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Microwave spectrum and substitution structure of syn thiobenzoic acid

Aaron J. Reynolds, Kenneth R. Leopold *

Department of Chemistry, University of Minnesota, 207 Pleasant St., SE, Minneapolis, MN 55455, United States

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ABSTRACT

The rotational spectrum of the *syn* conformer of thiobenzoic acid (C_6H_5COSH) has been observed by Fourier transform microwave spectroscopy in a supersonic jet. Spectra of all singly-substituted isotopologues involving ^{13}C, as well as the ^{18}O, ^{33}S, ^{34}S, and −SD derivatives have also been recorded. The isotopic data have been used to derive structural parameters of the molecular frame. The results are compared with density functional theory calculations at theM06-2X/6-311++G(d,p) level and show excellent agreement. The molecule is planar at the equilibrium geometry, and calculations of the energy profile for out-of-plane torsion of the SH group are presented. The *anti* conformer was not observed, consistent with calculations which indicate that it lies 2.6 kcal/mol higher in energy than the *syn* form.

1. Introduction

In this paper we report the microwave spectrum and structure of thiobenzoic acid (C_6H_5COSH, TBA). The literature on high resolution spectra of thiocarboxylic acids is relatively sparse compared with that for their more common oxygen analogues (RCOOH). Rotational spectra of thioformic acid (HCOSH) were recorded decades ago by Hocking and Winnewisser [1–4], and the microwave spectrum of thioacetic acid [5] has been more recently reported. Prior spectroscopic work on TBA appears limited, however. Renewed interest in thiocarboxylic acids stems from a recent report of thioformic acid formation on interstellar ice analogues [6] and its recent observation in the interstellar medium [7].

2. Theoretical and experimental methods

Calculations at the M06-2X/6–311++G(d,p) level of theory were performed for both the *syn* and *anti* forms of TBA using the ORCA quantum chemistry package [8,9]. The structures with atom numbering are shown in Fig. 1. As seen in the figure, the *syn* conformer is predicted to be planar. However, torsion about the C–S bond is expected and thus a scan of the electronic energy vs. the O13-C12-S14-H15 dihedral angle was also performed. The result of that scan with the angle stepped at 10 deg increments is shown in Fig. 2. As may be seen from the figure, the *syn* conformer is predicted to lie 2.6 kcal/mol lower in energy than the *anti* conformer, which is the configuration accessed by rotation of 168 deg about the C12-S14 bond. Predicted rotational constants for both the *syn* and *anti* structures are given in Table 1. Note that, while the *syn* form is fully planar, the *anti* configuration is not. At its lowest energy structure, the O13-C12-C6-C1 dihedral angle is calculated to be 28.8 deg, indicating that the phenyl group is bent out of conjugation with the carbonyl.

Details of our Fourier transform microwave spectrometer, which includes both cavity and broadband capabilities, have been presented elsewhere [10,11]. Spectra of the parent species between 6 and 18 GHz were taken using both broadband and cavity methods. Isotopologue spectra were observed only on the cavity instrument. Liquid TBA was placed in a small stainless steel reservoir situated close to the nozzle and argon at a pressure of ~ 0.5 atm was used to entrain the vapor. The Ar/TBA mixture was injected into a pulsed jet produced by expanding 1.3 atm of argon through a 0.8 mm cone nozzle for 1–2 μs. The injection was accomplished with a stainless steel hypodermic needle (0.016 in. ID) that was bent so as to introduce the argon/acid mixture along the axis of the expansion as described previously [12]. The pressure in the vacuum chamber was in the mid-10^{-5} torr range. Transition frequencies measured on the broadband instrument were accurate to 10 kHz and those on the cavity instrument were accurate to 3 kHz.

Thiobenzoic acid (90 %, boiling point 122 °C) was obtained from Sigma-Aldrich^{T} and the broadband spectrum of the parent was readily assigned using the DAPPERS package [13]. Only *a*- and *b*-type transitions were observed. The − SD form was studied using an isotopically enriched sample prepared via H/D exchange in a 1:6 mixture of C_6H_5COSH with D_2O. Hyperfine structure due to the deuterium nucleus was not resolved. Other isotopologues were observed in natural abundance. Once the parent form had been fully analyzed, the location and

* Corresponding author.
E-mail address: kleopold@umn.edu (K.R. Leopold).

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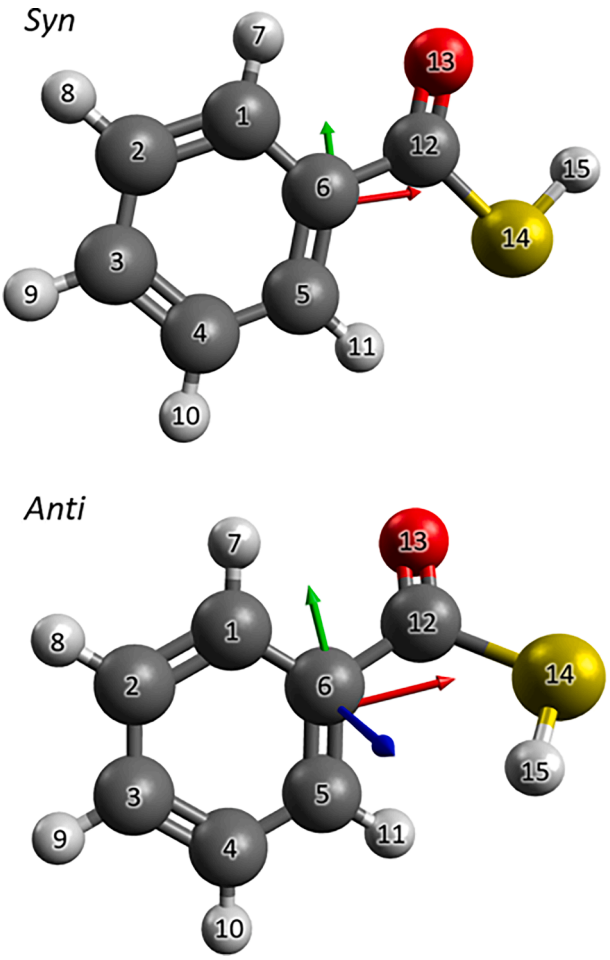

Fig. 1. The minimum energy structure of the *syn* and *anti* conformers of thiobenzoic acid, computed at the M06-2X/6-311++G(d,p) level of theory. The *a*-, *b*-, and *c*-inertial axes are shown in red, green, and blue, respectively. The *c*-axis is omitted for the planar *syn* conformer.

acquisition of the isotopic spectra were straightforward, with the exception of the ^{13}C6 substituted form. C6 lies very close to the center of mass of the molecule and thus some of the transitions were overlapped with parent spectra. For the ^{18}O and ^{33}S spectra, a slightly larger needle diameter (0.020 in) was used to increase the amount of TBA entering the jet. A representative spectrum obtained from a mixture containing both the parent and –SD forms is shown in Fig. 3.

Table 1
Calculated Rotational Constants for the Parent Forms of *syn* and *anti* Thiobenzoic Acid and Comparison with Observed Values.

Constant	M06-2X/6–311++G(d,p)		
	Syn	*anti*	Observed
A [MHz]	3156.3	3150.8	3130.30020(40)
B [MHz]	940.2	915.3	941.05205(13)
C [MHz]	724.4	733.6	724.454830(96)
$\|\mu_a\|$ [D]	1.9	3.2	
$\|\mu_b\|$ [D]	1.4	2.4	
$\|\mu_c\|$ [D]	0.0	0.9	

3. Results and discussion

Spectral frequencies were fit to the Watson A-reduced Hamiltonian in the I^r representation using Pickett's SPFIT program [14]. With the exception of δ_K which was found to be undetermined, quartic centrifugal distortion constants were employed in the fit of the parent derivative. For the other isotopologues, some distortion constants were constrained to their parent values as necessary depending on the scope of the data set. The fitted spectroscopic constants are presented in Tables 2 and 3. The microwave rms for the ^{33}S fit is seen to be somewhat larger than that of the other isotopologues studied (9 kHz) but inclusion of a χ_{ab} term in the fit yielded no improvement. The larger rms in the residuals is consistent with the larger (5–10 kHz) uncertainties in the spectral frequencies that resulted from low isotopic abundance and dilution of signal from the nuclear hyperfine splitting.

Values of the parent rotational constants are also included in Table 1, where it may be seen that the observed values of *B* and *C* are in excellent agreement with those predicted for the *syn* form. The calculated *A* rotational constants for both conformers are somewhat larger that the observed value, but neither overwhelmingly favors one form over the other. However, taken together with the substitution structure discussed below, as well as the calculated energy difference of 2.6 kcal/mol between the two conformers, it is reasonable to conclude that the observed spectrum indeed arises from the *syn* form.

With substitution on all atoms except the phenyl hydrogens, Kisiel's KRA program [15] was used to determine structural parameters of the molecular frame via Kraitchman analysis [16]. As noted above, the computed structure obtained at the M06-2X/6-311++G(d,p) level of theory is planar, consistent with the small negative observed inertial defect, $\Delta = (I_{cc} - I_{aa} - I_{bb}) = -0.8846$ u·Å^2 for the parent species. Thus, the system was initially constrained to planarity in the analysis and only the *A* and *B* rotational constants were used. However, an analysis without this constraint was also performed. The resulting vibrationally averaged inertial axis system coordinates for both analyses are shown in

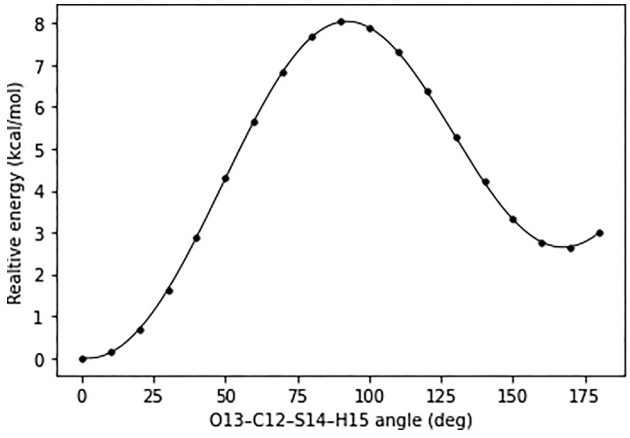

Fig. 2. Electronic energy as a function of the O13-C12-S14-H15 dihedral angle computed at the M06-2X/6-311++G(d,p) level of theory at 10 deg angular increments. A smooth curve is drawn through the points for ease of visualization.

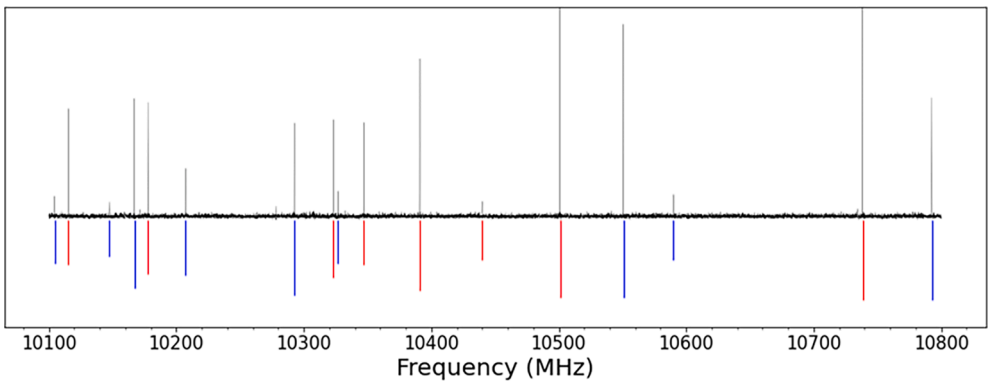

Fig. 3. A portion of the broadband spectrum containing a mixture of C_6H_5COSH and C_6H_5COSD. Top trace is the observed spectrum. Bottom trace is the calculated spectrum (parent in red, deuterated species in blue). This spectrum represents the average of 610,000 acquisitions.

Table 2
Spectroscopic Constants of the Parent and ^{13}C Substituted Forms of *syn* Thiobenzoic Acid.[a]

	Parent	**^{13}C1**	**^{13}C2**	**^{13}C3**
A [MHz]	3130.30020(40)	3101.0989(31)	3113.0297(10)	3127.7789(10)
B [MHz]	941.05205(13)	938.896480(71)	930.435725(83)	926.41473(10)
C [MHz]	724.454830(96)	721.60877(11)	717.23797(11)	715.61794(16)
Δ_J [kHz]	0.02841(65)	0.02594(69)	0.02436(98)	0.0261(12)
Δ_{JK} [kHz]	−0.0511(51)	[−0.0511]	[−0.0511]	[−0.0511]
Δ_K [kHz]	0.424(25)	[0.424]	[0.424]	[0.424]
δ_J [kHz]	0.00664(38)	[0.00664]	[0.00664]	[0.00664]
N^b	101	26	27	27
Microwave RMS [kHz]	4.0	1.6	2.7	1.8
	^{13}C4	**^{13}C5**	**^{13}C6**	**^{13}C12**
A [MHz]	3092.6094(10)	3105.66529(87)	3129.6742(63)	3124.4929(13)
B [MHz]	934.13739(10)	940.37336(10)	941.03581(26)	938.32329(17)
C [MHz]	718.337210(79)	722.731563(93)	724.414299(66)	722.52780(15)
Δ_J [kHz]	0.02583(93)	0.02779(97)	[0.2841]	0.0240(16)
Δ_{JK} [kHz]	[−0.0511]	[−0.0511]	[−0.0511]	[−0.0511]
Δ_K [kHz]	[0.424]	[0.424]	[0.424]	[0.424]
δ_J [kHz]	[0.00664]	[0.00664]	[0.00664]	[0.00664]
N^b	25	25	7	24
Microwave RMS [kHz]	1.3	1.2	0.9	2.1

(a) Numbers in square brackets were fixed at their parent values. Atom numbering refers to Fig. 1. (b) Number of distinct frequencies in the least squares fit.

Table 3
Spectroscopic Constants of −SD, ^{18}O, ^{33}S and ^{34}S Substituted Forms of *syn* Thiobenzoic Acid.[a]

	−SD15	**^{18}O13**	**^{33}S14**	**^{34}S14**
A [MHz]	3130.74101(58)	3025.1017(91)	3117.137(53)	3105.09565(14)
B [MHz]	920.563990(97)	931.50813(13)	931.06352(80)	921.419840(75)
C [MHz]	712.28998(11)	713.09959(11)	717.84213(77)	711.453000(60)
Δ_J [kHz]	0.02477(50)	[0.02841]	[0.02841]	0.02666(66)
Δ_{JK} [kHz]	−0.206(35)	[−0.0511]	[−0.0511]	[−0.0511]
Δ_K [kHz]	[0.424]	[0.424]	[0.424]	[0.424]
δ_J [kHz]	[0.00664]	[0.00664]	[0.00664]	[0.00664]
χ_{aa} [MHz]			−30.25(33)	
$(\chi_{bb} - \chi_{cc})$ [MHz]			−32.3(23)	
N^b	93	17	20	36
Microwave RMS [kHz]	4.2	2.3	9.2	1.3

(a) Numbers in square brackets were fixed at their parent values. Atom numbering refers to Fig. 1. (b) Number of distinct frequencies in the least squares fit.

Table 4, where the results are seen to be almost identical. All experimental coordinates are seen to be well determined except for the *b*-coordinate of the deuterium atom, which has a small imaginary value and is therefore taken to be zero. Table 5 gives the experimental bond lengths and bond angles and compares them with their theoretical counterparts. It can be seen in the table that there is quite good agreement between the theoretical and experimental structural parameters. The worst discrepancies are 0.097 Å and 5.6 deg for bond lengths and bond angles, respectively. Both involve the position of C6 which is the most difficult atom to locate due to its proximity to the center of mass. Relaxation of the planarity constraint in the Kraitchman analysis produced negligible changes in the experimentally determined geometry.

It is of interest to compare the structural features of the –COSH group with those of the –COOH group in related carboxylic acids. This is done

Table 4
Experimental Inertial Axis System Coordinates for *syn* Thiobenzoic Acid.

	Planar Analysis[a]		Non-planar Analysis		
	a **(Å)**	***b*** **(Å)**	***a*** **(Å)**	***b*** **(Å)**	***c*** **(Å)**
S14	2.40746(62)	−0.8285(18)	2.40724(62)	−0.82783(7)	0.0331(45)
C1	−1.1103(14)	1.2374(12)	−1.1099(14)	1.2370(12)	0.031(49)
*C*2	−2.47727(61)	0.9560(16)	−2.47686(61)	0.9549(16)	0.045(33)
C3	−2.91810(52)	−0.3655(41)	−2.91802(52)	−0.3649(41)	0.022(70)
C4	−1.99245(76)	−1.4129(11)	−1.99221(76)	−1.4125(11)	−0.031(48)
C5	−0.6227(24)	−1.1344(13)	−0.6208(24)	−1.1333(13)	−0.050(30)
C6	−0.096(16)	0.1801(85)	−0.089(17)	0.1766(86)	−0.036(42)
C12	1.2516(12)	0.5500(27)	1.2514(12)	0.5494(27)	−0.0256(59)
O13	1.65637(91)	1.69810(88)	1.65575(91)	1.69745(88)	−0.047(32)
H15	3.45905(44)	0.1532(98)*i*[b]	3.45794(44)	0.1776(85)*i*[b]	0.089(17)

(a) All *c*-coordinates are zero since the analysis was performed under the constraint of planarity. Signs are chosen based on the theoretical structure.
(b) Complex coordinate, taken to be zero in the calculation of bond lengths and bond angles.

in Table 6. Structural data obtained from both microwave and gas phase electron diffraction results are included for HCOOH, CH_3COOH, and C_6H_5COOH. The electron diffraction results are included because, in the case of C_6H_5COOH, which is most closely related to this paper, the only microwave study [22] did not include sufficient isotopic substitution to determine the relevant structural parameters. Thus, the data for HCOOH and CH_3COOH provide a measure of the degree to which parameter values determined from electron diffraction can be compared with results from microwave spectroscopy. It can be seen from the table that for HCOOH and CH_3COOH, distances determined from gas phase electron diffraction are in reasonable agreement with microwave values, typically a few thousandths of an angstrom (but up to 0.015 Å for r[C–O] of HCOOH). Angles are typically within 1.5 degrees. Moreover, it can be seen from the table that the C=O bond lengths, as well as the R–C=O angles are quite similar across all systems listed. As expected, the most notable difference is in the COH vs. CSH angle. In the carboxylic acids, this angle is slightly less than the tetrahedral angle, whereas for COSH, it is only 91.75(35) deg. This fully parallels the usual lack of sp^3 hybridization in third row elements compared with their second row counterparts. The C–S and S–H distances, of course, are longer than that C–O and O–H distances by about 0.4 Å, which is roughly consistent with the larger atomic size of sulfur [23].

Table 5
Experimental and Theoretical Bond Lengths and Bond Angles of *syn* Thiobenzoic Acid.[a]

	Experimental		M06-2X/6-311++G (d,p)
	Planar Analysis	Non-Planar Analysis	
R(C1-*C*2)	1.3957(15)	1.3959(16)	1.388
R (*C*2-C3)	1.3931(42)	1.3931(56)	1.393
R(C3-C4)	1.3978(33)	1.3981(33)	1.391
R(C4-C5)	1.3977(25)	1.3997(26)	1.390
R(C5-C6)	1.416(10)	1.413(10)	1.395
R(C6-C1)	1.465(13)	1.473(14)	1.396
R(C6-C12)	1.398(15)	1.392(17)	1.495
R(C12-O13)	1.2174(28)	1.2174(30)	1.199
R(C12-S14)	1.7989(27)	1.7989(36)	1.804
R(S14-H15)	1.3388(62)	1.3388(58)	1.341
∠(C1-*C*2-C3)	120.08(12)	120.07(25)	120.0
∠(*C*2-C3-C4)	120.08(8)	120.03(25)	120.2
∠(C3-C4-C5)	119.98(15)	119.96(15)	120.0
∠(C4-C5-C6)	123.31(62)	123.56(67)	119.9
∠(C5-C6-C1)	114.4(10)	114.0(11)	120.0
∠(C6-C1-*C*2)	122.16(51)	122.22(56)	120.0
∠(C6-C12-O13)	124.76(41)	124.93(44)	123.2
∠(C6-C12-S14)	114.63(41)	114.47(44)	115.8
∠(O13-C12-S14)	120.60(10)	120.61(13)	121.0
∠(C12-S14-H15)	91.75(35)	91.85(32)	92.4
∠(O13-C12-S14-H15)	0[b]	2.4(56)	0.0

(a) Bond lengths are in Å. Angles are in degrees.
(b) Assumed value.

The value of $\chi_{cc} = (-1/2)[\chi_{aa} + (\chi_{bb}-\chi_{cc})]$ is useful for comparison with other planar systems since it is independent of the orientation of the *a*- and *b*-inertial axes. From the ^{33}S constants in Table 3, we obtain $\chi_{cc} =$ 31.28(23) MHz. While many ^{33}S nuclear quadrupole coupling tensors have been determined [24], relatively few are for planar systems that also form chemically logical comparisons with TBA. Nevertheless, we note that the value for TBA is comparable to that of $^{33}SO_2$ (−23.8538 (22) [25]) and $^{33}S = CH_2$ (–38.083(18) MHz [26]), but quite different from that of ^{33}S-thiophene (20.9525(47) [27], $H_2^{33}S$ (41.4498(64) MHz [28]), and $(CH_3)_2^{33}S$ (48.0161(49) MHz [29]). Better comparisons would include other thiocarboxylic acids and, perhaps, thiophenols, but we are unaware of measurements of the ^{33}S quadrupole coupling tensor for such systems. Additional studies could provide an interesting line of inquiry.

As noted above, the *anti* conformer of TBA is calculated to lie 2.6 kcal/mol higher in energy than the *syn* form. Thus, its absence in the supersonic jet is expected and, indeed, no transitions were observed that could attributed to it. (Note that the calculated dipole moment components in Table 1 are somewhat larger for the *anti* form and suggest that the *a*- and *b*-type anti spectra should be about three times stronger than those of the *syn* conformer. However, this does not provide enough of an enhancement to overcome the greatly reduced Boltzman factor at a canonical jet temperature of ~ 2 K.) As noted above, while the *syn* form is calculated to be planar, the *anti* conformer is not, with about a 29 deg O13-C12-C6-C1 dihedral angle. The reason for this is not determined in the present work but it is plausibly a result of repulsion between the SH hydrogen and the nearest *ortho* hydrogen on the phenyl ring. Indeed, at the calculated equilibrium geometry of the *anti* form, the distance between the SH hydrogen and the nearest ortho hydrogen on the phenyl ring is 2.199 Å, which is exactly twice the van der Waals radius of hydrogen given by Pauling [30]. (A calculation of the *anti* conformer constrained to a planar geometry gives an H···H distance of 1.89 Å.) Thus, forcing the system into a planar configuration would bring the hydrogen atoms closer than the sum of their van der Waals radii and would be expected to raise the energy of the system.

CRediT authorship contribution statement

Aaron J. Reynolds: Formal analysis, Data curation. **Kenneth R. Leopold:** Conceptualization, Project administration, Validation, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

Table 6
Comparison of Structural Parameters of the COSH Group in Thiobenzoic Acid with Those of the COOH Group in Several Carboxylic Acids.[a]

	HCOOH		CH_3COOH		C_6H_5COOH	C_6H_5COSH
	MW[b]	GPED[b,c]	MW[d]	GPED[e]	GPED[f]	MW (This Work)
r[C–O(S)]	1.342(5)	1.357(3)	1.357(5)	1.364(3)	1.359(8)	1.7989(27)
r[C=O]	1.204(5)	1.213(3)	1.209(6)	1.214(3)	1.220(6)	1.2174(28)
r[O(S)–H]	0.972(5)	0.966(24)	0.970(3)	0.97 [h]	0.983(13)	1.3388(62)
∠[O=C–O(S)]	124.8(4)	123.55(46)	121.8(9)[g]	122.8(8)[g]	120.3(22)[g]	120.6(10)
∠[C–O(S)–H]	106.3(4)	–	105.9(5)	107.0 [h]	105.7(25)	91.75(35)
∠[R–C–O(S)][i]	112.0(15)	–	112.0(6)	110.6(6)	113.1(15)	114.63(41)
∠[R−C=O][i]	123.2(15)	–	126.2(7)	126.6(6)	126.6(16)	124.76(41)

(a) MW = Microwave; GPED = Gas Phase Electron Diffraction. Distances are in Å, angles are in degrees.
(b) Ref. [17].
(c) Ref. [18].
(d) Ref. [19].
(e) Ref. [20].
(f) Ref. [21].
(g) Calculated from the C–C–O and C–C=O angles assuming a planar heavy atom structure.
(h) Assumed value.
(i) For formic, acetic, and benzoic or thiobenzoic acids, R = H, the carbon of CH_3, and the carbon of C_6H_5 that is attached to the COOH or COSH group, respectively.

the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jms.2023.111787.

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