The Rotational Spectrum of Monothioformic Acid
IV. *cis*- and *trans*-$H^{13}C(:O)SH$ and $HC(:^{18}O)SH$

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The microwave and millimeter wave spectra of two isotopically substituted species of monothioformic acid, $H^{13}COSH$ and $HC^{18}OSH$, have been investigated. Over 60 rotational transitions in the ground vibrational state have been assigned and measured for both the *cis* and *trans* thiol rotamers, HC(:O)SH, of each isotopic species. Rotational constants and quartic centrifugal distortion comstants of $H^{13}COSH$ and $HC^{18}OSH$ have been determined from the observed spectra. These data have been combined with previously published results on HCOSH, DCOSH, HCOSD and $HCO^{34}SH$ to obtain complete substitutions structures for the planar *cis* and *trans* rotamers of HC(:O)SH. All of the in-plane bond angles as well as the SH distance are significantly different for the two rotamers. For the *cis* rotamer the HSC and HCS angles increase by more than 2°, the OCS angle decreases by more than 3°, and the SH bond shortens compared to the *trans* rotamer geometry. The *cis* structure is: $r(C-H) = 1.104 \pm 0.003$ Å, $r(C=O)$ 1.203 ± 0.003 Å, $r(C-S) = 1.771 \pm 0.003$ Å, $r(S-H) = 1.335 \pm 0.002$ Å, $\sphericalangle(OCS) = 122.5^\circ \pm 0.3^\circ$, $\sphericalangle(HSC) = 94.9^\circ \pm 0.2^\circ$ and $\sphericalangle(HCS) = 114.4^\circ \pm 0.2^\circ$; whereas the *trans* structure is: $r(C-S) = 1.104 \pm 0.003$ Å, $r(C=O) = 1.205 \pm 0.003$ Å, $r(C-S) = 1.768 \pm 0.003$ Å, $r(S-H) = 1.354 \pm 0.002$ Å, $\sphericalangle(OCS) = 125.9^\circ \pm 0.3^\circ$, $\sphericalangle(HSC) = 92.5^\circ \pm 0.2^\circ$ and $\sphericalangle(HCS) = 111.0^\circ \pm 0.2^\circ$.

I. Introduction

Over the past two decades, microwave spectroscopy has provided a wealth of diverse information on the phenomenon of rotational isomerism in small molecules [1, 2]. Unfortunately, in only a few instances has the complete molecular structure of each rotameric form of such a molecule been precisely determined. Aside from their intrinsic interest to the physical chemist, accurate geometrical structures of rotational isomers have become of increasing importance in recent years due to the systematic investigation of conformation-related problems by quantum chemists [3]. It has been shown that both *ab initio* [4] and semi empirical [5] calculations of torsional potential energy curves, dipole moments, etc. are a sensitive function of molecular geometry. Furthermore, fundamental insight into the nonbonded forces within molecules is clearly dependent upon reliable results from quantum chemical calculations. The experimental determination of accurate structures for each form of a molecule that occurs as two or more rotational isomers is thus highly desirable.

Monothioformic acid exists in two distinct isomeric forms [6] which are the planar *cis* and *trans* rotamers of the thiol configuration, HC(:O)SH. In a series of papers [7–9] we have presented the spectra of the four isotopic species HCOSH, DCOSH, HCOSD and $HCO^{34}SH$, together with their rotational and centrifugal distortion constants. These data enabled us to derive a preliminary molecular structure for each rotamer. Stark effect measurements on HCOSH, DCOSH and HCOSD gave precise values for the electric dipole moment components of each rotamer. The change in the magnitude of the dipole moment components upon isotopic substitution has been used to determine the direction of the electric dipole moment [9]. Finally the energy difference between the ground vibrational states of the *trans* and *cis* rotamers was determined from relative intensity measurements. The ground state of the *cis* rotamer is higher by 231.3(6) cm^{-1} than that of the *trans* rotamer.

We have undertaken to investigate the vibrational ground state spectra of the two remaining singly substituted isotopic species, $H^{13}C(:O)SH$ and $HC(:^{18}O)SH$. The aim of these measurements was twofold: firstly, it is desirable to obtain a complete

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substitution structure, since internuclear distances between related molecules are best compared by using substitution structures. Secondly, we wanted to provide for monothioformic acid a complete set of experimentally determined, precise molecular parameters which can be used as a firm basis in future theoretical model calculations.

II. Experimental Procedures

The rotational spectra of $H^{13}COSH$ and $HC^{18}OSH$ were observed using samples which had been enriched with carbon-13 and oxygen-18 respectively. Except for the use of the appropriately labelled formic acid as starting material these samples were prepared following exactly the previously described procedure[7]. This preparation was slightly modified from that described first by Engler and Gattow in 1972[10]. Formic acid enriched in carbon-13 by 90% was purchased from Merck Sharp and Dohme Canada Limited, while formic acid enriched in oxygen-18 by ~40% was purchased from Stohler Isotope Chemicals, Mass., U.S.A. In both cases the enriched formic acid was used without further purification.

The microwave and millimeter wave spectrometers and their mode of operation have been described previously[7]. All frequency measurements were made at room temperature with sample pressures of less than 10 mTorr. The accuracy of these measurements is estimated to be better than ± 30 kHz.

III. Rotational Spectra and Assignment

The two isotopic species of monothioformic acid studied int his work, $H^{13}C(:O)SH$ and $HC(:^{18}O)SH$, like the other isotopes of this molecule which have been previously investigated[7, 8], exhibit both strong *a*- and *b*-type rotational spectra. The assignment process was straightforward and was carried through following the usual bootstrap procedure[7]. Over 60 transitions have been measured and assigned for both the *cis* and *trans* rotamers of each of the two isotopic species. These transitions were selected from amongst the much larger number of observable lines in such a way as to provide a nearly uniform sampling of the accessible branches.

Figure 1 shows an X-band survey spectrum of a monothioformic acid sample enriched in carbon-13 by ~90%. Only a few selected absorption lines have been identified in the figure, although most of the strong transitions which fall in this region have been assigned. The important $1_{01}-0_{00}$ absorption lines of *cis*- and *trans*-$H^{13}C(:O)SH$ fall just above 11.6 GHz and are strikingly similar in appearance to those of the $HC(:^{18}O)SH$ species and the parent isotopic species. (For comparison see Fig. 1 of Reference[7].) This is illustrated more clearly in Fig. 2 which compares in greater detail the spectra of carbon-13 (~90%) and oxygen-18 (~40%) labelled HCOSH samples near the position of the $1_{01}-0_{00}$ lines in the 11.0 – 11.9 GHz region. These two spectra may be compared with similar recordings of the microwave spectra of HCOSH, DCOSH and HCOSD presented in Fig. 3 of Reference[8].

The characteristic features of the monothioformic acid spectrum may be summarized. Firstly, it has been found that for all of the isotopically substituted forms studied, the frequency shift of the $1_{01}-0_{00}$ transitions is largest for $HC(:^{18}O)SH$. Furthermore the $1_{01}-0_{00}$ transitions of *cis*- and *trans*-monothio-

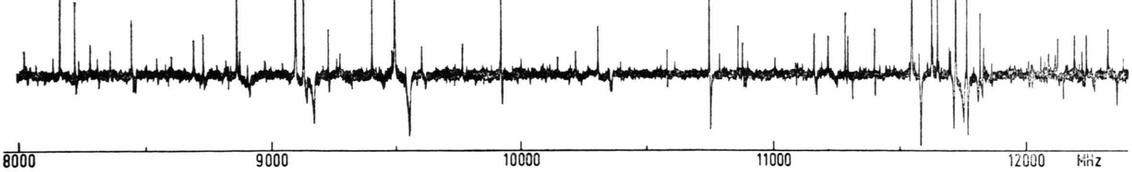


Fig. 1. Survey scan of the absorption spectrum of $H^{13}COSH$ from 8 to 12.4 GHz.

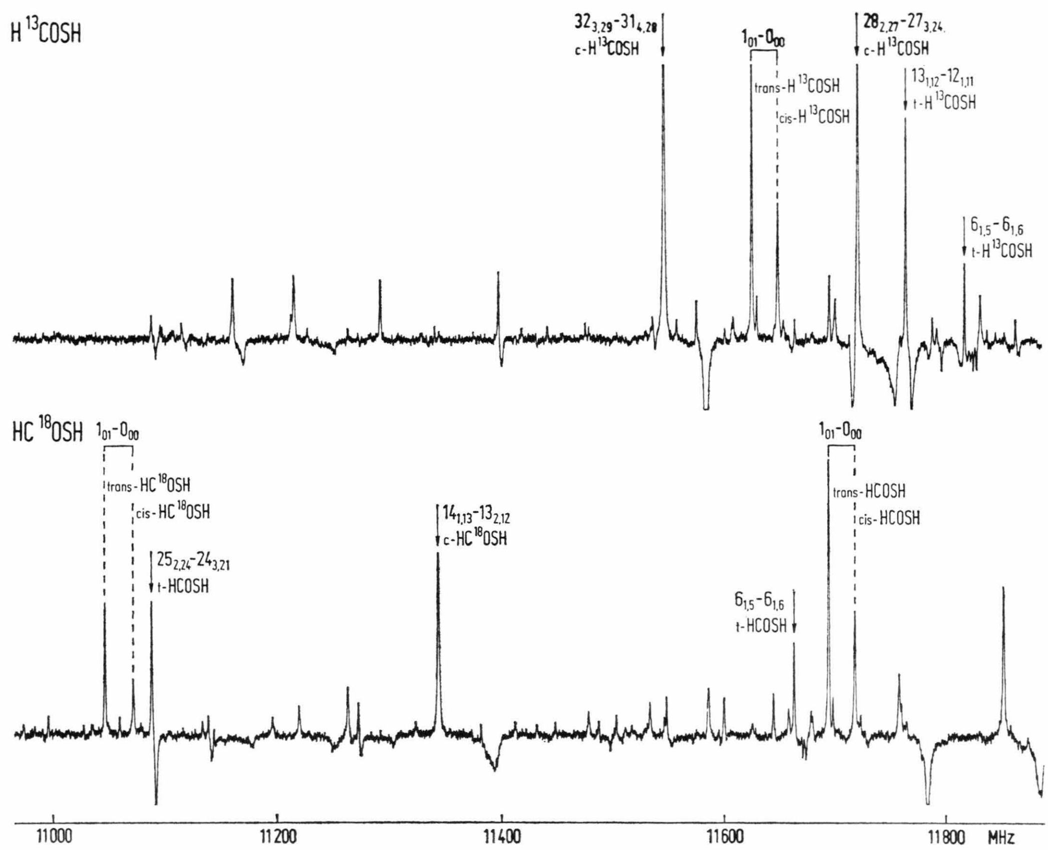


Fig. 2. Comparison of the absorption spectra of $H^{13}COSH$, HCOSH and $HC^{18}OSH$ in the region 11.0–11.9 GHz.

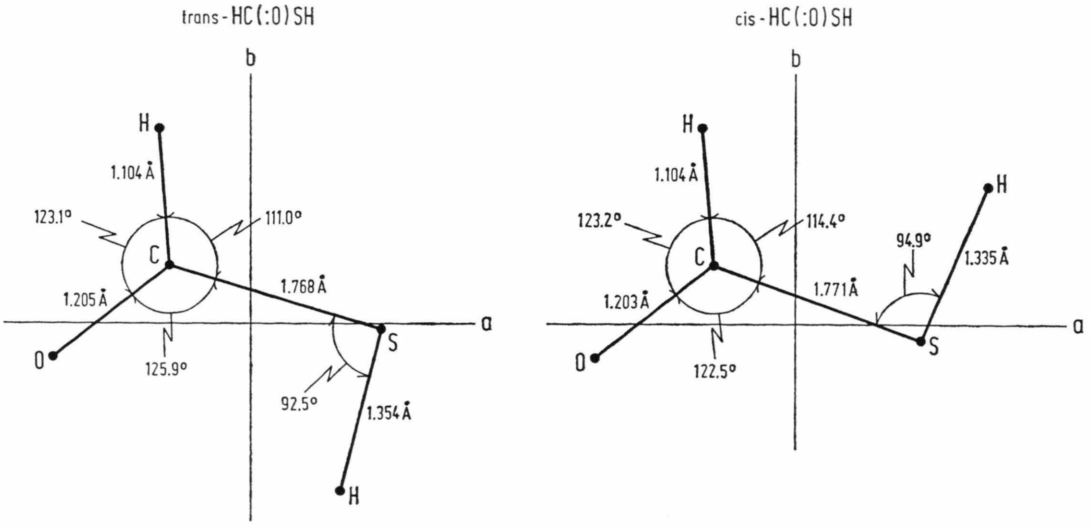


Fig. 3. Molecular structures of the two abundant isomers of monothioformic acid. On going from the *trans* to the *cis* rotamer the CSH and the HCS angles increase by more than two degress whereas the OCS angle decreases by 3.4°. The SH bond length shortens by 0.02 Å.

Table I. Observed *a*-type transitions of *cis*- and *trans*-$H^{13}COSH$ and $HC^{18}OSH$ in MHz.

Transition				$H^{13}COSH$				$HC^{18}OSH$			
				trans		*cis*		*trans*		*cis*	
J'	K_a' K_c'	J''	K_a'' K_c''	Observed	O−C	Observed	O−C	Observed	O−C	Observed	O−C
1	(0, 1)	0	(0, 0)	11625.830	0.003	11648.870	0.011	11046.830	0.003	11072.170	-0.003
2	(0, 2)	1	(0, 1)	23247.220	-0.008	23293.440	0.006	22090.130	-0.010	22140.950	0.001
2	(1, 2)	1	(1, 1)	22688.850	0.005	22740.535	0.007	21589.320	0.007	21645.435	0.046
2	(1, 1)	1	(1, 0)	23814.620	-0.013	23855.090	-0.018	22598.180	-0.013	22643.515	-0.008
3	(0, 3)	2	(0, 2)					33126.410	-0.015	33202.910	-0.027
3	(1, 3)	2	(1, 2)					32381.660	-0.005	32465.840	-0.005
3	(1, 2)	2	(1, 1)					33894.920	-0.005	33962.970	-0.014
3	(2, 2)	2	(2, 1)					33141.240	0.025	33217.370	0.030
3	(2, 1)	2	(2, 0)					33154.960	-0.019	33230.570	-0.035
7	(1, 7)	6	(1, 6)	79351.576	-0.015	79534.038	-0.019				
8	(0, 8)	7	(0, 7)	92637.244	-0.004	92833.152	0.027	88080.877	-0.001	88293.548	-0.004
8	(1, 8)	7	(1, 7)	90665.522	-0.026	90874.626	-0.020	86285.170	-0.000	86511.488	0.015
8	(1, 7)	7	(1, 6)	95161.751	-0.002	95326.205	0.001	90315.562	0.015	90498.983	-0.009
8	(2, 7)	7	(2, 6)	92949.454	-0.030	93135.361	0.011	88329.213	0.005	88533.328	-0.007
8	(2, 6)	7	(2, 5)	93312.003	0.000	93485.798	0.033	88616.746	-0.001	88810.512	0.012
8	(3, 6)	7	(3, 5)	93055.320	-0.010	93238.191	0.006	88414.067	-0.009	88615.691	0.029
8	(3, 5)	7	(3, 4)	93060.597	-0.004	93243.170	0.013	88417.750	-0.017	88619.132	0.005
8	(4, 5)	7	(4, 4)	93040.969[a]	0.010	93224.960[a]	0.030	88403.564[a]	0.010		
8	(4, 4)	7	(4, 3)	93040.969[a]	-0.018	93224.960[a]	0.005	88403.564[a]	-0.007		
8	(5, 4)	7	(5, 3)	93037.669	-0.009	93222.675[a]	0.028	88402.359[a]	-0.005		
8	(5, 3)	7	(5, 2)	93037.669[a]	-0.009	93222.675	0.028	88402.359	-0.005		
8	(6, 3)	7	(6, 2)	93040.076	-0.047	93226.097	0.002	88405.984	-0.041	88610.530	-0.012
8	(6, 2)	7	(6, 1)	93040.076[a]	-0.047	93226.097[a]	0.002	88405.984	-0.041	88610.530[a]	-0.012
8	(7, 2)	7	(7, 1)	93045.770[a]	-0.110	93232.897[a]	-0.044	88412.497[a]	-0.127	88618.133[a]	-0.060
8	(7, 1)	7	(7, 0)	93045.770[a]	-0.110	93232.897[a]	-0.044	88412.497[a]	-0.127	88618.133[a]	-0.060
13	(0, 13)	12	(0, 12)	149589.014	0.019	149934.845	-0.003				
13	(1, 13)	12	(1, 12)	147095.312	0.015	147440.766	-0.010				
13	(1, 12)	12	(1, 11)	154343.045	0.014	154618.685	-0.004				
13	(2, 12)	12	(2, 11)	150860.716	0.002	151166.946	-0.007				
13	(2, 11)	12	(2, 10)	152376.981	0.022	152634.740	0.023				
13	(3, 11)	12	(3, 10)	151293.651	0.021	151586.789	0.032				
13	(3, 10)	12	(3, 9)	151356.051	0.037	151645.615	0.007				
13	(4, 10)	12	(4, 9)	151238.682[a]	0.065	151534.111[a]	0.053				
13	(4, 9)	12	(4, 8)	151239.553	-0.018	151534.902	-0.034				
13	(5, 9)	12	(5, 8)	151209.045	0.019	151506.919	0.028				
13	(5, 8)	12	(5, 7)	151209.045[a]	0.011	151506.919[a]	0.021				
13	(6, 8)	12	(6, 7)	151200.055	-0.024	151499.983	-0.028				
13	(6, 7)	12	(6, 6)	151200.055[a]	-0.024	151499.983[a]	-0.028				
13	(7, 7)	12	(7, 6)	151201.684[a]	-0.116	151503.671[a]	-0.089				
13	(7, 6)	12	(7, 5)	151201.684[a]	-0.116	151503.671[a]	-0.089				
15	(1, 14)	14	(1, 13)	177894.922	0.016	178218.833	-0.019				
16	(0, 16)	15	(0, 15)					174520.277	0.010	174994.563	-0.018
16	(1, 16)	15	(1, 15)					172154.838	-0.022	172617.611	0.006
16	(1, 15)	15	(1, 14)					180089.805	-0.008	180473.342	0.018
16	(2, 15)	15	(2, 14)					176329.499	0.024	176745.539	0.007
16	(2, 14)	15	(2, 13)					178505.791	0.014	178849.530	0.005
16	(3, 14)	15	(3, 13)					176953.893	0.003	177349.642	-0.003
16	(3, 13)	15	(3, 12)					177077.749	0.011	177465.935	-0.018
16	(4, 13)	15	(4, 12)					176885.742	0.005	177284.009	0.011
16	(4, 12)	15	(4, 11)					176888.315	-0.016	177286.355	-0.014
16	(5, 12)	15	(5, 11)					176840.551[a]	-0.000		
16	(5, 11)	15	(5, 10)					176840.551[a]	-0.028		

[a] Not included in the fit.

Table I, continued

Transition				$H^{13}COSH$				$HC^{18}OSH$			
				trans		*cis*		*trans*		*cis*	
J'	K_a' K_c'	J''	K_a'' K_c''	Observed	O−C	Observed	O−C	Observed	O−C	Observed	O−C
5	(1, 4)	5	(1, 5)	8442.258	0.007	8358.197	0.014				
6	(1, 5)	6	(1, 6)	11817.775	0.001	11700.115	0.014	10590.930	0.002	10478.102	0.008
7	(1, 6)	7	(1, 7)					14119.215	0.006	13968.825	0.014
8	(1, 7)	8	(1, 8)	20250.505	0.005	20049.030	0.002			17956.345	0.015
9	(1, 8)	9	(1, 9)	25304.470	-0.009	25052.950	0.004				
10	(1, 9)	10	(1, 10)					27710.590	-0.007	27416.030	-0.010
11	(1, 10)	11	(1, 11)					33236.740	0.002	32883.955	-0.012
12	(1, 11)	12	(1, 12)					39255.730	0.007	38839.920	-0.002
15	(2, 13)	15	(2, 14)	9920.390	0.001	9602.748	0.005				
16	(2, 14)	16	(2, 15)			12219.940	0.000	10100.290	0.001		
17	(2, 15)	17	(2, 16)					12665.580	-0.002	12233.350	-0.007
18	(2, 16)	18	(2, 17)	19456.405	-0.003	18860.140	0.011	15650.105	0.002	15123.255	0.000
19	(2, 17)	19	(2, 18)	23654.870	-0.003	22942.985	-0.022				
21	(2, 19)	21	(2, 20)					27372.640	0.000		
22	(2, 20)	22	(2, 21)					32268.730	-0.003	31255.740	0.011
23	(2, 21)	23	(2, 22)					37681.880	0.004	36523.280	-0.016

formic acid occur always as a fairly closely spaced "doublet", in which the $1_{01}-0_{00}$ transition of the *cis* rotamer occurs for all isotopic species, with the exception of HCOSD, at slightly higher frequencies than the corresponding transition of the *trans* rotamer.

IV. Centrifugal Distortion Analysis

The measured rotational transition frequencies of *cis*- and *trans*-$H^{13}C(:O)SH$ and $HC(:^{18}O)SH$ were analysed using the reduced Hamiltonian reported by Watson[11] in which $\tilde{R}_6$ is set equal to zero. The analysis was performed in the I^r axis representation so that the Hamiltonian may be written as

$$\begin{aligned}\mathcal{H} = {}& {}^1\!/_2(\tilde{B}+\tilde{C})P^2 + [\tilde{A}-{}^1\!/_2(\tilde{B}+\tilde{C})]P_a^2 \\ & + {}^1\!/_2(\tilde{B}-\tilde{C})(P_b^2-P_c^2) - \Delta_J P^4 \\ & - \Delta_{JK} P^2 P_a^2 - \Delta_K P_a^4 - 2\,\delta_J P^2 (P_b^2 - P_c^2) \\ & - \delta_K [P_a^2 (P_b^2 - P_c^2) + (P_b^2 - P_c^2) P_a^2] \qquad (1)\end{aligned}$$

where P, P_a, P_b, and P_c are the operators for the total angular momentum and its components along the principal inertial axes. The parameters $\tilde{A}$, $\tilde{B}$ and $\tilde{C}$ are Watson's reduced rotational constants and the deltas are the quartic centrifugal distortion constants.

An iterative least squares procedure[12] was used to fit the observed spectra to the above Hamiltonian. To ensure that the results would not be seriously biased by the neglect of higher order distortion terms from the Hamiltonian, the data sets were restricted[7, 8] to include only transitions with J less than 25 and K_a less than 7. The observed and calculated transition frequencies are listed in Tables I and II, the spectroscopic constants are given in Table III.

Tables IV and V contain values of the rotational constants and centrifugal distortion constants for alternative formulations of the rotational Hamiltonian. These parameters, and their calculation from the spectroscopic constants (Table III), have been discussed in detail previously[7, 12, 13]. Watson's determinable parameters[11], which are invariant to a unitary transformation, are reported in Table IV. The constants presented in Table V were obtained by application of the planarity constraints (case 1 of Reference[12]).

V. Molecular Structure

The moments of inertia and the inertial defect of each of the isotopic species of monothioformic acid investigated to date are collected in Table VI. These numbers were calculated from the Kivelson and Wilson[14] rotational constants, α', β', γ', reported in Table V, of this paper, Table V of Ref.[7] and Table IX of Ref.[8] using the conversion factor $(\beta' \cdot I_b) = 505379.0(38)$ MHz·u·Å². The small positive values observed for the inertial defect strongly indicate that both rotamers are planar in their equilibrium configuration. This has been confirmed by calcula-

Table II. Observed *b*-type transitions of *cis*- and *trans*-$H^{13}COSH$ and $HC^{18}OSH$ in MHz.

Transition		$H^{13}COSH$				$HC^{18}OSH$			
		trans		*cis*		*trans*		*cis*	
J' K_a' K_c'	J'' K_a'' K_c''	Observed	O−C	Observed	O−C	Observed	O−C	Observed	O−C
3 (1, 3)	2 (0, 2)	87880.352	-0.031						
13 (1, 13)	12 (0, 12)					178416.125	-0.004	179772.577	0.010
14 (1, 14)	13 (0, 13)					186789.015	0.036	188178.133	0.007
11 (1, 10)	11 (0, 11)	75557.038	0.002	76077.649	0.001				
12 (1, 11)	12 (0, 12)	79812.739	0.010	80272.004	-0.012				
13 (1, 12)	13 (0, 13)	84566.774	0.009	84955.867	0.009				
14 (1, 13)	14 (0, 14)	89843.346	-0.002	90153.174	0.011	86419.701	0.014	86849.608	0.034
15 (1, 14)	15 (0, 15)	95663.757	0.005	95885.273	0.000	91500.815	-0.004	91848.582	0.005
6 (2, 5)	6 (1, 6)							174195.052[a]	-0.073
7 (2, 6)	7 (1, 7)							175960.194	-0.032
8 (2, 7)	8 (1, 8)					175482.247	-0.042	177982.086	-0.002
9 (2, 8)	9 (1, 9)			179065.739	-0.037	177787.659	0.026	180262.281	0.000
10 (2, 9)	10 (1, 10)					180355.932	0.001		
8 (2, 6)	8 (1, 7)	154936.333	-0.029	157344.589	-0.020				
10 (2, 8)	10 (1, 9)	150942.795	-0.001	153360.038	-0.016				
12 (2, 10)	12 (1, 11)	146847.679	0.013	149252.236	0.022				
1 (1, 1)	2 (0, 2)					33105.090	-0.002	33923.180	-0.018
2 (1, 2)	3 (0, 3)	18990.210	-0.005	19709.035	0.025				
3 (1, 3)	4 (0, 4)					9797.460	-0.011	10576.740	-0.009
6 (0, 6)	5 (1, 5)	19008.985	0.000	18333.810	0.005	14396.060	0.006	13649.120	0.009
7 (0, 7)	6 (1, 6)					26788.850	0.002		
8 (0, 8)	7 (1, 7)					39354.730	0.005	38637.870	0.002
11 (0, 11)	10 (1, 10)	86071.111	0.008	85473.488	0.015				
12 (0, 12)	11 (1, 11)					90897.586	-0.017	90256.780	0.011
16 (0, 16)	15 (1, 15)	154705.123	0.011	154275.794	0.013				
10 (2, 9)	11 (1, 10)	18097.960	-0.008	20356.265	-0.009	28566.760	-0.017		
11 (2, 10)	12 (1, 11)					14641.330	-0.016	17129.390	-0.020
13 (1, 12)	12 (2, 11)	11764.700	-0.008	9495.270	-0.003				
14 (1, 13)	13 (2, 12)			24757.340	-0.009	13842.310	-0.006	11346.030	-0.010
15 (1, 14)	14 (2, 13)					28385.080	-0.021		
18 (1, 17)	17 (2, 16)	90085.650	-0.038	87785.876	-0.040				
19 (1, 18)	18 (2, 17)							85811.875	-0.040
14 (2, 12)	15 (1, 15)					37939.470	0.005	39594.940	-0.004
15 (2, 13)	16 (1, 16)					32963.020	-0.005	34483.020	0.005
16 (2, 14)	17 (1, 17)	23807.820	-0.003	24886.940	0.000	28623.130	0.006	29993.740	0.005
17 (2, 15)	18 (1, 18)	20740.350	-0.002	21646.180	0.012				
18 (2, 16)	19 (1, 19)	18486.530	-0.002	19204.540	0.001				
21 (2, 19)	22 (1, 22)					17505.515	-0.003	17919.325	-0.004
22 (2, 20)	23 (1, 23)					17550.870	0.003	17734.590	0.002
23 (2, 21)	24 (1, 24)	20108.335	0.003	19698.010	-0.002				
14 (3, 12)	15 (2, 13)	91695.998	0.009	95490.749	-0.007				
19 (3, 17)	20 (2, 18)	20341.280	0.002	24388.845	0.008	39590.030	-0.006		
20 (3, 18)	21 (2, 19)			9097.765	0.005			29870.960	0.009
21 (3, 19)	22 (2, 20)					10948.330	0.009	15450.500	0.008
22 (2, 20)	21 (3, 19)	10747.665	0.007						
23 (2, 21)	22 (3, 20)			22582.845	0.034				
24 (2, 22)	23 (3, 21)							14376.125	0.032
15 (3, 12)	16 (2, 15)	91118.494	-0.019	94529.061	0.030				
17 (3, 14)	18 (2, 17)							86837.966	0.020
22 (3, 19)	23 (2, 22)	22833.990	0.012	25624.510	-0.003	36326.470	-0.008		
23 (3, 20)	24 (2, 23)					27850.800	0.008	30988.940	-0.004

[a] Not included in the fit.

Table III. Rotational constants and centrifugal distortion constants of monothioformic acid [a].

	cis-$H^{13}C(:O)SH$	*trans*-$H^{13}C(:O)SH$	
$\tilde{A}$	61295.6325 (39)	60503.9010 (37)	MHz
$\tilde{B}$	6103.12450 (39)	6094.40708 (36)	MHz
$\tilde{C}$	5545.74954 (39)	5531.43327 (36)	MHz
Δ_J	3.62686 (81)	3.38315 (76)	kHz
Δ_{JK}	−46.448 (14)	−41.664 (13)	kHz
Δ_K	1281.86 (38)	1232.70 (35)	kHz
δ_J	0.466269 (75)	0.437076 (72)	kHz
δ_K	17.485 (28)	16.374 (25)	kHz
σ [b]	18.7	16.8	kHz
N [c]	60	57	
	cis-$HC(:^{18}O)SH$	*trans*-$HC(:^{18}O)SH$	
$\tilde{A}$	61850.9798 (37)	60972.0319 (33)	MHz
$\tilde{B}$	5785.66443 (36)	5775.67561 (31)	MHz
$\tilde{C}$	5286.52128 (36)	5271.16418 (31)	MHz
Δ_J	3.29749 (66)	3.06850 (60)	kHz
Δ_{JK}	−47.478 (13)	−42.807 (12)	**kHz**
Δ_K	1296.41 (48)	1240.91 (56)	kHz
δ_J	0.403526 (75)	0.378236 (68)	kHz
δ_K	15.864 (25)	14.827 (20)	kHz
σ [b]	17.4	14.4	kHz
N [c]	61	64	

[a] The numbers in parentheses are standard errors.

[b] Standard deviation of the fit.

[c] The number of equally weighted transitions included in the fit.

Table IV. Watson's determinable rotational constants and quartic centrifugal distortion constants of monothioformic acid [a, b].

	cis-$H^{13}C(:O)SH$	*trans*-$H^{13}C(:O)SH$	
$\mathfrak{A}$	61295.6397 (39)	60503.9077 (37)	MHz
$\mathfrak{B}$	6103.04940 (40)	6094.33856 (36)	MHz
$\mathfrak{C}$	5545.74625 (40)	5531.43200 (36)	MHz
τ'_{aaaa}	−4956.1 (15)	−4777.7 (14)	kHz
τ'_{bbbb}	−18.2376 (33)	−17.0292 (31)	kHz
τ'_{cccc}	−10.7773 (33)	−10.0360 (31)	kHz
τ_1	142.271 (57)	126.059 (52)	kHz
τ_2'	0.8763 (56)	0.4230 (52)	kHz
$\Delta\tau'_{cccc}$	−0.0192 (12)	−0.0240 (12)	kHz
	cis-$HC(:^{18}O)SH$	*trans*-$HC(:^{18}O)SH$	
$\mathfrak{A}$	61850.9864 (37)	60972.0381 (33)	MHz
$\mathfrak{B}$	5785.59101 (36)	5775.60853 (31)	MHz
$\mathfrak{C}$	5286.51293 (36)	5271.15792 (31)	MHz
τ'_{aaaa}	−5008.9 (19)	−4804.7 (22)	kHz
τ'_{bbbb}	−16.4182 (27)	−15.2999 (25)	kHz
τ'_{cccc}	−9.9618 (27)	−9.2481 (25)	kHz
τ_1	150.343 (54)	134.404 (48)	kHz
τ_2'	1.6729 (49)	1.2841 (44)	kHz
$\Delta\tau'_{cccc}$	−0.0145 (11)	−0.01942 (91)	kHz

[a] The numbers in parentheses are standard errors.

[b] $\tau_2' = \tau_2/(\alpha+\beta+\gamma)$; where α, β and γ are rotational constants defined by Kivelson and Wilson [14]. See also References [11–13].

Table V. Rotation constants and quartic centrifugal distortion constants derived from the planarity relations [a].

	cis-$H^{13}C(:O)SH$	*trans*-$H^{13}C(:O)SH$	
α'	61295.615	60503.884	MHz
β'	6103.0719	6094.3574	MHz
γ'	5545.8108	5531.4910	MHz
$h^4\,\tau_{aabb}$	147.16	134.70	kHz
$h^4\,\tau_{bbcc}$	−13.854	−12.903	kHz
$h^4\,\tau_{aacc}$	80.946	71.031	kHz
$h^4\,\tau_{abab}$	−35.992	−33.383	kHz
	cis-$HC(:^{18}O)SH$	*trans*-$HC(:^{18}O)SH$	
α'	61850.964	60972.018	MHz
β'	5785.6167	5775.6306	MHz
γ'	5286.5767	5271.2163	MHz
$h^4\,\tau_{aabb}$	143.52	131.36	kHz
$h^4\,\tau_{bbcc}$	−12.660	−11.762	kHz
$h^4\,\tau_{aacc}$	83.232	73.508	kHz
$h^4\,\tau_{abab}$	−31.873	−29.352	kHz

[a] Calculated using the planarity relations as described in Ref. [12], case 1.

tions of the inertial defect based on preliminary harmonic force fields [15].

The substitution coordinates [16] of all five atoms in each of the two rotamers of HC(:O)SH were calculated from the ground state moments of inertia given in Table VI using Kraitchman's equations [17] for a planar molecule

$$|a| = \left\{\frac{\Delta I_b}{\mu}\left(1+\frac{\Delta I_a}{I_a - I_b}\right)\right\}^{\frac{1}{2}} \tag{2 a}$$

$$|b| = \left\{\frac{\Delta I_a}{\mu}\left(1+\frac{\Delta I_b}{I_b - I_a}\right)\right\}^{\frac{1}{2}} \tag{2 b}$$

where $\Delta I_g = I_g' - I_g$ is the change in the gth moment of inertia on isotopic substitution and μ is the reduced mass. Since the b-coordinate of the sulfur atom in each rotamer was found to be less than the minimum distance (0.15 Å) that Costain [16] has suggested can be safely determined by Kraitchman's equations, it was recalculated using the centre of mass condition

$$\sum_i m_i\, b_i = 0\,. \tag{3}$$

Final values for the various coordinates are presented in Table VII. The uncertainty in these numbers due to measurement error in the rotational constants is less than one digit in the last significant figure in every case. However it is well known that vibrational effects can unfortunately cause substitution coordinates to differ from the equilibrium, r_e,

Table VI. Moments of inertia and inertial defect of monothioformic acid [a, b].

	HC(:O)SH	DC(:O)SH	$H^{13}C$(:O)SH	HC(:^{18}O)SH	HC(:O)^{34}SH	HC(:O)SD
cis						
I_a	8.0311061	10.441015	8.2449454	8.1709155	8.0586761	9.1823310
I_b	82.386996	82.959319	82.807316	87.350930	84.397154	84.862428
I_c	90.491625	93.484010	91.128063	95.596645	92.529521	94.113324
Δ	0.073523	0.083676	0.075802	0.074800	0.073691	0.068565
trans						
I_a	8.1465341	10.535131	8.3528356	8.2887039	8.1494571	9.9464884
I_b	82.507420	83.068581	82.925724	87.501960	84.626461	83.036931
I_c	90.737200	93.696914	91.363974	95.875216	92.859191	93.069387
Δ	0.083246	0.093202	0.085414	0.084552	0.083273	0.085968

[a] All constants are for the ground vibrational state and are measured in units of $uÅ^2$. [b] $\Delta = I_c - I_b - I_a$.

Table VII. Substitution coordinates of *cis*- and *trans*-HC(:O)SH [a, b].

	cis-HC(:O)SH	*trans*-HC(:O)SH
a(H)	-0.7478 ± 0.0020	-0.7406 ± 0.0020
a(C)	-0.6515 ± 0.0023	-0.6500 ± 0.0023
a(O)	-1.5975 ± 0.0005	-1.6024 ± 0.0005
a(S)	1.0194 ± 0.0007	1.0468 ± 0.0007
a(H) [c]	1.5688 ± 0.0010	0.7224 ± 0.0021
b(H)	1.5660 ± 0.0010	1.5590 ± 0.0010
b(C)	0.4667 ± 0.0032	0.4584 ± 0.0033
b(O)	-0.2772 ± 0.0027	-0.2795 ± 0.0027
b(S) [d]	-0.1204 ± 0.0018	-0.0387 ± 0.0018
b(H) [c]	1.0960 ± 0.0014	-1.3530 ± 0.0011

[a] All coordinates are measured in Å units relative to the principal axis system of *cis*- or *trans*-HC(:O)SH.

[b] The error limits are estimates of the possible deviation from the equilibrium coordinates due to vibrational effects.

[c] Labile hydrogen atom.

[d] This coordinate was fixed using the center of mass relation; the substitution values are -0.1210 ± 0.0062 Å for *cis*- and -0.0394 ± 0.0190 Å for *trans* species.

coordinates by as much as several thousands of an angstrom.

The importance of vibrational contributions to the r_s structural parameters determined for monothioformic acid was investigated in the following way: If $\delta(\Delta I) = \Delta I^0 - \Delta I^e$ is the deviation of a ground state moment of inertia difference from its equilibrium value, then for a planar near prolate asymmetric top molecule [such as *cis*- or *trans*-HC(:O)SH] the deviation of the corresponding r_s coordinate from its equilibrium value, δr_s, is given by

$$\delta r_s \cong \delta(\Delta I)/2\,\mu\,r_s\,. \tag{4}$$

Costain [18] found $\delta(\Delta I) \cong -0.0024\ u \cdot Å^2$ for substitution of the central nitrogen atom in nitrous oxide, N_2O. He further suggested that this might be a fairly typical result. Recently, Schwendeman [19] has proposed that the "Costain Rule", with $|\delta(\Delta I)| = 0.003\ u \cdot Å^2$, should be adopted as a means of obtaining realistic error estimates for r_s structures. The error limits reported in Table VII, for all coordinates except $b(S)$, were calculated using Eq. (4) with Schwendeman's value of $\delta(\Delta I)$. The error limits on $b(S)$ were obtained by propagation of errors through the center of mass relation.

Equations (2) are strictly valid only for a rigid planar molecule. Since the relation $I_c - I_b - I_a = 0$ is also valid for such a molecule, Eqs. (2) may be rewritten in terms of (I_b, I_c) or (I_a, I_c). For the purpose of calculating an r_s structure from ground state moments of inertia there does not appear to be any reason to presume that one form of Kraitchman's equations is inherently better than the other two. Consequently the structures of *cis*- and *trans*-HC(:O)SH were also determined using the two alternative formulations of Equations (2). In each instance the small sulfur b-coordinate was obtained by applying the center of mass relation. The resulting bond lengths and angles for all of the structures are summarized in Table VIII. The observed variations in the structural parameters obtained for each rotamer by the different methods are compatible with the error estimates determined using the "Costain Rule".

A majority of the r_s structures reported in the literature for planar molecules to date have been calculated using only one set of moment of inertia data. Normally, the (I_a, I_b) data has been the preferred set, although in some instance, where only approximate I_a values could be obtained, structures calculated from (I_b, I_c) have been published. Thus,

Table VIII. Substitution structure, of *cis*- and *trans*-HC(:O)SH [a, b].

cis	(I_b, I_c)	(I_a, I_c)	(I_a, I_b)	
r(C–H)	1.1044	1.1041	1.1036 ± 0.0033	Å
r(C=O)	1.2057	1.2022	1.2034 ± 0.0032	Å
r(C–S)	1.7720	1.7728	1.7711 ± 0.0026	Å
r(S–H)	1.3330	1.3341	1.3348 ± 0.0021	Å
∢(OCS)	122.24	122.43	122.46 ± 0.25	degree
∢(HSC)	94.90	94.90	94.95 ± 0.15	degree
∢(HCS)	114.45	114.60	114.37 ± 0.20	degree
$\Sigma m_i a_i$	0.05129	0.01949	0.05085	uÅ
$\Sigma m_i a_i b_i$	0.05768	0.03933	0.06124	uÅ^2
$I_a^0 - I_a^s$	−0.00413	0.04253	0.04279	uÅ^2
$I_b^0 - I_b^s$	0.20461	0.15752	0.20363	uÅ^2
$I_c^0 - I_c^s$	0.27400	0.27358	0.31994	uÅ^2
trans	(I_b, I_c)	(I_a, I_c)	(I_a, I_b)	
r(C–H)	1.1052	1.1048	1.1043 ± 0.0034	Å
r(C=O)	1.2071	1.2037	1.2048 ± 0.0032	Å
r(C–S)	1.7689	1.7698	1.7681 ± 0.0025	Å
r(S–H)	1.3545	1.3534	1.3538 ± 0.0021	Å
∢(OCS)	125.68	125.88	125.90 ± 0.26	degree
∢(HSC)	92.55	92.52	92.46 ± 0.15	degree
∢(HCS)	111.11	111.27	111.04 ± 0.20	degree
$\Sigma m_i a_i$	0.02221	−0.00629	0.02180	uÅ
$\Sigma m_i a_i b_i$	0.14641	0.12427	0.14603	uÅ^2
$I_a^0 - I_a^s$	−0.01907	0.03250	0.03286	uÅ^2
$I_b^0 - I_b^s$	0.25268	0.20144	0.25161	uÅ^2
$I_c^0 - I_c^s$	0.31686	0.31718	0.36772	uÅ^2

[a] In each case the small b-coordinate of the sulfur atom has been fixed using the center of mass relation.

[b] The error limits on the structural parameters calculated from the (I_a, I_b) data were obtained by propagation of the errors given in Table VII.

for the purpose of comparison with other molecules, the structures obtained in this work from (I_a, I_b) should be the appropriate ones. These structures are illustrated in Figure 3.

VI. Discussion

The structures determined for the two rotamers of monothioformic acid in this work differ significantly from each other. Similar differences were observed between the preliminary structures reported earlier [8]. A qualitative explanation for these differences in terms of nonbonded forces has been presented [8] and will not be repeated here.

The bond lengths and angles determined for the formyl group in monothioformic acid and a number of related molecules are compared in Table IX. Only structures determined by microwave spectroscopy (preferably r_s structures) have been included in Table IX in order to avoid the model problems encountered when structures determined by different techniques are compared [33]. The range in values of the formyl group parameters is seen to be very small: discounting the acetaldehyde r_0 structure $\Delta r(\mathrm{C=O}) = 0.038$ Å, $\Delta r(\mathrm{C-H}) = 0.013$ Å, Δ∢(HCO) = 5.7° and Δ∢(OCX) = 5.3°. Nonetheless, there do appear to be some definite trends to the variations in at least the first three of these parameters. The molecules have been organized in Table IX according to C = O bond length, from smallest (HCOF) to largest (*trans*-CH_2CHCO). It will be noted that this is roughly equivalent to a listing based on increasing C – H bond length or decreasing HCO angle. Furthermore, the observed changes are strongly correlated with the electronegativity of the substituent X: electron attracting substituents shorten the C = O and C – H bonds and increase the HCO angle, while electron donating groups have the opposite influence. The explanation for this behaviour likely involves both inductive effects [22] and contribution from resonance structures such as [34, 35]

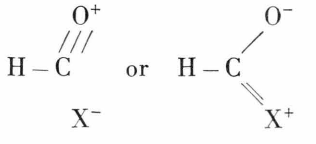


Table IX. Structure of the formyl group in monothioformic acid and related molecules[a].

Molecule	r(C=O)	r(C–H)	$\sphericalangle$(HCO)	$\sphericalangle$(OCX)	Ref.
HCOF	1.181 ± 0.005	1.095 ± 0.008	127.3 ± 3.0	122.8 ± 0.5	20
HCOOCHO[b]	1.184 ± 0.003	1.098 ± 0.004	126.9 ± 0.5	120.6 ± 0.3	21
HCOCl[c]	1.188 ± 0.003	1.096 ± 0.003	126.5 ± 0.4	123.5 ± 0.4	22
HCOOCHO[b]	1.197 ± 0.003	1.095 ± 0.003	125.3 ± 0.3	125.9 ± 0.3	21
$HCOOCH_3$	1.200 ± 0.010	1.101 ± 0.010	124.8 ± 1.0	125.9 ± 1.0	23
trans-HCOOH[d]	1.202 ± 0.010	1.097 ± 0.005	124.1 ± 2.0	124.9 ± 1.0	24
cis-HCOSH	1.203 ± 0.003	1.104 ± 0.003	123.2 ± 0.3	122.5 ± 0.3	
H_2CO[c]	1.204 ± 0.003	1.102 ± 0.003	121.7 ± 0.3	121.7 ± 0.3	25
trans-HCOSH	1.205 ± 0.003	1.104 ± 0.003	123.1 ± 0.3	125.9 ± 0.3	
CH_2OHCHO[c]	1.209 ± 0.003	1.102 ± 0.003	122.0 ± 0.3	122.7 ± 0.3	26
HCCCHO[c]	1.215 ± 0.003	1.106 ± 0.003	122.3 ± 0.3	123.8 ± 0.3	27
CH_3CHO[e]	1.216 ± 0.002	1.114 ± 0.015	118.6 ± 0.7	123.9 ± 0.1	28
NH_2CHO	1.219 ± 0.012	1.098 ± 0.010	122.5 ± 2.0	124.7 ± 0.3	29
trans-CH_2CHCHO	1.219 ± 0.005	1.108 ± 0.003	121.6 ± 0.3	123.3 ± 0.3	30

[a] All structures, except where otherwise indicated, are r_s structures; bond lengths are measured in Å units and angles in degrees.

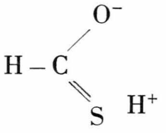
[b] The two formyl groups in formic anhydride have different structures.

[c] The error limits given for formyl chloride, formaldehyde, glycolaldehyde and propynal were estimated by the present authors; the original authors either gave no error limits or gave errors reflecting only measurement uncertainty.

[d] A rather different structure to that quoted here has more recently been reported for the *trans* rotamer of formic acid by Bellet et al.[31]. However, these authors apparently used questionable substitution values for several small coordinates[32] and hence it is expected that the earlier structure of Kwei and Curl[24] is to be preferred. The *cis* rotamer of formic acid has recently been detected but an accurate structure is not yet available.

[e] This is an r_0 structure; some caution should be used in comparing it to the other (r_s) structures.

Table X presents a comparison of the SH group structural parameters of the few thiols whose molecular structure has been completely determined by microwave spectroscopy. The SH bond lengths show only a very small range in values (0.032 Å) with a slight indication that this bond is a bit longer than normal in monothioformic acid. This could be attributed to a small degree of ionic character as represented by the resonance structures.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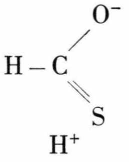
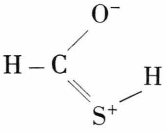


A contribution from these resonance forms would also be consistent with the short (0.04 Å shorter than the sum of the single bond radii[41]) CS bond length observed in both rotamers of HC(:O)SH. However, the different carbon atom hybridizations[42] (~ sp^2 in monothioformic acid and ~ sp^3 in the mercaptans) as well as contributions from the resonance forms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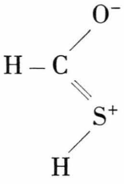

Table X. Structure of the SH group in several thiols[a].

Molecule	r(S–H)	r(C–S)	$\sphericalangle$(HSX)	Ref.
trans-HCOSH	1.354 ± 0.002	1.768 ± 0.003	92.5 ± 0.2	
cis-HCOSH	1.335 ± 0.002	1.771 ± 0.003	94.9 ± 0.2	
CH_3SH[b]	1.335 ± 0.010	1.819 ± 0.005	96.5 ± 0.5	36
trans-CH_3CH_2SH	1.322 ± 0.006	1.820 ± 0.005	96.2 ± 0.4	37
gauche-CH_3CH_2SH	1.336 ± 0.010	1.814 ± 0.009	96.0 ± 0.5	38
HSSH[b]	1.327 ± 0.003		91.3 ± 0.5	39
H_2S[c]	1.337 ± 0.002		91.9 ± 0.3	40

[a] All structures, except where otherwise indicated, are r_s structures; bond lengths are measured in Å units and angles in degrees.

[b] This is an r_0 structure; some caution should be used in comparing it to the r_s structures.

[c] The error limits given for hydrogen sulfide were estimated by the present authors.

must also play a role in the CS bond shortening. Some double bond character in the CS bond in HC(:O)SH is also to be expected on the basis of the observed planarity of both rotamers. Lastly, the variation in the HSX bond angles reported in Table X would appear to be due largely to steric repulsions.

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