Supplementary Material

Toward an intimate understanding of the structural properties and the conformational preference of oxoesters and thioesters: gas and crystal structure and conformational analysis of Dimethyl Monothiocarbonate, $CH_3OC(O)SCH_3$

Mauricio F. Erben, Roland Boese, Carlos O. Della Védova, Heinz Oberhammer, and Helge Willner

Table of contents for supporting information

Table SM1. Observed and Calculated Vibrational Data for (sp,sp) and (sp,ap) conformers of $CH_3OC(O)SCH_3$.

IR(gas)[a]	**Raman(liq)**[b]	**MP2 6-311++G****[c]		**B3LYP 6-311++G(3df,2p)**[d]		**Symmetry species/ Approximate description of mode**[e]
		(sp,sp)	(sp,ap)	(sp,sp)	(sp,ap)	
		88 (<1)	56 (<1)	97 (<1)	99 (<1)	*a*"/ torsion SCH_3
		108 (1)	132 (<1)	109 (<1)	122 (<1)	*a*"/ torsion OCH_3
		131 (<1)	145 (<1)	126 (<1)	144 (<1)	*a*"/ torsion C-S
		168 (<1)	167 (<1)	159 (<1)	167 (<1)	*a*"/ torsión C-O
	198 w	195 (<1)	200 (<1)	184 (<1)	183 (<1)	*a*'/ def O–C–S
	320 m	312 (4)	316 (3)	297 (<1)	300 (3)	*a*'/ def antisym C–S–C
	395 s	401 (2)	425 (1)	386 (3)	411 (1)	*a*'/ def sym C–O–C
	502 s	520 (<1)	482 (<1)	497 (2)	460 (<1)	*a*'/ rock C=O
679 (2)		675(2)	671 (2)	687 (<1)	684 (<1)	*a*"/ def oop C=O
	723 s	763 (<1)	757 (<1)	714 (2)	705 (2)	*a*'/ stretch S–CH_3
815 (5)	818 m	839 (5)	836 (5)	827 (<1)	826 (5)	*a*'/ stretch sym O–C–S
873 (3)	954 w	1003 (3)	997 (3)	973 (4)	969 (1)	*a*'/ stretch O–CH_3
969 (2)	982	1004 (1)	1000 (1)	981 (1)	977 (<1)	*a*'/$\rho_{as}SCH_3$
		1031 (<1)	1034 (2)	1003 (<1)	1003 (4)	*a*'/ rock S–CH_3
		1192 (<1)	1192 (<1)	1174 (<1)	1166 (100)	*a*"/$\rho_{as}OCH_3$
1151 (100)	1194 vw	1205 (100)	1193 (100)	1178 (100)	1174 (<1)	*a*'/ stretch antisym O–C–S
A {1188, 1196, 1200} (42)		1233 (57)	1224 (15)	1215 (18)	1208 (7)	*a*'/ rock O–CH_3
1318(3)		1399 (<1)	1403 (2)	1359 (<1)	1361 (1)	*a*'/ def sym S–CH_3
1436 (5)		1461 (2)	1461 (2)	1464 (1)	1468 (2)	*a*'/ def sym O–CH_3
1442 (9)	1442 m,broad	1492 (1)	1491 (1)	1472 (2)	1470 (2)	*a*"/ def antisym S–CH_3
		1495 (3)	1496 (4)	1479 (2)	1482 (4)	*a*'/ def antisym S–CH_3

		1504 (2)	1501 (2)	1488 (2)	1486 (2)	*a*"/ def antisym O–CH_3
		1521 (3)	1521 (3)	1501 (2)	1501 (2)	*a*'/ def antisym O–CH_3
$\left\{\begin{matrix}1729\\1740\end{matrix}\right.$ (52)	1712 m	1768 (53)	1764 (66)	1764 (45)	1761 (68)	*a*'/ stretch C=O
A $\left\{\begin{matrix}2842\\2848\\2853\end{matrix}\right.$ (1) $\left\{\begin{matrix}2940\\2946\end{matrix}\right.$ (1) $\left\{\begin{matrix}2968\\2962\end{matrix}\right.$ (2) $\left\{\begin{matrix}3005\\3020\end{matrix}\right.$ (<1)	2838 s 2936 vs 2955 vs 3013 s	3100 (7)	3099 (3)	3051 (5)	3054 (6)	*a*'/ sym stretch OCH_3
		3101 (2)	3102 (6)	3056 (2)	3056 (2)	*a*'/ sym stretch SCH_3
		3195 (3)	3189 (1)	3123 (3)	3128 (2)	*a*"/ antisym stretch OCH_3
		3203 (1)	3198 (3)	3142 (<1)	3137 (2)	*a*'/ antisym stretch SCH_3
		3211 (1)	3213 (1)	3149 (<1)	3151 (1)	*a*"/ antisym stretch SCH_3
		3229 (2)	3227 (2)	3156 (2)	3156 (1)	*a*'/ antisym stretch OCH_3

[a] In parentheses relative absorbance at band maximum. The band contour is indicated. [b] Liquid, room temperature, band intensities: vs= very strong, s= strong, m= medium, w= weak, vw= very weak. [c] In parentheses relative band strength of (sp,sp) and (sp,ap) rotamers; 100≡ 471 and 501 km/mol, respectively. [d] In parentheses relative band strength of (sp,sp) and (sp,ap) rotamers; 100≡ 600 and 524 km/mol, respectively. [e] (sp,sp) conformer.

Table SM2. Interatomic Distances, Experimental and Calculated Vibrational Amplitudes and Vibrational Corrections for $CH_3OC(O)SCH_3$ (Without Distances Involving Hydrogens). [a]

	Distance	Ampl. (exp)		Ampl. (calc) [b]	$\Delta r = r_{h1} - r_a$
C=O	1.20	0.036(5)	*l*1	0.038	0.001
C1–O2	1.33	0.045 [c]		0.045	0.002
C2–O2	1.44	0.048 [c]		0.048	0.002
S–C	1.76 – 1.80	0.049 [c]		0.049	0.001
O1···O2	2.26	0.051 [c]		0.051	0.004
C1···C2	2.30	0.075(8)	*l*2	0.063	0.003
C2···O1	2.62	0.088(18)	*l*3	0.095	-0.002
S···O1	2.66	0.061(7)	*l*4	0.056	0.004
C1···C3	2.72	0.070(22)	*l*5	0.080	0.004
C3···O1	2.89	0.093(25)	*l*6	0.119	-0.007
S···C2	3.85	0.075(8)	*l*2	0.067	0.018
C3···O2	3.93	0.070(22)	*l*5	0.076	0.019
C2···C3	5.02	0.088(18)	*l*3	0.098	0.020

[a] Values in Å, error limits are 3σ values. For atom numbering see Figure 4. [b] B3LYP/6-31G*. [c] Not refined.

Table SM3. Crystal data and structure refinement for $CH_3OC(O)SCH_3$

Empirical formula	$C_3 H_6 O_2 S$
Formula weight	106.14 Da
Density (calculated)	1.356 g cm^{-3}
F(000)	448
Temperature	203(2) K
Crystal size	0.3 mm
Crystal color	colorless
Crystal description	cylindric
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 12.6406(9) Å α = 90° b = 4.1678(3) Å β = 98.1640(10)°, c = 19.9399(14) Å, γ = 90°
Volume	1039.86(13) $Å^3$
Z	8
Cell measurement reflections used	2640
Cell measurement theta min/max	2.44° to 28.28°
Diffractometer control software	Bruker AXS SMART Vers. 5.054 1997/98
Diffractometer measurement device	Siemens SMART CCD area detector system
Diffractometer measurement method	Omega data collection at 0.3° scan width one run with 740 frames, phi = 0°, chi = 0°
Theta range for data collection	2.05° to 28.29°
Completeness to theta = 28.29°	89.1 %
Index ranges	-7<=h<=16, -4<=k<=4, -26<=l<=26
Computing data reduction	Bruker AXS SAINT program Vers. 6.02A

Absorption coefficient	0.489 mm^{-1}
Computing absorption correction	Bruker AXS SADABS program multiscan V2.03
Absorption correction details	R.H. Blessing, Acta Cryst. (1995) A51 33-38
Max. / min. transmission	1.00 / 0.93
$R_{(merg)}$ before/after correction	0.0162 / 0.0111
Computing structure solution	Bruker AXS SHELXTL Vers. 5.10 DOS/WIN95/NT
Computing structure refinement	Bruker AXS SHELXTL Vers. 5.10 DOS/WIN95/NT
Refinement method	Full-matrix least-squares on F^2
Reflections collected	3850
Independent reflections	2311 [$R_{(int)}$ = 0.0102]
Data / restraints / parameters	2037 / 0 / 110
Goodness-of-fit on F^2	1.025
Weighting details	$w = 1/[\sigma^2 (Fo^2) + (0.0489*P)^2 + 0.1961*P]$ where $P = (Fo^2+2Fc^2)/3$
Final R indices [I>2sigma(I)]	R_1 = 0.0265, wR_2 = 0.0802
R indices (all data)	R_1 = 0.0307, wR_2 = 0.0841
Extinction coefficient	0.018(3)
Largest diff. peak and hole	0.242 and -0.173 $eÅ^{-3}$
Treatment of hydrogen atoms: Riding model on idealized geometries with the 1.5 fold for methyl groups isotropic displacement parameters of the equivalent Uij of the corresponding carbon atom; Comment The crystallization was performed on the diffractometer at a temperature of 205 K with a miniature zone melting procedure using focused infrared-laser-radiation according to: R. Boese, M.Nussbaumer, "In Situ crystallisation Techniques", in: "Organic Crystal Chemistry", Ed. D.W. Jones, Oxford University Press, Oxford,England, (1994) 20-37	

Table SM4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $CH_3OC(O)SCH_3$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1)	6599(1)	5982(1)	1823(1)	48(1)
S(2)	1793(1)	4013(1)	1829(1)	44(1)
O(1)	4879(1)	3328(2)	1303(1)	47(1)
O(2)	6184(1)	2983(3)	647(1)	56(1)
O(3)	1867(1)	6699(2)	706(1)	43(1)
O(4)	230(1)	6923(3)	1026(1)	52(1)
C(1)	4164(1)	1574(4)	797(1)	55(1)
C(2)	5863(1)	3837(3)	1153(1)	39(1)
C(3)	7832(1)	6428(4)	1489(1)	58(1)
C(11)	1479(1)	8430(4)	92(1)	51(1)
C(12)	1149(1)	6134(3)	1124(1)	37(1)
C(13)	685(1)	3385(4)	2285(1)	57(1)

Table SM5. Hydrogen coordinates (x 10^4) and displacement parameters ($Å^2$ x 10^3) for $CH_3OC(O)SCH_3$.

	x	y	z	U(eq)
H(1A)	4040	2826	383	83
H(1B)	3489	1201	963	83
H(1C)	4484	-467	706	83
H(3A)	8137	4327	1433	87
H(3B)	8325	7687	1801	87
H(3C)	7703	7507	1054	87
H(11A)	921	7190	-176	77
H(11B)	2062	8772	-168	77
H(11C)	1192	10486	206	77
H(13A)	411	5442	2410	85
H(13B)	919	2148	2691	85
H(13C)	126	2224	2001	85

Table SM6. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $CH_3OC(O)SCH_3$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
S(1)	49(1)	55(1)	40(1)	-7(1)	11(1)	-3(1)
S(2)	38(1)	52(1)	42(1)	3(1)	5(1)	1(1)
O(1)	40(1)	55(1)	47(1)	-3(1)	11(1)	0(1)
O(2)	51(1)	76(1)	42(1)	-12(1)	14(1)	-3(1)
O(3)	39(1)	52(1)	41(1)	1(1)	11(1)	-1(1)
O(4)	35(1)	70(1)	51(1)	8(1)	7(1)	4(1)
C(1)	43(1)	59(1)	63(1)	-3(1)	3(1)	-2(1)
C(2)	40(1)	39(1)	37(1)	5(1)	8(1)	6(1)
C(3)	46(1)	71(1)	59(1)	-7(1)	13(1)	-11(1)
C(11)	56(1)	59(1)	39(1)	1(1)	10(1)	-5(1)
C(12)	36(1)	39(1)	35(1)	-7(1)	5(1)	-4(1)
C(13)	58(1)	65(1)	51(1)	10(1)	21(1)	5(1)

Table SM 7. Electronic Energies (E), Zero Point Energies (ZPE), and Number of Imaginary Frequencies for Conformers and Transition States (TS) of $CH_3OC(O)SCH_3$ Calculated at different Levels of Approximation.

Conformer	Method	E, hartree	ZPE, hartree	Nº of imag. frequencies
(sp,sp)	MP2/6-31+G*	-665.2243288	0.093065	0
	MP2/6-311++G(d,p)	-665.410587	0.092370	0
	B3LYP/6-31+G(d)	-666.5900465	0.091450	0
	B3LYP/6-311++G(3df,2p)	-666.7158243	0.090701	0
(ap,sp)	MP2/6-31+G*	-665.2152488	0.093022	0
	MP2/6-311++G(d,p)	-665.4019399	0.092194	0
	B3LYP/6-31+G(d)	-666.5818594	0.091403	0
	B3LYP/6-311++G(3df,2p)	-666.7084075	0.090639	0
(sp,ap)	MP2/6-31+G*	-665.2209601	0.093127	0
	MP2/6-311++G(d,p)	-665.4070627	0.092270	0
	B3LYP/6-31+G(d)	-666.5867868	0.091432	0
	B3LYP/6-311++G(3df,2p)	-666.7124907	0.090689	0
TS1[a]	B3LYP/6-31+G*	-666.5738444	0.090657	1
	B3LYP/ 6-311++G(3df,2p)	-666.7002206	0.089910	1
TS2[b]	B3LYP/6-31+G*	-666.5743593	0.091134	1
	B3LYP/ 6-311++G(3df,2p)	-666.6995025	0.090347	1

[a] TS1: rotational TS connecting the (sp,sp) and the (ap,sp) conformers, [b] TS2: rotational TS connecting the (sp,sp) and the (sp,ap) conformers.

Table SM8. Cartesian Coordinates of the Optimized Structure for (sp,sp) at the MP2/6-31+G* Level of Approximation

Atom	X	Y	Z
O	0.359692	1.380134	-0.000036
C	0.308339	0.159301	-0.000181
O	1.380395	-0.664555	-0.000023
C	2.657430	0.019597	0.000090
S	-1.165435	-0.813104	-0.000002
C	-2.356155	0.548672	0.000074
H	-3.346419	0.087622	0.000171
H	-2.239951	1.165911	-0.891044
H	-2.239801	1.165957	0.891139
H	3.396034	-0.779192	0.000210
H	2.749262	0.639706	0.892930
H	2.749456	0.639619	-0.892791

Table SM9. Cartesian Coordinates of the Optimized Structure for (ap,sp) at the MP2/6-31+G* Level of Approximation

Atom	X	Y	Z
O	-0.299185	1.756697	0.000015
C	0.243725	0.667834	-0.000048
O	1.594680	0.568928	0.000002
C	2.225982	-0.728838	0.000014
S	-0.656125	-0.874142	-0.000007
C	-2.320627	-0.170040	0.000013
H	-3.009429	-1.017780	0.000032
H	-2.479385	0.437757	-0.890603
H	-2.479357	0.437774	0.890622
H	3.292673	-0.511641	0.000061
H	1.957563	-1.289272	-0.898513
H	1.957488	-1.289294	0.898505

Table SM10. Cartesian Coordinates of the Optimized Structure for (sp,ap) at the MP2/6-31+G* Level of Approximation

Atom	X	Y	Z
O	1.050142	-1.536984	0.000025
C	0.367714	-0.524730	-0.000092
O	0.861602	0.738343	-0.000030
C	2.311105	0.797399	0.000028
S	-1.395906	-0.581867	0.000014
C	-1.847849	1.172520	0.000008
H	-2.940718	1.196708	0.000071
H	-1.477196	1.676416	-0.892529
H	-1.477092	1.676454	0.892481
H	2.541880	1.860826	0.000067
H	2.703955	0.308761	-0.892478
H	2.703888	0.308712	0.892536

Table SM11. Cartesian Coordinates of the Optimized Structure for (sp,sp) at the MP2/6-311++G(d,p) Level of Approximation

Atom	X	Y	Z
O	-0.361333	1.369838	0.000000
C	-0.310696	0.160365	-0.000058
O	-1.375541	-0.663620	-0.000012
C	-2.641800	0.019897	0.000024
S	1.163748	-0.812394	0.000006
C	2.344329	0.553208	0.000012
H	3.336131	0.097153	0.000060
H	2.225560	1.167915	0.891630
H	2.225623	1.167866	-0.891648
H	-3.389892	-0.769986	0.000065
H	-2.736731	0.642378	-0.891024
H	-2.736664	0.642408	0.891058

Table SM12. Cartesian Coordinates of the Optimized Structure for (ap,sp) at the MP2/6-311++G(d,p) Level of Approximation

Atom	X	Y	Z
O	0.296101	1.747315	-0.000014
C	-0.246365	0.670995	-0.000005
O	-1.592470	0.569736	0.000012
C	-2.203617	-0.726448	0.000011
S	0.651647	-0.874841	-0.000020
C	2.308457	-0.162920	0.000027
H	3.000977	-1.006726	0.000019
H	2.463691	0.443722	0.891096
H	2.463724	0.443764	-0.891009
H	-3.274942	-0.533810	0.000029
H	-1.929832	-1.287842	0.896496
H	-1.929860	-1.287827	-0.896492

Table SM13. Cartesian Coordinates of the Optimized Structure for (sp,ap) at the MP2/6-311++G(d,p) Level of Approximation

Atom	X	Y	Z
O	1.050647	-1.524453	0.000000
C	0.372522	-0.522581	-0.000007
O	0.858939	0.736901	0.000000
C	2.298399	0.793217	0.000002
S	-1.392173	-0.582862	0.000002
C	-1.844799	1.167884	-0.000001
H	-2.936940	1.188810	-0.000009
H	-1.476795	1.671605	-0.892806
H	-1.476807	1.671604	0.892809
H	2.540272	1.854184	0.000003
H	2.695813	0.304448	-0.890544
H	2.695811	0.304447	0.890549

Table SM14. Cartesian Coordinates of the Optimized Structure for (sp,sp) at the B3LYP/6-31+G(d) Level of Approximation

Atom	X	Y	Z
O	0.367420	1.385147	0.000000
C	0.319849	0.174182	0.000002
O	1.387645	-0.645947	0.000002
C	2.676299	0.003967	-0.000001
S	-1.166752	-0.813658	-0.000001
C	-2.395596	0.538172	0.000000
H	-3.375776	0.054060	-0.000001
H	-2.289143	1.156955	-0.892957
H	-2.289144	1.156953	0.892958
H	3.402626	-0.808663	-0.000065
H	2.787840	0.623800	0.893326
H	2.787790	0.623899	-0.893266

Table SM15. Cartesian Coordinates of the Optimized Structure for (ap,sp) at the B3LYP|6-31+G(d) Level of Approximation

Atom	X	Y	Z
O	-0.261185	1.762327	-0.000034
C	0.260899	0.674329	0.000109
O	1.603572	0.549860	-0.000011
C	2.238301	-0.739369	-0.000023
S	-0.674732	-0.870500	0.000008
C	-2.354980	-0.156485	-0.000020
H	-3.043654	-1.005284	-0.000085
H	-2.510125	0.451860	-0.892526
H	-2.510187	0.451776	0.892532
H	3.307825	-0.526906	-0.000092
H	1.973668	-1.305907	-0.898454
H	1.973778	-1.305872	0.898462

Table SM16. Cartesian Coordinates of the Optimized Structure for (sp,ap) at the B3LYP/6-31+G(d) Level of Approximation

Atom	X	Y	Z
O	-1.052287	-1.539653	0.000034
C	-0.385401	-0.528842	0.000028
O	-0.882383	0.725493	-0.000014
C	-2.324924	0.816045	-0.000016
S	1.396227	-0.586074	-0.000033
C	1.892622	1.176991	0.000034
H	2.986440	1.171840	0.000001
H	1.532646	1.688246	0.894582
H	1.532593	1.688329	-0.894446
H	-2.541362	1.884377	-0.000129
H	-2.733185	0.336346	0.892835
H	-2.733200	0.336150	-0.892753

Table SM17. Cartesian Coordinates of the Optimized Structure for (sp,sp) at the B3LYP|6-311++G(3df,2p) Level of Approximation

Atom	X	Y	Z
O	-0.366047	1.377193	-0.000112
C	-0.317455	0.176423	-0.000271
O	-1.379331	-0.642752	-0.000020
C	-2.666020	0.000871	0.000166
S	1.161547	-0.805953	-0.000039
C	2.385641	0.531328	0.000171
H	3.358703	0.045233	0.000316
H	2.279392	1.145239	0.889466
H	2.279667	1.145264	-0.889140
H	-3.391105	-0.806327	0.000383
H	-2.780859	0.619199	-0.887828
H	-2.780521	0.619373	0.888082

Table SM18. Cartesian Coordinates of the Optimized Structure for (ap,sp) at the B3LYP|6-311++G(3df,2p) Level of Approximation

Atom	X	Y	Z
O	0.259079	1.755067	-0.000211
C	-0.258055	0.675255	-0.000097
O	-1.595048	0.547800	0.000154
C	-2.220954	-0.740184	0.000243
S	0.669226	-0.861640	-0.000385
C	2.339978	-0.161712	0.000493
H	3.020011	-1.010695	0.000427
H	2.494916	0.441663	0.889497
H	2.495568	0.442323	-0.887949
H	-3.288295	-0.541440	0.000451
H	-1.953773	-1.304368	0.893408
H	-1.954110	-1.304325	-0.893050

Table SM19. Cartesian Coordinates of the Optimized Structure for (sp,ap) at the B3LYP/6-311++G(3df,2p) Level of Approximation

Atom	X	Y	Z
O	-1.040467	-1.530997	0.000173
C	-0.383383	-0.525159	-0.000384
O	-0.882281	0.721783	-0.000193
C	-2.320957	0.808806	0.000120
S	1.388364	-0.579408	0.000015
C	1.891155	1.168009	0.000096
H	2.979309	1.154629	0.000315
H	1.534313	1.675154	0.890992
H	1.534669	1.675129	-0.890957
H	-2.544646	1.870666	0.000193
H	-2.728000	0.329344	0.887557
H	-2.728381	0.329380	-0.887161

Table SM20. Cartesian Coordinates of the Optimized Structure for the Transition State TS (sp,sp) → (ap,sp) at the B3LYP/6-31+G* Level of Approximation

Atom	X	Y	Z
O	0.018545	1.674247	0.046118
C	0.300492	0.525180	-0.184574
O	1.554635	0.111275	-0.534205
C	2.344754	-0.523484	0.489174
S	-0.866299	-0.826363	-0.211849
C	-2.372432	0.054635	0.330273
H	-3.176524	-0.685789	0.339132
H	-2.613179	0.856673	-0.369882
H	-2.237683	0.467599	1.331969
H	3.276866	-0.813005	0.002924
H	1.837665	-1.411400	0.882372
H	2.551315	0.185572	1.298531

Table SM21. Cartesian Coordinates of the Optimized Structure for the Transition State TS (sp,sp) → (ap,sp) at the B3LYP/ 6-311++G(3df,2p) Level of Approximation

Atom	X	Y	Z
O	0.022364	1.665744	0.049912
C	0.296024	0.525644	-0.182422
O	1.543674	0.106704	-0.535341
C	2.335066	-0.521662	0.483771
S	-0.862306	-0.818289	-0.207758
C	-2.361626	0.050733	0.324757
H	-3.157715	-0.690373	0.335075
H	-2.601662	0.844039	-0.376786
H	-2.228074	0.464878	1.319872
H	3.257428	-0.828066	-0.000093
H	1.825551	-1.395274	0.892056
H	2.556268	0.189554	1.280807

Table SM22. Cartesian Coordinates of the Optimized Structure for the Transition State TS (sp,sp) → (sp,ap) at the B3LYP/6-31+G* Level of Approximation

Atom	X	Y	Z
O	-0.733944	1.389488	0.574205
C	-0.349641	0.420986	-0.035669
O	-1.120224	-0.630555	-0.362069
C	-2.498740	-0.553192	0.071903
S	1.356119	0.194936	-0.656641
C	2.026811	-0.692578	0.806506
H	3.083873	-0.868842	0.590230
H	1.526609	-1.653819	0.947819
H	1.944816	-0.078736	1.706818
H	-2.958931	-1.475582	-0.281820
H	-2.983112	0.320004	-0.371971
H	-2.548404	-0.484763	1.161637

Table SM23. Cartesian Coordinates of the Optimized Structure for the Transition State TS (sp,sp) → (sp,ap) at the B3LYP/6-311++G(3df,2p) Level of Approximation

Atom	X	Y	Z
O	-0.727872	1.384397	0.563316
C	-0.348920	0.419776	-0.035728
O	-1.116581	-0.627977	-0.356839
C	-2.491190	-0.549412	0.073965
S	1.350308	0.188364	-0.652796
C	2.021030	-0.683585	0.803682
H	3.071564	-0.856980	0.581644
H	1.524508	-1.639537	0.949482
H	1.941458	-0.065178	1.694107
H	-2.953186	-1.469338	-0.268725
H	-2.975604	0.316085	-0.373096
H	-2.543560	-0.470909	1.157990

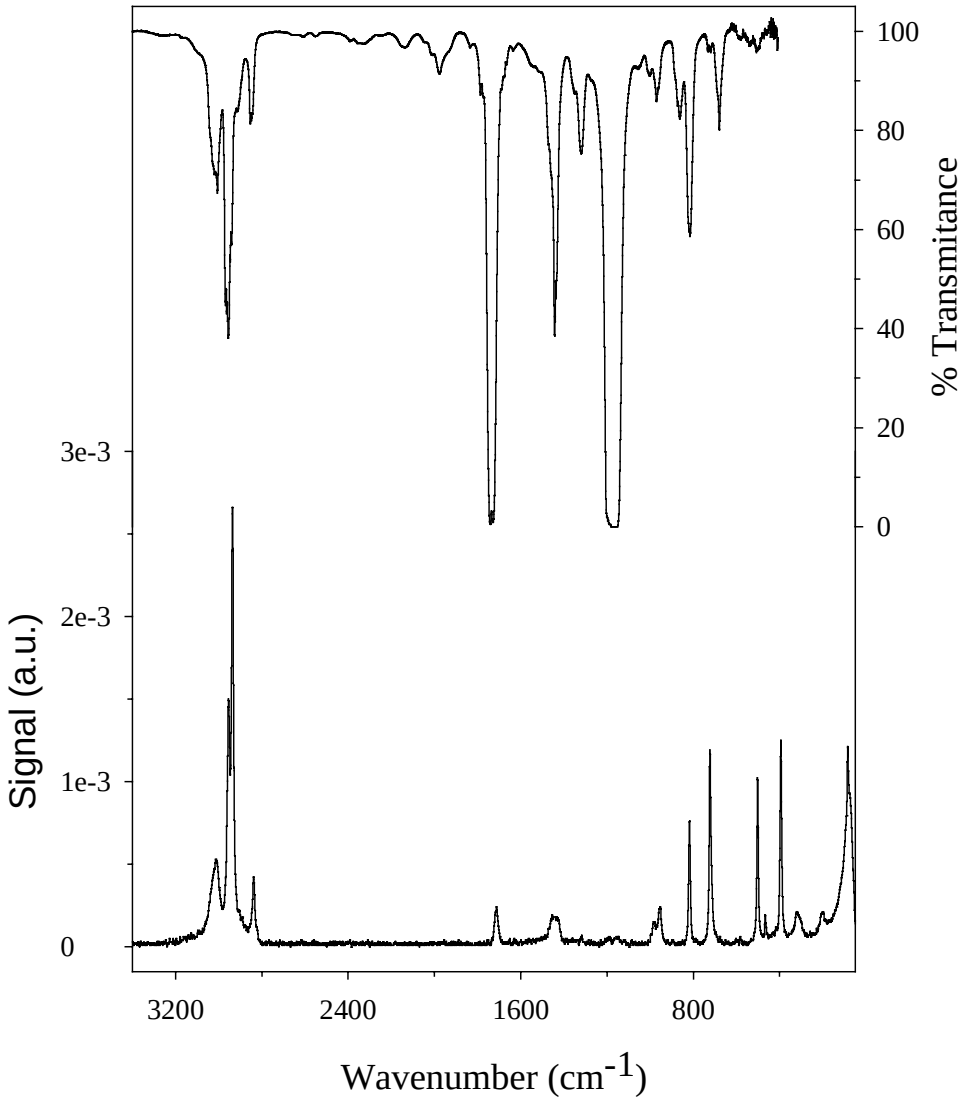

Figure SM1. Upper trace: IR (gas) spectrum of $CH_3OC(O)SCH_3$ (8.8 mbar at 200 mm optical path length and 300 K). Lower trace: Raman (liquid) spectrum of $CH_3OC(O)SCH_3$.

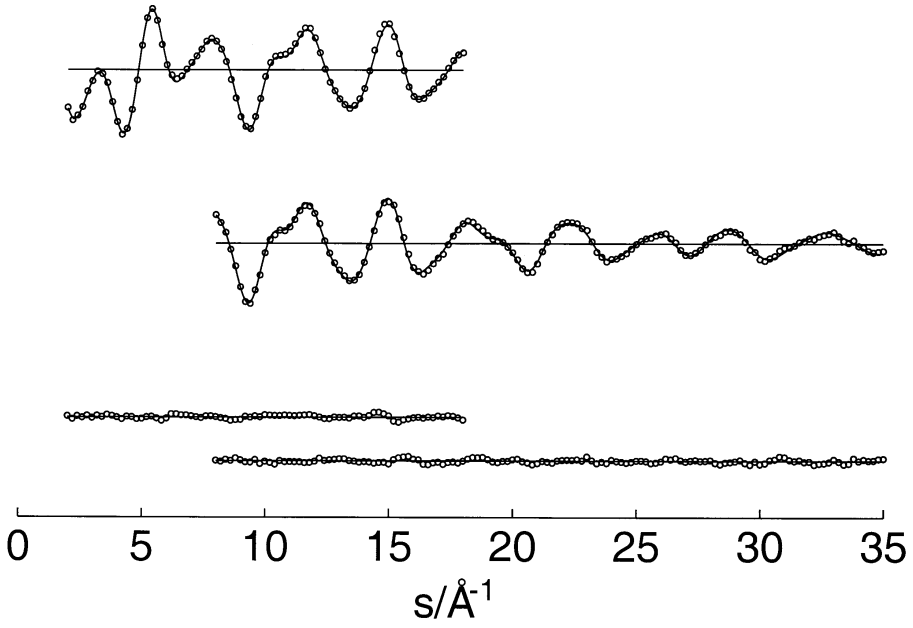

Figure SM2. Experimental (dots) and calculated (full line) molecular intensities for long (above) and short (below) nozzle-to-plate distances and residuals for $CH_3OC(O)SCH_3$.