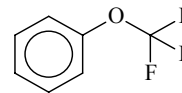


783 C₇H₅F₃OED, MW, vibrational spectroscopy, *ab initio* and DFT calculations**(Trifluoromethoxy)benzene** α,α,α -TrifluoroanisoleC_s assumed (perpendicular conformer, see comment)

r_a	Å ^{a)}	θ_a	deg ^{a)}
C(1)–C(2) ^{b)}	1.393(3)	C–C(1)–C	122.9(10)
C(2)–C(3) ^{b)}	1.398(3)	C–C(4)–C	119.2(14)
C(3)–C(4) ^{b)}	1.398(3)	C(1)–O–C(7)	115.9(6)
O–C(1) ^{b)}	1.390(16)	F–C–F	107.4(8)
O–C(7) ^{b)}	1.334(16)	tilt(CF ₃) ^{c)}	3.2 ^{d)}
C(7)–F(1) ^{b)}	1.327(6)	ϕ^e	3.6 ^{d)}
C(7)–F(2,3) ^{b)}	1.342(6)		
C–H	1.083(11)		



Two independent reports [1,2] were published almost simultaneously. There is an unsettled uncertainty regarding the conformation of the CF₃ group around the C(1)–O bond studied by ED and spectroscopic experiments in the gas phase and by quantum chemical calculations. Nevertheless, predominance of the perpendicular conformer I, with the O–C(7) bond lying in the plane perpendicular to the benzene ring, in the gas phase is unquestionable, as stated below.

The parameters of the frame structure reported in [1] are listed above: the C–H bonds were assumed to bisect the adjacent CCC angle. Differences in the values reported in [2] are generally insignificant. In both ED studies, the nozzle was at room temperature.

The perpendicular conformer I was observed in [1] by ED and MW experiments. Though the presence of a planar conformer II, with the O–C(7) bond lying in the ring plane, could not be excluded in the ED analysis (12(18)%), no evidence of its presence was obtained by MW and matrix IR experiments (<10%). MP2/6-31G* calculations supported this conclusion, predicting that the energy difference was 1.3 kcal mol^{−1}, but B3LYP/6-31G* calculations suggested coexistence of these conformers with only a slight energy difference and a low barrier, 0.27 kcal mol^{−1}, between the two forms.

On the other hand, the ED, IR and Raman experiments in [2] favored a mixture of conformers I (70(21)%) and II (30(21)%) with uncertainty of 3 σ , I being estimated to be *ca.* 0.4 kcal mol^{−1} more stable than II with a barrier of 2.8 kcal mol^{−1}. However, significant discrepancies similar to that mentioned above was reported between the predictions at various levels of theory on the relative stability of these conformers.

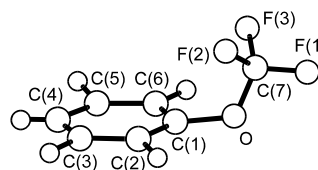
^{a)} Twice the estimated standard errors.

^{b)} Differences in the C–C, O–C and C–F bond lengths were assumed at the values from MP2/6-311G(2d) calculations.

^{c)} Tilt angle between the symmetry axis of the CF₃ group and the O–C(7) bond, towards the oxygen lone pairs.

^{d)} Assumed at the value from MP2/6-311G(2d) calculations.

^{e)} Angle between the O–C(1) bond and the benzene plane.



[1] Federsel, D., Herrmann, A., Christen, D., Sander, S., Willner, H., Oberhammer, H.: J. Mol. Struct. **567-568** (2001) 127.

[2] Shishkov, I.F., Geise, H.J., Van Alsenoy, C., Khristenko, L.V., Vilkov, L.V., Senyavian, V.M., Van der Veken, B., Herrebout, W., Lokshin, B.V., Garkusha, O.G.: J. Mol. Struct. **567-568** (2001) 339.