Supplementary Material

Conformational and vibrational analysis of trifluoroacetyl triflate, $CF_3C(O)OSO_2CF_3$

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Table S1. Geometrical parameters (distances in Å and angles in degrees) for the *syn-anti* and *syn-gauche* conformers of $CF_3C(O)OSO_2CF_3$ calculated with the B3LYP/cc-pvtz approximation.

Geometrical Parameter	*syn-anti*	*syn-gauche*
C1–C2	1.5525	1.5534
C2=O8	1.1836	1.1814
C2–O6	1.3681	1.3768
O6–S7	1.6834	1.6763
S7=O4	1.4335	1.4325
S7=O5	1.4335	1.4316
S7–C3	1.8918	1.8944
C1–F9	1.3259	1.3267
C1–F10	1.3385	1.3384
C1–F11	1.3385	1.3372
C3–F12	1.3264	1.3252
C3–F13	1.3226	1.3214
C3–F14	1.3226	1.3245
F9–C1–F10	109.0	108.9
F9–C1–F11	109.0	109.0
F12–C3–F13	110.1	110.1
F12–C3–F14	110.1	110.1
C1–C2=O8	125.0	124.8
O8=C2–O6	126.7	127.5
C2–O6–S7	119.5	123.7
O6–S7=O4	109.1	110.0
O4=S7=O5	109.1	103.5
O4=S7–C3	108.6	109.4
F9–C1–C2=O8	0.0	–0.2
O8=C2–O6–S7	0.0	–15.7
C2–O6–S7–C3	180.0	83.4
O6–S7–C3–F12	180.0	174.1

Table S2. Cartesian coordinates (in Å) of the *syn-anti* conformer of $CF_3C(O)OSO_2CF_3$ calculated with the B3LYP/cc-pvtz approximation.

Atom	*x*	*y*	*z*
C1	–2.6201	–0.4100	0.0000
C2	–1.4731	0.6362	0.0000
C3	2.2175	–0.7310	0.0000
O4	1.3116	1.4920	1.2665
O5	1.3116	1.4919	–1.2665
O6	–0.2802	–0.0336	0.0000
S7	1.1602	0.8377	0.0000
O8	–1.6256	1.8099	0.0000
F9	–3.7925	0.2091	0.0000
F10	–2.5362	–1.1865	0.0000
F11	–2.5361	–1.1866	–1.0869
F12	3.4825	–0.3323	0.0000
F13	1.9663	–1.4439	1.08540
F14	1.9663	–1.4440	–1.0853
F14	–2.6201	–0.4100	0.0000

Table S3. Cartesian coordinates (in Å) of the *syn-gauche* conformer of $CF_3C(O)OSO_2CF_3$ calculated with the B3LYP/cc-pvtz approximation.

Atom	*x*	*y*	*z*
C1	–2.6496	–0.0928	0.1781
C2	–1.2429	–0.2058	0.4710
C3	2.1070	–0.7068	–0.2007
O4	1.2072	1.1770	1.5552
O5	1.5946	1.8556	–0.8509
O6	–0.3551	0.4714	–0.3344
S7	1.1886	0.9132	0.1473
O8	–1.0066	–0.7913	1.4696
F9	–3.5353	–0.7552	0.5547
F10	–2.6317	–0.6104	–1.4122
F11	–3.0196	1.1899	–0.2559
F12	3.3932	–0.4717	0.0158
F13	1.6775	–1.6635	0.6033
F14	1.9130	–1.0535	–1.4642
F14	–2.6496	–0.0928	0.1781

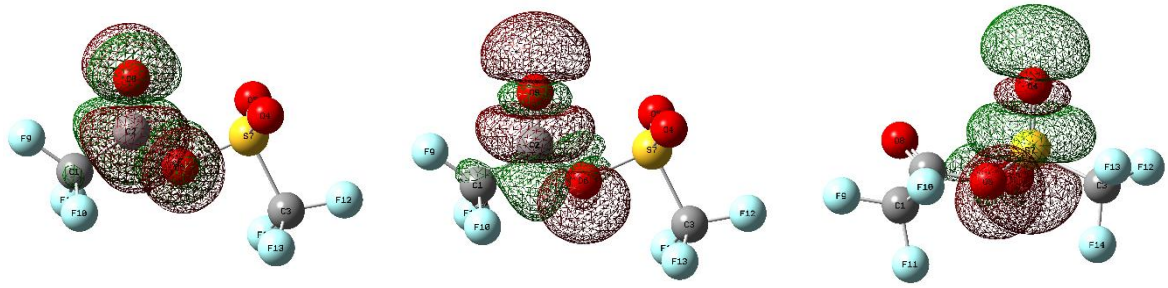
Table S4. Wavenumbers, IR and Raman intensities (I), and tentative assignment, calculated with the B3LYP/cc-pvtz approximation for the *syn-anti* and *syn-gauche* conformers of $CF_3C(O)OSO_2CF_3$.

syn-anti			*syn-gauche*			Tentative assignment[a]
ν (cm^{-1})	**I IR ($Km.mol^{-1}$)**	**I Raman ($Å^4.amu^{-1}$)**	**ν (cm^{-1})**	**I IR ($Km.mol^{-1}$)**	**I Raman ($Å^4.amu^{-1}$)**	
1882	241	9	1892	220	8	ν C=O
1426	220	5	1434	195	6	ν_{as} SO_2
1301	47	3	1293	52	3	ν C−C
1242	224	<1	1242	381	1	ν_{as} CF_3 (−SO_2)
1236	262	3	1234	216	5	ν_{as} CF_3 (−SO_2)
1231	198	3	1231	174	1	ν_{as} CF_3 (−C=O)
1225	170	9	1225	36	11	ν_s SO_2
1179	223	1	1182	260	1	ν_{as} CF_3 (−C=O)
1106	231	6	1106	251	5	ν_s CF_3 (−C=O)
1061	637	<1	1043	592	1	ν C−O
852	97	7	843	38	3	δ OCO
770	3	2	770	7	2	ν_s CF_3 (−SO_2)
765	15	<1	774	41	2	$\delta_{o.o.p.}$ (C=O)
741	55	<1	734	45	<1	δ_s CF_3 (−C=O)
686	291	19	686	271	19	ν S−O
587	62	1	594	120	1	ω SO_2
566	52	3	575	40	2	ν C−S
556	<1	2	554	<1	2	δ CF_3 (−SO_2)
544	5	3	547	3	3	δ CF_3 (−SO_2)
519	8	1	517	3	1	δ CF_3 (−C=O)
489	43	1	487	48	1	δ SO_2
432	8	2	428	<1	1	δ O=S=O
415	1	3	381	3	2	δ C−C=O
325	1	3	335	0	2	δ F−C−C
320	<1	2	314	1	2	ω CF_3 (−SO_2)
300	1	4	284	1	4	δ F−C−C
257	5	4	277	2	4	δ F−C−S
236	1	1	243	3	2	ω CF_3 (−C=O)
186	2	4	200	8	2	δ C−O−S
183	3	<1	180	2	<1	ρ SO_2
159	3	1	149	1	1	δ O–S–C
67	<1	<1	121	<1	<1	τ
64	<1	<1	73	<1	<1	τ
57	<1	<1	34	<1	<1	τ
35	<1	<1	29	<1	<1	τ
19	<1	<1	20	<1	<1	τ

[a] ν stretching; δ deformation; ρ rocking; ω wagging; τ torsion; *as* antisymmetric; *s* symmetric; *o.o.p.* out of plane

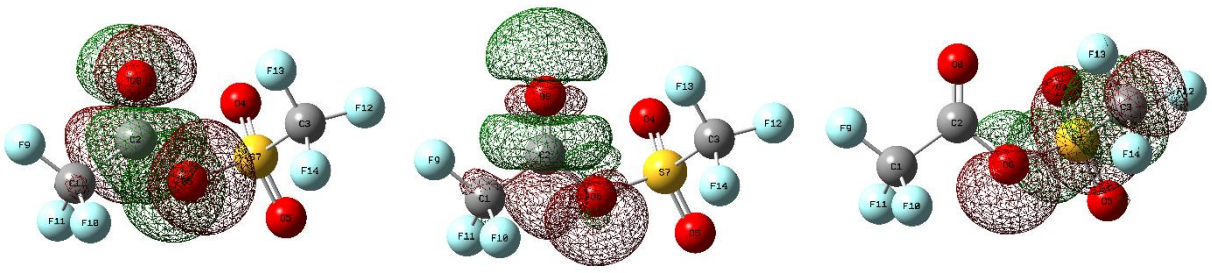
Table S5. Percentage of the *syn-anti* conformer of $CF_3C(O)OSO_2CF_3$ estimated from the relative intensities of selected IR bands of the Ar-matrix FTIR spectrum of TFAT. I, using the relationship of the absorption coefficients of the involved bands when the concentrations of the two rotamers becomes equal after the randomization process (in this case, broad-band UV-visible irradiation of the matrix for 50 min); II) through the use of the absorption coefficients obtained from the B3LYP/cc-pvtz approximation.

Normal Mode	*(% syn-anti)*$_I$	*(% syn-anti)*$_{II}$
ν C=O	59	58
ν C–O	71	76
δ OCO	63	57



(**a**) lpπ O → π* C=O (**b**) lpσ O → σ* C=O (**c**) lpσ O → σ* S=O

Figure S1. Schematic representation of the hyperconjugative and anomeric interactions in the *syn-anti* conformer of trifluoroacetyl triflate calculated with the NBO formalism using the B3LYP/cc-pvtz approximation: (**a**) lpπ O → π* C=O; (**b**) lpσ O → σ* C=O; (**c**) lpσ O → σ* S=O.



(**a**) lpπ O → π* C=O (**b**) lpσ O → σ* C=O (**c**) lpσ O → σ* S–C

Figure S2. Schematic representation of the hyperconjugative and anomeric interactions in the *syn-gauche* conformer of trifluoroacetyl triflate calculated with the NBO formalism using the B3LYP/cc-pvtz approximation: (**a**) lpπ O → π* C=O; (**b**) lpσ O → σ* C=O; (**c**) lpσ O → σ* S–C.