Methoxycarbonyl Trifluoromethyl Disulfide, $CH_3OC(O)SSCF_3$: Synthesis, Structure and Conformational Properties

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Electronic Suplemmentary Information (ESI)

Table S1. Experimental and calculated (B3LYP/6-311++G**) vibrational data (cm^{-1}) for $CH_3OC(O)SSCF_3$.

Table S2. Crystal data and structure refinement for $CH_3OC(O)SSCF_3$.

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for $CH_3OC(O)SSCF_3$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table S4. Bond lengths [Å] and angles [°] for $CH_3OC(O)SSCF_3$.

Table S5. Anisotropic displacement parameters (Å^2x 10^3) for $CH_3OC(O)SSCF_3$. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 a^{*2} U11 + ... + 2 h k a* b* U12].

Table S6. Hydrogen coordinates (x 10^4) and i displacement parameters (Å^2 x 10^3) for $CH_3OC(O)SSCF_3$.

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Table S7. Torsion angles [°] for $CH_3OC(O)SSCF_3$.

Table S1.

	Experimental		Calculated[c]		Assignment/
			B3LYP/6-311++G**		**(Approximated description)[f]**
Mode	**IR[a]**	**Raman[b]**	**s-s-g[d]**	**s-a-g[e]**	
ν_1	3014 vvw	3041 vvw	3173 (1)	3174 (1)	$\nu_{as}(CH_3)$
ν_2	2967 w	2962 s	3140 (2)	3141 (2)	$\nu_{as}(CH_3)$
		2917			$\nu_4 + \nu_{10}$
ν_3	2902 vvw	2896 vvw	3127 (2)		$\nu_s(CH_3)$, s-s-g
	2849 vvw	2843 w		3061 (5)	$\nu_s(CH_3)$, s-a-g
	2349				2 x ν_{10}
ν_4	1782 s	1762 vw	1821 (41)		$\nu(C=O)$, s-s-g
	1750 R 1747 Q m 1743 P	1724 vvw		1788 (69)	$\nu(C=O)$, s-a-g
ν_5		1493 m	1495 (2)	1494 (2)	$\delta_{as}(CH_3)$
ν_6			1484 (2)	1484 (2)	$\delta_{as}(CH_3)$
ν_7	1440 vw	1457 w	1467 (2)	1467 (3)	$\delta_s(CH_3)$
ν_8			1210 (19)	1217 (59)	$\rho_s(CH_3O)$
ν_9	1297 vvw		1167 (3)	1186 (75)	$\rho_{as}(CH_3)$
ν_{10}	1180 s	1158 vw	1165 (100)	1167 (< 1)	$\nu_{as}(C-O-C)$
ν_{11}	1159 s		1152 (24)	1148 (46)	$\nu_{as}(CF_3)$
ν_{12}			1139 (37)	1138 (29)	$\nu_{as}(CF_3)$
ν_{13}	1115 vs	1102 vvw	1090 (99)	1088 (100)	$\nu_s(CF_3)$
ν_{14}	971 vvw	937 m	954 (1)	966 (2)	$\nu_s(C-O-C)$
ν_{15}	812 w	811 s	820 (7)	825 (9)	$\delta(C-O-C)$
ν_{16}	757 w	755 vs	749 (3)	749 (3)	$\delta_s(CF_3)$
ν_{17}	671 vw		675 (2)	674 (2)	δoop (O−C(O)S)
ν_{18}		568 w	558 (< 1)	555 (< 1)	$\rho(CF_3)$
ν_{19}			534 (< 1)	534 (< 1)	$\delta_s(CF_2)$
ν_{20}		541 m	516 (< 1)	505 (< 1)	$\nu(S-S)$
ν_{21}		483 s	472 (2)	446 (1)	$\nu((O)C-S)$
ν_{22}		452 s	446 (2)	437 (1)	$\nu(S-CF_3)$

ν_{23}		415 vvw	371 (1)	387 (1)	$\tau(C-O-C-S)$
ν_{24}		378 s	329 (1)	326 (< 1)	$\rho_{as}(SCF_3)$
ν_{25}		319 s	311 (2)	309 (< 1)	$\rho_{as}(OCH_3)$
ν_{26}		256 m	245 (1)	257 (2)	$\tau(C-O-C=O)$
ν_{27}		152 m	167 (< 1)	170 (< 1)	$\tau_{oop}(C-O-C-S)$
ν_{28}			145 (< 1)	146 (< 1)	$\rho(CH_3-O)$
ν_{29}			135 (< 1)	132 (< 1)	$\tau(CH_3-O)$
ν_{30}			114 (< 1)	113 (< 1)	$\rho(CH_3)$
ν_{31}		79 m	59 (< 1)	59 (< 1)	$\rho_s(CH_3 + OC(O))$
ν_{32}			45 (< 1)	45 (< 1)	$\tau(CF_3)$
ν_{33}			37 (< 1)	39 (< 1)	$\rho(SCF_3)$

[a] band intensity: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, vvw = very very weak; [b] liquid at room temperature; [c] In parentheses relative band strengths for the two most stable forms, IR intensities [100% ≡ 619 Km/mol for syn-syn-gauche form] and [100% ≡ 512 Km/mol for syn-anti-gauche form]. [d] s-s-g refers to the most stable conformer syn-syn-gauche. [e] s-a-g refers to the second stable conformer syn-anti-gauche. [f] Except specified, bands in the spectra arise from vibration of both s-s-g and s-a-g forms.

Table S2.

Empirical formula	$C_3 H_3 F_3 O_2 S_2$
Formula weight	192.17 Da
Density (calculated)	1.765 g cm^{-3}
F(000)	384
Temperature	190(2) K
Crystal size	0.3 mm diameter
Crystal color	colorless
Crystal description	cylindric
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P\ \bar{1}$
Unit cell dimensions	a = 6.4698(5) Å α = 97.219(6)º
	b = 9.0499(8) Å β = 93.131(5)º
	c = 12.5700(11) Å γ = 96.888(5)º
Volume	723.07(11) Å^3
Z	4
Cell measurement reflections used	9901
Cell measurement theta min/max	2.28° to 27.03°
Diffractometer control software	Bruker AXS APEX 2 Vers. 2.0-2 2006
Diffractometer measurement device	Siemens SMART three axis goniometer with APEX II area detector system
Diffractometer measurement method	Data collection strategy APEX 2/COSMO chi + / - 10°
Theta range for data collection	1.64° to 27.90°
Completeness to theta = 27.90°	76.2 %
Index ranges	-5<=h<=5, -11<=k<=11, 0<=l<=16
Computing data reduction	Bruker AXS APEX 2 Vers. 2.0-2 2006
Absorption coefficient	0.730 mm^{-1}
Empirical absorption correction	Bruker AXS TWINABS Vers. 1.05
Max. / min. transmission	0.97 / 0.81
R(merg) before/after correction	0.0534 / 0.0509
Computing structure solution	Bruker AXS SHELXTL Vers. 6.12 W95/98/NT/2000/ME
Computing structure refinement	Bruker AXS SHELXTL Vers. 6.12 W95/98/NT/2000/ME
Refinement method	Full-matrix least-squares on F^2
Reflections collected	36644
Independent reflections	7516 [R(int) = 0.069]
Data / restraints / parameters	5296 / 0 / 184
Goodness-of-fit on F2	1.031
Weighting details	w = 1/[σ^2 (Fo^2)+ (0.1365*P)^2+0.2533*P] where P = (Fo^2+2Fc^2)/3
Final R indices [I>2sigma(I)]	$R1$ = 0.0631, $wR2$ = 0.1900
R indices (all data)	$R1$ = 0.0887, $wR2$ = 0.2186
Extinction coefficient	0.004(5)
Largest diff. peak and hole	0.563 and -0.357 eÅ^{-3}

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for ocoss_m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S11	2060(2)	2230(1)	6248(1)	45(1)
S21	-1058(2)	2159(1)	6255(1)	47(1)
O11	-716(4)	1558(3)	4130(2)	52(1)
O21	-3897(5)	1672(2)	4771(2)	48(1)
C11	2795(7)	4205(4)	6213(3)	52(1)
C21	-1850(7)	1741(3)	4838(2)	40(1)
C31	-4915(7)	1387(4)	3692(3)	57(1)
F11	2176(5)	5056(3)	7044(2)	94(1)
F21	2056(4)	4669(3)	5336(2)	91(1)
F31	4852(4)	4463(3)	6252(2)	73(1)
S12	3799(2)	8330(1)	1004(1)	45(1)
S22	6860(2)	8198(1)	880(1)	45(1)
O12	5730(4)	8116(2)	-1219(2)	48(1)
O22	9108(5)	8059(3)	-679(2)	54(1)
C12	2788(6)	6365(3)	867(3)	46(1)
C22	7096(7)	8113(3)	-553(2)	42(1)
C32	9717(7)	7959(5)	-1781(3)	63(1)
F12	795(4)	6279(2)	1114(2)	64(1)
F22	2824(4)	5674(2)	-128(2)	67(1)
F32	3755(4)	5597(2)	1511(2)	72(1)

Table S4. Bond lengths [Å] and angles [°] for ocoss_m.

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S11-C11	1.801(3)	F21-C11-F31	107.9(3)
S11-S21	2.0110(15)	F21-C11-F11	107.3(3)
S21-C21	1.806(3)	F31-C11-F11	107.4(3)
O11-C21	1.193(4)	F21-C11-S11	113.1(3)
O21-C21	1.316(4)	F31-C11-S11	108.2(2)
O21-C31	1.455(4)	F11-C11-S11	112.8(3)
C11-F21	1.314(4)	O11-C21-O21	128.5(3)
C11-F31	1.320(5)	O11-C21-S21	125.9(3)
C11-F11	1.328(5)	O21-C21-S21	105.6(2)
S12-C12	1.803(3)	C12-S12-S22	100.59(13)
S12-S22	2.0116(14)	C22-S22-S12	102.39(15)
S22-C22	1.808(3)	C22-O22-C32	116.0(3)
O12-C22	1.185(4)	F32-C12-F22	107.3(3)
O22-C22	1.326(4)	F32-C12-F12	107.3(3)
O22-C32	1.455(4)	F22-C12-F12	107.8(3)
C12-F32	1.312(4)	F32-C12-S12	114.1(3)
C12-F22	1.329(4)	F22-C12-S12	112.8(2)
C12-F12	1.338(4)	F12-C12-S12	107.2(2)
		O12-C22-O22	128.4(3)
C11-S11-S21	100.26(15)	O12-C22-S22	126.6(3)
C21-S21-S11	101.71(14)	O22-C22-S22	105.0(2)
C21-O21-C31	116.1(3)		

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Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $CH_3OC(O)SSCF_3$. The anisotropic displacement factor exponent takes the form: $-2\pi^2\ [\ h^2\ a^{*2}\ U_{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S11	39(1)	51(1)	47(1)	10(1)	-1(1)	11(1)
S21	40(1)	67(1)	33(1)	5(1)	7(1)	4(1)
O11	46(2)	73(1)	36(1)	-2(1)	8(1)	9(1)
O21	34(2)	65(1)	43(1)	4(1)	1(1)	3(1)
C11	34(3)	55(2)	68(2)	11(2)	-1(2)	7(2)
C21	45(3)	41(1)	34(1)	5(1)	4(1)	2(1)
C31	54(3)	65(2)	48(2)	5(1)	-8(2)	1(2)
F11	83(2)	66(1)	126(2)	-23(1)	29(2)	8(1)
F21	78(2)	78(2)	121(2)	58(2)	-27(2)	-8(1)
F31	43(2)	78(1)	92(2)	6(1)	-1(1)	-3(1)
S12	43(1)	42(1)	50(1)	0(1)	9(1)	10(1)
S22	38(1)	61(1)	34(1)	4(1)	0(1)	1(1)
O12	45(2)	62(1)	37(1)	8(1)	-4(1)	7(1)
O22	34(2)	84(2)	45(1)	14(1)	7(1)	10(1)
C12	35(3)	48(2)	52(2)	2(1)	5(2)	3(1)
C22	50(3)	39(1)	38(2)	7(1)	3(2)	5(1)
C32	54(3)	84(2)	52(2)	8(2)	20(2)	6(2)
F12	34(2)	76(1)	80(2)	7(1)	10(1)	0(1)
F22	67(2)	61(1)	66(1)	-17(1)	11(1)	-4(1)
F32	62(2)	63(1)	95(2)	35(1)	-4(1)	9(1)

Table S6. Hydrogen coordinates (x 10^4) and i displacement parameters ($Å^2$ x 10^3) for $CH_3OC(O)SSCF_3$.

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	x	y	z	U(eq)
H3A1	-4359	2134	3262	85
H3B1	-6387	1427	3744	85
H3C1	-4697	408	3358	85
H3A2	8861	7130	-2209	94
H3B2	11158	7792	-1787	94
H3C2	9546	8871	-2078	94

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Table S7. Torsion angles [°] for $CH_3OC(O)SSCF_3$.

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C11-S11-S21-C21	92.74(15)
S21-S11-C11-F21	-63.2(3)
S21-S11-C11-F31	177.4(2)
S21-S11-C11-F11	58.7(3)
C31-O21-C21-O11	-2.4(4)
C31-O21-C21-S21	178.2(2)
S11-S21-C21-O11	0.5(3)
S11-S21-C21-O21	179.87(16)
C12-S12-S22-C22	89.37(14)
S22-S12-C12-F32	51.1(3)
S22-S12-C12-F22	-71.7(3)
S22-S12-C12-F12	169.81(19)
C32-O22-C22-O12	-1.5(4)
C32-O22-C22-S22	179.0(2)
S12-S22-C22-O12	-0.9(3)
S12-S22-C22-O22	178.56(16)

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