the prolate limit of −1.

It was not attempted to combine rotational constants with GED data in the determination of the geometric structure. Since FPAN possesses four torsional vibrations around single bonds (C−C, O−C, O−O, and O−N), it is expected to undergo several large-amplitude motions. In such cases the traditional methods for calculating vibrational corrections ($\Delta r = r_a - r_z$ and $\Delta B^i = B^i_0 - B^i_z$), which are derived for small amplitude vibrations, cannot be applied.

Quantum Chemical Calculations

The geometries of syn and anti conformers for both peroxynitrates were fully optimized with ab initio (HF/3-21G, HF/6-31G*, and MP2/6-31G*) and DFT methods (B3PW91/6-31G* and B3PW91/6-311+G*) using the Gaussian 94 program suite.[21] The calculated energy differences between syn and anti conformers are listed in Table 7. For both compounds the syn form

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Table 8. Experimental Skeletal Geometric Parameters of Peroxides with Electron-Withdrawing Substituents

	O−O (Å)	O−C (Å)	O−N (Å)	O−O−C (deg)	O−O−N (deg)	ϕ(COOX) (deg)
CF_3OOCF_3[a]	1.419(20)	1.399(9)		107.2(12)		123.3(40)
FC(O)OOC(O)F[b]	1.419(9)	1.355(4)		109.4(9)		83.5(14)
$FC(O)OONO_2$[c]	1.420(6)	1.355[10][e]	1.514(6)	107.5(10)	106.7(12)	86.2(14)
CF_3OONO_2[d]	1.414(8)	1.378[12][e]	1.523(7)	107.7(14)	108.4(13)	105.1(16)
$CH_3C(O)OONO_2$	1.418(12)	1.395(12)	1.492(7)	107.3(13)	108.6(20)	84.7(13)
$CF_3C(O)OONO_2$	1.408(8)	1.360[10][e]	1.526(10)	107.6(20)	109.9(15)	85.8(29)

[a] Reference 25. [b] Reference 26. [c] Reference 27. [d] Reference 28. [e] Not refined in GED analysis. Estimated uncertainty is in brackets.

is predicted to be strongly favored. The CH_3 and CF_3 groups adopt eclipsed orientations with respect to the carbonyl C═O bond. The barrier to internal rotation of the CF_3 group in FPAN is predicted to be 1.1 kcal mol^{-1} (B3PW91/6-31G*). Calculated geometric parameters are given together with experimental values in the respective tables. Furthermore, we calculated the vibrational frequencies with the HF/3-21G method. The Cartesian force constants were multiplied with a scale factor of 0.85 except for torsional vibrations, which were not scaled. Vibrational amplitudes were derived from this force field with the program ASYM40.[22] Geometric parameters for the syn conformer of PAN (without dihedral angles), derived with the B3LYP method, have been reported in the literature.[23] When our studies were completed, we learned about recent quantum chemical calculations (MP2 and B3LYP with 6-31G* basis sets) for PAN.[24] In these structure optimizations, however, the O−C and C−C single bond lengths were erroneously set to be equal. Therefore, these results do not correspond to a correct structure optimization and the MP2 values do not agree with ours, neither regarding structural parameters nor energy differences.

Discussion

In the GED experiment for PAN and FPAN and in the microwave spectra for FPAN only, the syn conformer (C═O bond syn to O−O bond) was observed, in agreement with our theoretical calculations. These calculations reproduce all geometric parameters satisfactorily except for the O−N bond length. The HF/3-21G values are slightly too short, and the MP2/6-31G* values are too long by 0.05−0.06 Å. Only the DFT method reproduces these distances correctly.

Table 8 compares skeletal geometric parameters of some peroxides with electron-withdrawing substituents. The atom bonded to the peroxide group is either an sp^3-hybridized carbon atom (CF_3) or an sp^2-hybridized carbon (RC(O)) or nitrogen atom (NO_2). The O−O bond lengths in these compounds vary between 1.41 and 1.42 Å and are considerably shorter than those in peroxides with electropositive substituents (1.464 Å in HOOH,[29] 1.457(12) Å in MeOOMe[30]). The most interesting geometric parameter in the peroxynitrates is the O−N bond length, which correlates with their low thermal stability. These bonds (1.49−1.53 Å) are extremely long compared to those of covalent nitrates with electropositive substituents (1.383(5) Å in Me_3SiONO_2,[31] 1.406(5) Å in $HONO_2$,[32] and 1.402(5) Å in $MeONO_2$ [33]). In some peroxides this bond is even longer than that in $FONO_2$ (1.507(4) Å).[34] The O−N bond in PAN (1.492(7) Å) is remarkably shorter than that in FPAN (1.526(10) Å). This is surprising because the experimental O−N bond energies (28(1) kcal mol^{-1}) are equal within their experimental uncertainties[3,9] and four bonds lie between the H or F and the O−N bond. On the other hand, the experimental trend is reproduced very well by the computational methods, which predict this bond to be 0.02−0.04 Å shorter in PAN than in FPAN (see Tables 1 and 3). The dihedral angles around the O−O bond are smaller than 90° in peroxides with two sp^2-hybridized substituents (RC(O) or NO_2). If both substituents are sp^3-hybridized, the dihedral angle is about 120° (123.3(40)° in CF_3OOCF_3 [25] and 119(4)° in MeOOMe[30]). This angle is intermediate in CF_3OONO_2 (105.1(16)° [28]), which contains one sp^3- and one sp^2-hybridized substituent.

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