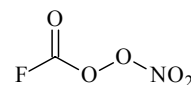


32 **CFNO₅**ED, *ab initio* and DFT calculations**Fluorocarbonyl nitro peroxide**

Fluorocarbonyl peroxyxynitrate

C₁ (*syn*)

r_a	Å ^{a)}	θ_a	deg ^{a)}
O(1)–O(2)	1.420(6)	O(2)–O(1)–C	107.5(10)
O(1)–C	1.355 ^{b)}	O(1)–O(2)–N	106.7(12)
O(2)–N	1.514(6)	O(1)–C=O(3)	128.8 ^{b)}
C=O(3)	1.165 ^{b)}	O(1)–C–F	104.3 ^{b)}
C–F	1.320 ^{b)}	O(2)–N=O (mean)	114.4(6)
N=O	1.192(4)	O(2)–N=O(4) ^{c)}	110.9(8)
		O(2)–N=O(5) ^{c)}	117.9(8)
		$\tau_1(\text{FCO})$ ^{d)}	5.6(43)
		$\tau_2(\text{NO}_2)$ ^{d)}	4.9(9)
		τ_3 ^{e)}	86.2(14)



According to the vibrational and NMR spectra, the molecule exists at room temperature only as a *syn* conformer (O=C–O–O chain is in the *syn* position). The energy of the *anti* conformer was predicted to be 1.8 kcal mol^{–1} higher than that of the *syn* form by HF/3-21G calculations. In ED analysis, FCO(3)O(1) and O(2)NO(4)O(5) groups were assumed to be planar according to results of these calculations.

The nozzle was at room temperature.

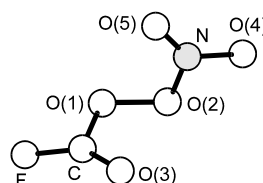
^{a)} Three times the estimated standard errors including a systematic error.

^{b)} Geometric parameters of FC(O)O group were constrained to experimental values for bis(fluorocarbonyl) peroxide, FC(O)–O–O–C(O)F, from the literature.

^{c)} Difference between O(2)–N=O angles was constrained to the mean value from HF/3-21G and LDF/DZP calculations.

^{d)} Torsional angles of the FCO(3) and NO₂ groups around O–C and O–N bonds, respectively; $\tau_{1,2} = 0^\circ$ when the O–O bond is eclipsed with respect to the C=O(3) and N=O(5) bonds, respectively. Both torsions lead to a decrease of the O(3)...O(5) distance.

^{e)} C–O–O–N torsional angle from the *syn* position.



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