

s-cis and *s-trans* Conformers of Formic, Thioformic and Dithioformic Acids

An *Ab Initio* Study

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Ab initio SCF-MO calculations have been carried out for formic, thioformic and dithioformic acids using the 6-31G* basis set. Fully optimized geometries, atomic charges, relative stabilities and harmonic force fields for *s-cis* and *s-trans* conformers of these molecules have been determined and the effects of oxygen-by-sulphur substitution analysed. A realistic description of the molecular charge distribution can be reached by introducing a quantum-mechanical correction to the Mulliken atomic charges, derived from the 'charge'-'charge flux'-'overlap' (CCFO) model. Unlike reported theoretical results, the present *ab initio* calculations yield relative stabilities of the thioformic acid conformers in agreement with experiment [*s-cis* (thiol) > *s-trans* (thiol) > *s-cis* (thione) > *s-trans* (thione)]. The success of these *ab initio* calculations should be partially ascribed to the inclusion of polarization functions on all non-hydrogen atoms.

Dithio compounds constitute an ideal resonance Raman (RR) probe for monitoring catalytic events within an enzyme's active site.¹⁻³ The catalytic hydrolysis of substrates containing the RC(=O)O fragment by cysteine proteases (*e.g.* papain) proceeds through the formation of a thiolacyl enzyme, RC(=O)S-Enz. Using a thion-substituted substrate, it is possible to generate an enzyme-substrate intermediate that contains the chromophore -C(=S)S-, thus differing from the 'natural' intermediate by a single atom substitution (=O → =S).

Interpretation of the RR spectra of dithioenzyme-substrate intermediates has relied heavily on joint Raman and crystallographic studies on suitable model compounds.⁴⁻⁶ While our understanding of some of these probes has reached a sophisticated level, it is apparent that the assessment of changes in molecular properties produced by oxygen-by-sulphur substitutions in molecules containing the -C(=X)Y-, (X, Y = O or S) fragment has a major interest to further our understanding of the active site data.

We have recently initiated a systematic approach to the study of thione- and thiol-substituted carboxylic acids and esters using *ab initio* quantum-mechanical calculations.⁷⁻⁹ The results obtained for HCSSH using the 3-21G basis set⁸ were compared with previous data on HCOOH, HC(=O)SH and HC(=S)OH,¹⁰ and revealed a remarkable similarity between molecular properties of dithioformic and thioformic acids. This trend was also observed along the series of the corresponding methyl esters, HCSSCH₃ resembling more HC(=O)SCH₃ than the compounds possessing an oxygen ester atom.^{7,9}

The importance of mesomerism in determining the properties of this kind of molecule (fig. 1) is well known, in particular, for their ground conformational state (the *s-cis* form). We have proposed⁸ that the main effect resulting from C(=O)O → C(=O)S or C(=S)O → C(=S)S substitutions is originated in the poorer conjugating properties of the sulphur 3p orbitals as compared with those of the oxygen 2p orbitals.

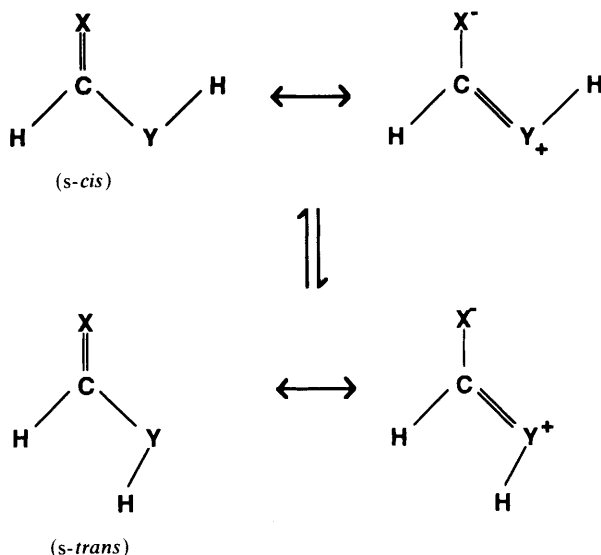
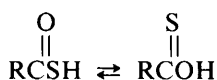


Fig. 1. Canonical forms showing the mesomerism in both *s-cis* and *s-trans* conformers of $\text{HC}(=\text{X})\text{YH}$ ($\text{X}, \text{Y} = \text{O}$ or S).

The calculations carried out with the 3-21G and 4-31G basis sets had elucidated the main trends exhibited by the carboxyl and thiocarboxyl compounds.⁷⁻¹⁰ However, the relative stabilities of the various thioacid conformers are not in agreement with the experimental evidence. Thus, additional studies with larger basis sets are required.

Monothio carboxylic acids exist as a tautomeric mixture of thiol and thione forms.



In general, the thiol structures predominate over the thione forms. A detailed microwave and millimetre wave spectroscopic study performed on thioformic acid led to the identification of the most stable forms of this molecule in gaseous phase (the thiol forms), the *s-trans* rotamer lying at higher energy than the *s-cis* rotamer by $2.767 \text{ kJ mol}^{-1}$.¹¹ Whereas early i.r. and proton n.m.r. investigations had suggested the presence of a thione form in the conformational equilibrium,¹² microwave and millimetre wave spectral data do not show any evidence of this form.¹¹ However, as the energy difference between the most stable thione form and the less stable thiol form of thioformic acid should not be large,¹³⁻¹⁴ the thione form has probably evaded clear experimental identification.

Several calculations have been performed on HCSOH .^{9,10,15} However, both EHT and CNDO/2 results¹⁵ do not agree with experimental evidence, as the first do not predict the occurrence of both thiol and thione alkyl esters of thioformic acid, and the second predicts the thione conformers to be the most stable forms. In addition, while 3-21G and 4-31G results present a much better agreement with experiment than the semi-empirical results, the stability of the *s-cis* thione form has been wrongly calculated to be greater than that of the *s-trans* thiol form.⁹⁻¹⁰

In order to improve the quality of the theoretical results and, in particular, reach a better description of the charge distribution over the $\text{C}(=\text{X})\text{Y}$ group ($\text{X}, \text{Y} = \text{O}$ or S), we have considered a larger basis set by adding more primitive gaussians to the atomic

core regions and polarization functions to all non-hydrogen atoms. The fundamental idea was to work with a more efficient and well balanced basis set, like the 6-31G*, to correctly represent the electronic distribution in the inner and outer regions of the molecular space. The reliability of the results obtained with the extended 6-31G* basis set allows us to use them as a starting point to perform both charge distribution and normal coordinate analysis.

Computational Methods

The *ab initio* SCF-MO calculations were carried out with the 6-31G* basis set¹⁶ using the GAUSSIAN 82 program system¹⁷ running on a VAX 8530 computer.

Molecular geometries were fully optimized by the force gradient method with analytical gradient¹⁸; the bond lengths within *ca.* 1 pm, the bond angles within *ca.* 0.1°. The maximum residual force on each internal coordinate was set up to 3×10^{-4} hartree bohr⁻¹† or hartree rad⁻¹. Harmonic force constants were evaluated numerically from the energies and forces for all studied conformers and scaled to reproduce the experimental frequencies. The scaling procedure followed the scheme proposed in ref. (19) and (20): the force constants were grouped according to the type of coordinate involved (coupling constants in a single group), a separate scaling factor was ascribed to each group and the complete force field was then scaled to the experimental frequencies.

Vibrational calculations were performed using the GMAT and FPRT programs,²¹ adapted to a DG/Eclipse MV8000 computer. The observed frequency parameters, $\lambda_i = 4\pi^2 c^2 v_i^2$, were weighted by $1/\lambda_i^2(\text{obs})$, in all refinements.

Infrared intensity parameters were examined using the atomic polar tensor (APT) formalism²² and the CCFO model,²³⁻²⁴ within the numerical difference approximation,

$$\partial p_\sigma / \partial \sigma_\alpha \approx \Delta p_\sigma / \Delta \sigma_\alpha \quad \text{with } \Delta \sigma = 1 \text{ pm} \quad (1)$$

where p represents the electric dipole moment along the σ axis and α refers to a specific atom in the molecule.

Results and Discussion

Molecular Geometries and Energies

The 6-31G* relative stabilities and electric dipole moments of the *s-cis* and *s-trans* conformers of the molecules considered in this study are listed in table 1. For comparison, other theoretical and experimental data are also presented in this table. Both the energy and the dipole moment values improve significantly over previous theoretical results.

For all the HC(=X)YH (X, Y=O or S) molecules, the *s-cis* form is more stable than the *s-trans* form, the energy difference reaching a minimum for X=O and Y=S and a maximum for X=S and Y=O (see table 1) and exceeding 25 kJ mol⁻¹ when Y=O.

The intramolecular effects that make *s-cis* conformers more stable than *s-trans* forms have already been analysed in detail, the most important ones being an extended *s-cis* π electronic delocalization and the occurrence of hydrogen bonding.^{7,9} Thus, the increase of the (*s-trans*)-(*s-cis*) energy difference along the series thioformic < dithioformic < formic < thionformic acids can be ascribed both to the improved conjugating properties of the oxygen 2p orbitals as compared to those of the sulphur 3p orbitals, and to the stronger O—H...X hydrogen bond interaction as compared with a S—H...X interaction.

The importance of the above-mentioned intramolecular interactions in *s-cis* conformations reflects also in the large changes produced by the HC(=X)QH \rightarrow HC(=X)SH

† 1 bohr $\approx 5.29177 \times 10^{-11}$ m.

1948 *The s-cis and s-trans Conformers of Formic, Thioformic and Dithioformic Acids***Table 1.** 6-31G* *ab initio* relative stabilities and dipole moments of *s-cis* and *s-trans* HC(=X)YH (X, Y = O or S) conformers and enhancement of *s-cis* → *s-trans* polarity

molecule		$\Delta E/\text{kJ mol}^{-1}$			p/D			$\Delta p/D$		
		6-31G*	4-31G ⁺ ^a	exptl ^b	6-31G*	4-31G ⁺	exptl ^b	6-31G*	4-31G ⁺	exptl ^b
HCOOH	<i>s-cis</i>	0.0	0.0	0.0	1.59	1.56	1.42	0.00	0.00	0.00
	<i>s-trans</i>	25.6	27.8	17.1	4.37	4.75	3.79	2.78	3.19	2.37
HC(=O)SH	<i>s-cis</i>	0.0	0.0	0.0	1.51	2.00	1.54	0.00	0.00	0.00
	<i>s-trans</i>	6.3	10.2	2.8	3.35	3.69	2.87	1.84	1.69	1.33
HC(=S)OH	<i>s-cis</i>	0.0	0.0		2.00	1.07		0.00	0.00	
	<i>s-trans</i>	27.4	28.5		4.48	3.93		2.48	2.86	
HCSSH	<i>s-cis</i>	0.0			1.80			0.00		
	<i>s-trans</i>	7.5			3.33			1.53		

^a 4-31G+ values from ref. (10); ^b experimental values from ref. (11) and (25).

Table 2. Basis set dependence of the relative stabilities (kJ mol⁻¹) of the *s-cis* and *s-trans* conformers of thioformic acid

molecule	exptl ^a	6-31G* ^b	4-31G ⁺ ^c	3-21G ⁺ ^d	3-21G ^d
<i>s-cis</i> thiol	0.0	0.0	0.0	19.2	34.1
<i>s-trans</i> thiol	2.77	6.3	10.2	26.9	45.8
<i>s-cis</i> thione		13.0	9.6	0.0	0.0
<i>s-trans</i> thione		40.2	38.1	32.0	32.0

^a Ref. (11). ^b This work. ^c Ref. (10). ^d Ref. (9).

substitution on the electric dipole moments of these forms, both for X=O or S ($|\Delta p| \approx -1D^\dagger$; see table 1), as compared with the reduction of the dipole moment of the *s-trans* conformers by a few tenths of a debye.

As mentioned in the introduction, previous theoretical studies could not adequately reproduce the experimental data concerning the relative stabilities of the thioformic acid tautomers.^{10,11} Table 2 allows us to compare the results now obtained with the literature values. Unlike the previous calculations, the 6-31G* calculations yield relative stabilities of the thioformic acid conformers in agreement with experiment [*s-cis*(thiol) > *s-trans*(thiol) > *s-cis*(thione) > *s-trans*(thione)]. The success of the 6-31G* calculations should be partially ascribed to the inclusion of polarization functions on all non-hydrogen atoms.

The 6-31G* fully optimized geometries of the molecules studied herein are presented in table 3. The changes in bond lengths and bond angles associated with the *s-cis* → *s-trans* isomerization can be summarized as follows and confirm the results previously obtained with the 3-21G and 4-31G basis sets:⁷⁻¹⁰

(i) the C=X bond is shortened and the C—Y bond lengthened, indicating a smaller electronic delocalization in *s-trans* forms;

(ii) the Y—H bond is shortened as expected, considering the intramolecular hydrogen bond presented by *s-cis* forms. This interaction can also partially explain the shortening of the C=X bond;

[†] 1 D = 3.335 64 × 10⁻³⁰ C m.

Table 3. 6-31G* calculated and experimental molecular geometries of HC(=X)H, and *s-cis* and *s-trans* HC(=X)YH conformers (X, Y = O or S)^a

coordinate	formic acid						thiolformic acid			
	formaldehyde		<i>s-cis</i>		<i>s-trans</i>		<i>s-cis</i>		<i>s-trans</i>	
	exptl ^{26,27}	calcd	exptl ²⁸	calcd	exptl ²⁹	calcd	exptl ¹¹	calcd	exptl. ¹¹	calcd
C—H	109.9	109.2	109.7	108.4	110.5	109.0	110.4	108.9	110.4	109.0
C=O	120.3	118.4	120.3	118.2	119.5	117.6	120.5	118.0	120.3	117.9
C—Y			134.2	132.3	135.2	132.8	176.8	177.4	177.1	177.7
Y—H			97.2	95.3	95.6	94.8	135.4	132.5	133.5	132.6
H—C=O	121.8	122.1	123.2	124.7	123.3	124.1	123.1	123.4	123.2	123.2
O=C—Y			124.8	124.9	122.1	122.0	125.9	125.1	122.5	122.4
C—Y—H			106.3	108.7	109.7	111.6	92.5	95.9	94.9	96.7

coordinate	thioformaldehyde		thionformic acid		dithioformic acid		
	exptl ³⁰	calcd	<i>s-cis</i> (calcd)	<i>s-trans</i> (calcd)	<i>s-cis</i>	exptl ³¹	calcd <i>s-trans</i> (calcd)
C—H	109.3	107.8	107.6	108.1	110.0	107.9	107.8
C=S	161.1	159.7	161.9	160.9	162.5	161.0	160.8
C—Y			130.7	131.6	173.3	173.6	174.2
Y—H			95.4	94.9	135.7	132.5	132.6
H—C=S	121.6	122.3	123.0	121.6	121.2	120.9	121.1
S=C—Y			126.7	124.3	127.8	128.8	124.7
C—Y—H			110.0	111.8	94.3	97.6	97.5

^a Bond lengths in pm; angles in degrees.**Table 4.** C=X bond length dependence with rotational isomerism in HC(=X)YH molecules (X=O or S)

molecule	C=X _(<i>s-cis</i>) pm	C=X _(<i>s-trans</i>) pm	ΔC=X _{(<i>s-cis</i>)-(<i>s-trans</i>)} pm	ΔC=X/C=X _(<i>s-cis</i>)
thionformic acid	161.9	160.9	1.0	6.2 × 10 ⁻³
formic acid	118.2	117.6	0.6	5.1 × 10 ⁻³
dithioformic acid	161.0	160.8	0.2	1.2 × 10 ⁻³
thiolformic acid	118.0	117.9	0.1	0.8 × 10 ⁻³

(iii) the H—C—Y (=360°—HCX—XCY) and C—Y—H angles increase, mainly due to the repulsive H···H electrostatic interactions in *s-trans* forms;

(iv) the X=C—Y angle decreases, suggesting the opening of the heavy-atom backbone in *s-cis* forms to make way for the hydrogen atom.

As was noted for energies, the structural changes associated with the rotational isomerism reveal well defined trends, the changes in the C=X bond length upon *s-cis* → *s-trans* isomerization increasing along the series thiolformic < dithioformic < formic < thionformic acids (table 4).

Charge-distribution Analysis

Fig. 2 presents values of standard (ζ^M) and corrected (ζ^{corr}) Mulliken atomic charges for the HC(=X)YH molecules, as calculated with the 6-31G* basis set. Corrected values

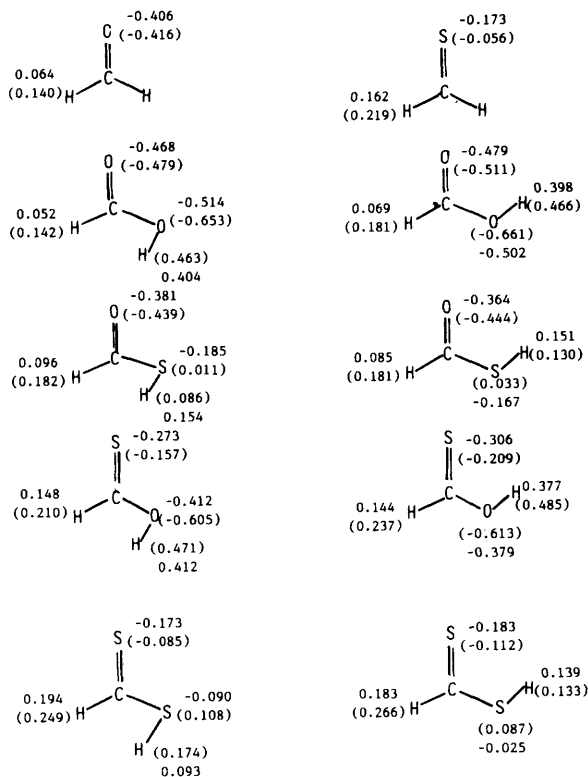
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Fig. 2. 6-31G* calculated standard and corrected Mulliken atomic charges for both *s-cis* and *s-trans* conformers of $\text{HC}(=\text{X})\text{YH}$ ($\text{X}, \text{Y} = \text{O}$ or S). The standard values are given in parentheses.

have been obtained using the $\Delta_{\text{OV},\alpha}$ element of the overlap tensor derived from the CCFO model,²³ in order to reproduce the SCF dipole moments from atomic charges^{24,32,33}. It has been shown³⁴ that this correction is useful to reduce the large basis set dependence of Mulliken charges^{35,36} and to improve description of intramolecular interactions.^{34,37}

The corrected Mulliken charges are given by

$$\zeta_{\alpha}^{\text{corr}} = \zeta_{\alpha}^{\text{M}} + \Delta_{\text{ov},\alpha}^{\text{xx}} \quad (2)$$

where x is the cartesian axis perpendicular to the molecular plane.

The hydrogen atomic charges adjacent to the $\text{C}=\text{X}$ group, with $\text{X}=\text{O}$ or S , become significantly less positive after correction, especially for the hydrogen atoms of aldehyde CH bonds (see fig. 2). This reflects the importance of the $\Delta_{\text{ov},\alpha}^{\text{xx}}$ term in accounting for the back-donation effect from the *trans* lone pair of the X heteroatom to the σ^* antibonding orbital of CH bond. This effect was also considered to explain both the observed values of the stretching frequencies of isolated CH groups in similar molecules,³⁸ and the charges on hydrogen atoms, as evaluated from infrared intensities in formaldehyde and ethene.³⁹

The $\Delta_{\text{OV},\alpha}^{\text{xx}}$ correction also allows one to correct the sign for charges on sulphur atoms of CSH groups. In contrast to $\zeta_{\text{S}}^{\text{M}}$, $\zeta_{\text{S}}^{\text{corr}}$ becomes negative, in agreement with the known chemical reactivity of sulphur in a CSH group.⁴⁰

By comparing ζ^{corr} and ζ^{M} for various heteroatoms (fig. 3) and the corresponding calculated dipole moment values (table 5), in particular those of H_2CO and H_2CS , one

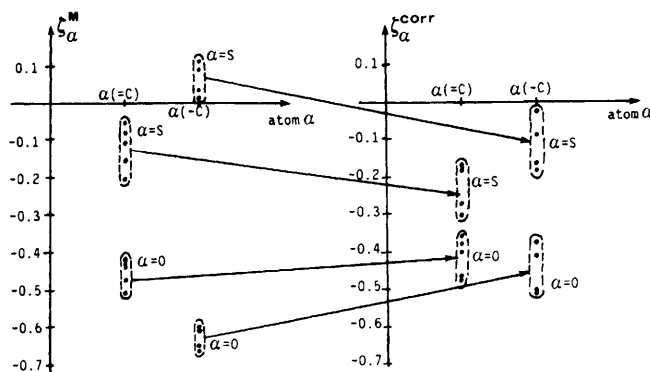


Fig. 3. Changes in the 6-31G* calculated Mulliken charges of O and S atoms upon correction by the $\Delta_{OV,\alpha}$ term (see text).

concludes that the Mulliken charges systematically overestimate the polarity of C=O bonds and underestimate the polarity of C=S bonds.

The reliability of ζ^{corr} to reproduce calculated quadrupole moments (table 5) is not as good as for dipole moments, though, in general, the correction improves much over the Mulliken charges.^{32,37} However, it is important to point out that the use of atomic point charges to represent quadrupole moments is naïve, especially when lone-pair moments are involved.

The corrected charges also reproduce the increase of polarity associated with the *s-cis* \rightarrow *s-trans* isomerization in the studied molecules (see table 1), whereas the values obtained from the Mulliken charges are considerably lower.

Normal-coordinate Analysis

The usual quantum-mechanical procedure to evaluate molecular force constants is to carry out the calculations under the Hartree-Fock approximation using a medium or extended-size basis set and scale the *ab initio* force constants to reproduce the experimental values. The scaling is necessary for a reliable prediction of vibrational spectra.⁴¹⁻⁴³

The 6-31G* complete harmonic in-plane and out-of-plane force fields of the molecules considered in this study are compiled in table 6. Experimental and *ab initio* vibrational frequencies for the *s-cis* conformers are compared in tables 7-10. These tables also contain the frequencies after scaling the force constants to the selected experimental values, and the potential-energy distribution (PED). The scaling factors, constrained by conservation of PED, are presented in table 11. The calculated frequencies of the *s-trans* conformers are listed in tables 12-15. Full transferability of the scaling factors between rotational isomers was assumed.

Formic Acid

Various force fields have been published for this molecule.^{28,44,47-49} In particular, a valence harmonic force field has been derived from the vibrational spectra of 24 different isotopic species.⁴⁴ Despite the large amount of experimental data and the excellent agreement between calculated and experimental frequencies, this force field could not yield a satisfactory PED.^{28,48} On the other hand, *ab initio* MO vibrational calculations usually yield accurately described normal modes,⁴¹⁻⁴³ though the frequencies are generally overestimated. By combining *ab initio* and empirical methods of calculation, a significantly improved force field for formic acid is obtained.

1952 *The s-cis and s-trans Conformers of Formic, Thioformic and Dithioformic Acids***Table 5.** In-plane components of dipole and quadrupole moments obtained from SCF, ζ^{corr} and ζ^{M} calculations using the 6-31G* basis set

molecule and selected cartesian axes orientation	type of calculation	μ_z/D	μ_y/D	$Q_{ZZ}/10^{-26} \text{ Fr cm}^2 a$	$Q_{YY}/10^{-26} \text{ Fr cm}^2 a$
	SCF	2.66	0.00	-0.45	0.42
	ζ^{corr}	2.66	0.00	-0.21	0.40
	ζ^{M}	3.14	0.00	0.34	0.69
	SCF	2.23	0.00	3.16	-2.06
	ζ^{corr}	2.22	0.00	2.27	-0.17
	ζ^{M}	1.64	0.00	1.03	0.07
	SCF	-1.58	-0.23	-7.96	7.23
	ζ^{corr}	-1.58	-0.23	-6.56	6.26
	ζ^{M}	-1.39	0.45	-8.10	8.19
	SCF	-3.98	1.86	1.29	-1.08
	ζ^{corr}	-3.98	1.84	1.21	-0.60
	ζ^{M}	-4.15	2.75	1.30	-0.21
	SCF	-1.40	-0.57	-2.20	2.53
	ζ^{corr}	-1.40	-0.58	-2.06	1.30
	ζ^{M}	-2.81	-1.79	-2.21	1.73
	SCF	-3.36	-0.07	1.67	-1.08
	ζ^{corr}	-3.35	-0.06	0.61	-1.03
	ζ^{M}	-3.83	-1.01	-0.55	0.01
	SCF	1.53	1.28	1.16	-0.32
	ζ^{corr}	1.53	1.24	2.23	-1.33
	ζ^{M}	0.43	0.44	2.17	-1.01
	SCF	0.96	4.37	-4.08	6.88
	ζ^{corr}	0.96	4.37	-1.96	5.16
	ζ^{M}	-0.38	3.98	-3.11	6.67
	SCF	-1.80	0.09	-5.01	6.41
	ζ^{corr}	-1.80	0.09	-3.66	4.71
	ζ^{M}	-2.05	-0.09	-2.07	4.40
	SCF	-2.86	1.71	1.74	0.53
	ζ^{corr}	-2.86	1.71	0.60	1.51
	ζ^{M}	-2.68	0.83	1.09	1.56

^a 1 Fr cm² \approx 3.33564 \times 10⁻¹⁴ C m².

Table 6. 6-31G* calculated force constants for *s-cis* and *s-trans* HC(=X)YH conformers (X, Y = O or S)^a

	HCOOH		<i>s-trans</i>	
	<i>s-cis</i>			
O-H	9.14	9.43		
C-H	-0.03	0.01	5.74	
C=O	-0.09	-0.03	0.51	17.41
C-O	0.14	0.22	0.28	7.96
C-O-H	0.22	0.04	0.01	0.39
H-C-O	0.04	0.07	-0.49	0.52
O=C-O	-0.12	-0.14	0.24	0.49
H-COO		0.78	0.08	-0.18
O=C-OH		-0.12	0.19	0.66
				-0.02
				0.11
HC(=O)SH				
	<i>s-cis</i>		<i>s-trans</i>	
S-H	4.96	4.92		
C-H	-0.01	0.02	5.68	
C=O	0.02	0.01	0.53	16.91
C-S	0.00	0.15	16.74	
C-S-H	0.03	0.02	-0.02	0.17
H-C-S	0.03	0.02	-0.54	0.30
O=C-S	-0.06	-0.12	-0.05	0.42
H-COS		0.65	0.07	-0.12
O=C-SH		-0.09	0.14	0.55
				-0.01
				0.11

(continued overleaf)

Table 6. (continued)

	HC(=S)OH			<i>s-trans</i>		
	<i>s-cis</i>			<i>s-trans</i>		
O-H	9.04			9.31		
C-H	-0.03	6.28		0.01	6.03	
C=S	-0.08	0.10	7.06	-0.06	0.14	7.34
C-O	0.23	0.21	1.17	0.03	0.24	1.14
C-O-H	0.20	0.03	0.01	0.09	0.00	0.46
H-C-O	0.04	0.09	-0.27	-0.07	0.08	-0.31
S=C-O	-0.07	-0.07	0.22	0.08	-0.08	0.06
H-CSO			0.54			0.54
S=C-OH			1.85			1.82
			0.72			0.57
			-0.16			-0.04
			0.22			0.12
			HCSSH			
			<i>s-cis</i>			<i>s-trans</i>
S-H	4.95			4.90		
C-H	-0.02	6.12		0.02	6.12	
C=S	0.00	0.13	7.27	0.00	0.14	7.41
C-S	0.02	0.11	0.79	-0.01	0.07	0.78
C-S-H	0.02	0.02	-0.02	-0.02	-0.03	0.06
H-C-S	0.03	0.09	-0.32	-0.02	0.04	-0.33
S=C-S	-0.06	-0.05	0.05	0.07	-0.04	0.01
H-CSS			0.64			0.29
S=C-SH			1.65			1.55
			0.63			0.48
			-0.14			-0.03
			0.18			0.12

^a The units of force constants are compatible with the energy measured in aJ, bond lengths in Å = 100 pm, and bond angles in rad.

Table 7. Calculated and observed vibrational frequencies (cm^{-1}) and PEDs of *s-cis* formic acid^a

obsd ^{4a}	<i>ab initio</i>	scaled	symmetry	PED ^b	$\Delta(\text{obsd-scaled})$
3569	4040	3569	1A'	$\nu\text{OH}[100]$	0
2938	3319	2939	2A'	$\nu\text{CH}[100]$	-1
1774	2035	1771	3A'	$\nu\text{C}=\text{O}[76] + \delta\text{CH}[26] + \nu\text{CO}[10]$	3
1380	1553	1381	4A'	$\delta\text{CH}[72] + \nu\text{C}=\text{O}[19]$	-1
1218	1440	1212	5A'	$\nu\text{CO}[45] + \delta\text{COH}[26] + \delta\text{OCO}[23]$	6
1103	1275	1105	6A'	$\delta\text{COH}[60] + \nu\text{CO}[38]$	-2
1036	1193	1036	1A''	$\gamma\text{CH}[105]$	0
638	716	638	2A''	$\tau\text{CO}[100]$	0
626	692	631	7A'	$\delta\text{OCO}[83] + \delta\text{COH}[13] + \nu\text{CO}[9]$	-5

^a Absolute mean error in frequencies calculated with the 6-31G* scaled force field, 2 cm^{-1} . ^b PEDs smaller than 5 are not presented.

Table 8. Calculated and observed vibrational frequencies (cm^{-1}) and PEDs of *s-cis* thioformic acid^a

obsd ¹²	<i>ab initio</i>	scaled	symmetry	PED ^b	$\Delta(\text{obsd-scaled})$
2850	3223	2848	1A'	$\nu\text{CH}[100]$	2
2540	2934	2540	2A'	$\nu\text{SH}[100]$	0
1660	1993	1663	3A'	$\nu\text{C}=\text{O}[99] + \delta\text{CH}[11]$	-3
1339	1527	1339	4A'	$\delta\text{CH}[81]$	0
946	1061	946	1A''	$\gamma\text{CH}[106]$	0
	1059	922	5A'	$\delta\text{CSH}[70] + \delta\text{OCS}[14] + \nu\text{CS}[36]$	—
690	769	691	6A'	$\nu\text{CS}[77] + \delta\text{OCS}[26] + \delta\text{CSH}[24] + \delta\text{CH}[14]$	-1
430 ^c	477	427	7A'	$\delta\text{OCS}[94] + \delta\text{CH}[33] + \nu\text{CS}[18] + \delta\text{CSH}[12]$	3
300 ^c	424	300	2A''	$\tau\text{CS}[111] + \gamma\text{CH}[13]$	0

^a Absolute mean error in frequencies calculated with the 6-31G* scaled force field, 1 cm^{-1} . ^b PEDs smaller than 5 are not presented. ^c From ref. (11).

Table 9. Calculated and observed vibrational frequencies (cm^{-1}) and PEDs of *s-cis* thionformic acid^a

obsd ¹²	<i>ab initio</i>	scaled	symmetry	PED ^b	$\Delta(\text{obsd-scaled})$
	4018	3548	1A'	$\nu\text{OH}[100]$	—
	3384	2989	2A'	$\nu\text{CH}[100]$	—
1402 ^{c,d}	1627	1460	3A'	$\delta\text{CH}[89] + \nu\text{C}=\text{S}[12] + \delta\text{COH}[10] + \nu\text{CO}[8]$	—
1235 ^d	1428	1238	4A'	$\nu\text{CO}[76] + \nu\text{C}=\text{S}[12] + \delta\text{COH}[10]$	-3
1160 ^d	1355	1160	5A'	$\delta\text{COH}[66] + \delta\text{CH}[16] + \nu\text{C}=\text{S}[10] + \nu\text{CO}[10]$	0
	1078	962	1A''	$\gamma\text{CH}[97]$	—
	1027	935	6A'	$\nu\text{C}=\text{S}[67] + \delta\text{COH}[14] + \nu\text{CO}[13] + \delta\text{SCO}[9]$	—
666	731	666	2A''	$\tau\text{CO}[121] + \gamma\text{CH}[24]$	0
	511	443	7A'	$\delta\text{SCO}[10] + \delta\text{CH}[15] + \delta\text{COH}[6]$	—

^a Absolute mean error in frequencies calculated with the 6-31G* scaled force field, 1 cm^{-1} . ^b PEDs smaller than 5 are not presented. ^c Frequency not considered in the scaling procedure. ^d In ref. (12) and (15) this band has been assigned differently (see text).

Table 10. Calculated and observed vibrational frequencies (cm^{-1}) and PEDs of *s-cis* dithioformic acid^a

obsd ^{45 h}	<i>ab initio</i>	scaled	symmetry	PED ^c	$\Delta(\text{obsd-scaled})$
2860 ^d	3341	2957	1A'	$\nu\text{CH}[100]$	—
2495 ^d	2932	2538	2A'	$\nu\text{SH}[100]$	—
1432 ^d	1478	1381	3A'	$\delta\text{CH}[70] + \nu\text{C}=\text{S}[28] + \nu\text{CS}[8]$	—
1048	1158	1047	4A'	$\nu\text{C}=\text{S}[54] + \delta\text{CH}[30] + \nu\text{CS}[9]$	1
922	1060	922	5A'	$\delta\text{CSH}[87] + \nu\text{CS}[5]$	0
893	955	893	1A''	$\gamma\text{CH}[103]$	0
711	757	711	6A'	$\nu\text{CS}[67] + \delta\text{SCS}[22] + \nu\text{C}=\text{S}[10]$ $+ \delta\text{CSH}[7]$	0
(378)	447	378	2A''	$\tau\text{CS}[103]$	0
(312)	358	332	7A'	$\delta\text{SCS}[79] + \nu\text{CS}[13] + \nu\text{C}=\text{S}[5]$	-20

^a Absolute mean error in frequencies calculated with the 6-31G* scaled force field, 4 cm^{-1} . ^b Values in parentheses have been calculated using the PF2 molecular mechanics force field.^{9,46} ^c PEDs smaller than 5 are not presented. ^d Frequency not considered in the scaling procedure.

Table 11. 6-31G* Scaling factors^a

coordinate	scaling factor
O—H	0.780
S—H	0.749
C—H	0.781
C=O	0.689
C=S	0.874
C—O	0.757
C—S	0.793
C—O—H	0.676
C—S—H	0.758
H—C—O	0.847
H—C—S	0.778
X=C—Y (X, Y=O or S)	0.764
H—COO o.o.p.	0.730
H—CSO o.o.p.	0.794
H—CSS o.o.p.	0.837
O=C—O—H	0.781
O=C—S—H	0.513
S=C—O—H	0.850
S=C—S—H	0.650

^a Scaling factors for interaction force constants are: 0.537 (HCOOH), 0.723 (HC=OSH), 0.866 (HC=SOH) and 0.364 (HCSSH).

Table 12. Calculated vibrational frequencies (cm^{-1}) and PEDs of *s-trans* formic acid.

<i>ab initio</i>	scaled	symmetry	PED ^a
4108	3628	1A'	$\nu\text{OH}[100]$
3227	2860	2A'	$\nu\text{CH}[100]$
2081	1804	3A'	$\nu\text{C}=\text{O}[77] + \delta\text{CH}[27] + \nu\text{CO}[8]$
1583	1412	4A'	$\delta\text{CH}[73] + \nu\text{C}=\text{O}[18]$
1426	1234	5A'	$\nu\text{CO}[52] + \delta\text{COH}[45] + \delta\text{OCO}[15]$
1238	1044	6A'	$\delta\text{COH}[49] + \nu\text{CO}[35]$
1179	1009	1A''	$\gamma\text{CH}[100]$
724	659	7A'	$\delta\text{OCO}[88] + \nu\text{CO}[8] + \delta\text{COH}[7] + \delta\text{CH}[6]$
517	457	2A''	$\tau\text{CO}[99]$

^a PEDs smaller than 5 are not presented.

Table 13. Calculated vibrational frequencies (cm^{-1}) and PEDs of *s-trans* thiolformic acid^a

<i>ab initio</i>	scaled	symmetry	PED ^b
3213	2839	1A'	$\nu\text{CH}[100]$
2923	2530	2A'	$\nu\text{SH}[100]$
2000	1667	3A'	$\nu\text{C}=\text{O}[100] + \delta\text{CH}[10]$
1524	1338	4A'	$\delta\text{CH}[84]$
1095	955	5A'	$\delta\text{CSH}[77] + \nu\text{CS}[9] + \delta\text{OCS}[9]$
1047	931	1A''	$\gamma\text{CH}[100]$
723	707	6A'	$\nu\text{CS}[68] + \delta\text{OCS}[28] + \delta\text{CSH}[16] + \delta\text{CH}[10]$
463	416	7A'	$\delta\text{OCS}[99] + \delta\text{CH}[33] + \nu\text{CS}[24] + \delta\text{CSH}[12]$
362	259	2A''	$\tau\text{CS}[100]$

^a Observed values for δOCS and τCS vibrations¹¹ are 430 and 384 cm^{-1} , respectively; ^b PEDs smaller than 5 are not presented.

Table 14. Calculated vibrational frequencies (cm^{-1}) and PEDs of *s-trans* thionformic acid

<i>ab initio</i>	scaled	symmetry	PED ^a
4080	3602	1A'	$\nu\text{OH}[100]$
3313	2926	2A'	$\nu\text{CH}[100]$
1643	1486	3A'	$\nu\text{CH}[89] + \nu\text{C}=\text{S}[16] + \nu\text{CO}[8] + \delta\text{COH}[7]$
1406	1227	4A'	$\nu\text{CO}[29] + \nu\text{C}=\text{S}[21] + \delta\text{COH}[18] + \delta\text{CH}[17]$
1366	1152	5A'	$\nu\text{CO}[63] + \delta\text{COH}[60] + \delta\text{SCO}[6]$
1043	929	1A''	$\gamma\text{CH}[100]$
1028	934	6A'	$\nu\text{C}=\text{S}[61] + \delta\text{COH}[16] + \delta\text{SCO}[9] + \nu\text{CO}[9]$
524	483	2A''	$\tau\text{CO}[100]$
515	447	7A'	$\delta\text{SCO}[104] + \delta\text{CH}[14]$

^a PEDs smaller than 5 are not presented.

Table 15. Calculated vibrational frequencies (cm^{-1}) and PEDs of *s-trans* dithioformic acid

<i>ab initio</i>	scaled	symmetry	PED ^a
3342	2957	1A'	$\nu\text{CH}[100]$
2918	2526	2A'	$\nu\text{SH}[100]$
1459	1375	3A'	$\delta\text{CH}[71] + \nu\text{C}=\text{S}[30] + \nu\text{CS}[6]$
1202	1057	4A'	$\nu\text{C}=\text{S}[750] + \delta\text{CH}[29] + \delta\text{CSH}[10]$
1050	949	5A'	$\delta\text{CSH}[78] + \nu\text{CS}[16] + \nu\text{C}=\text{S}[7]$
918	843	1A''	$\gamma\text{CH}[100]$
784	704	6A'	$\tau\text{CS}[63] + \delta\text{SCS}[19] + \delta\text{CSH}[9] + \nu\text{C}=\text{S}[9]$
365	294	2A''	$\tau\text{CS}[100]$
533	319	7A'	$\delta\text{SCS}[83] + \nu\text{CS}[13]$

^a PEDs smaller than 5 are not presented.

The calculated frequencies for *s-cis* HCOOH show an excellent agreement with experimental values⁴⁴ (absolute mean error = 2 cm^{-1} or 0.2%; see table 7). In addition, the high degree of coupling between the CO stretching and the COH in-plane bending motions clearly stands out from the calculated PED of 5A' and 6A' normal modes. Comparison with other PEDs^{44,47,49} shows that the present calculations stress the importance of vibrational coupling between CH in-plane bending and C=O stretching oscillators, thus reflecting the oxygen-to-CH bond back-donation effect.

When applied to other isotopic species, the present force field confirms its reliability, the absolute mean errors in frequencies being of similar magnitude to those obtained for the light isotopomer.

Thioformic Acid

The infrared spectrum of this acid suggests the presence of both thiol and thione forms in the tautomeric equilibrium at room temperature.¹² Normal coordinate calculations based on these spectral assignments yield a vibrational force field that fits nicely the observed frequencies.¹⁵ This force field was derived from a set of force constants taken from similar molecules by iteratively improving the results. While this method of force field parameterization is commonly used, it is not sufficiently reliable, especially when the experimental data available are scarce or the band assignments are doubtful.

In general, previous band assignments and calculated PEDs^{12,15} for *s-cis* thioformic acid are in accord with our results. However, our force field predicts that the CSH in-plane bending vibration occurs at 921 cm^{-1} , where it is likely to overlap with the strong i.r. band at 946 cm^{-1} . The calculated frequency for this mode is near the values observed in similar molecules, like HCSSH (922 cm^{-1} ⁴³), CCl_3COSH (908 cm^{-1} ¹⁴) and CH_3CSSH (910 cm^{-1} ⁵⁰). Instead, the 727 cm^{-1} band, previously assigned to this vibration,^{12,15} should be ascribed to the CS stretching mode of the *s-trans* thiol form (calculated at 707 cm^{-1}). Polymeric species also absorb at approximately the same wavenumber (the trimer absorbs at 726 cm^{-1} ¹²).

The OCS bending and torsional vibrations were initially expected to occur at too high frequencies.¹⁵ This misassignment, which resulted from lack of the corresponding experimental frequencies, stresses the risk of transferring force constants between different molecules.

The frequencies obtained for *s-trans* thioformic acid are very similar to those of the *s-cis* form (see table 13). This fact, together with the small equilibrium population of this conformer at room temperature, makes the assignment of spectral bands to this form rather difficult. In fact, a large majority of *s-trans* thiol bands are expected to

overlap with the most intense bands of the *s-cis* form. Exceptions to this rule are the CS stretching mode, herein ascribed to the 727 cm^{-1} band, and the low frequency OCS bending and torsional modes. The experimental values for these modes presented in table 13 have been derived in ref. (11) from the HCOSH microwave spectrum.

The calculated (6-31G*/scaled) and observed OCS bending frequencies for the *s-trans* thiol form show reasonable agreement; however, the torsional mode is significantly underestimated by these calculations. This results from assuming direct transferability of scaling factors between rotational isomers. In the case of low-frequency and strongly anharmonic torsional vibrations this assumption does not seem to work well.

The previously proposed band assignments of *s-cis* thionformic acid^{12,15} are not in consonance with our results, except for the 666 cm^{-1} band, ascribed to the torsional vibration of this form.

The large difference between the 6-31G* calculated CH stretching frequencies of *s-cis* thione and thiol tautomers (*ca.* 150 cm^{-1}) clearly indicates that the *s-cis* thione form cannot contribute to the infrared band at 2850 cm^{-1} , as proposed in ref. (15). Instead, this band should be ascribed only to the thiol conformers. In fact, our calculations predict that the CH stretching vibration of the thione form should appear at a significantly higher frequency (*ca.* 2990 cm^{-1}).

A somewhat similar situation is observed for the 1339 cm^{-1} band and the CH in-plane bending vibration. The calculations indicate that this mode occurs at quite different frequencies for the thione and the thiol forms. In particular, the 1339 cm^{-1} band should correspond to the thiol vibrations while the low intensity band at 1402 cm^{-1} (not previously assigned^{12,15}) may be due to the thione form (calculated value, 1460 cm^{-1}).

Also, the previously proposed assignment of the 1235 cm^{-1} band to the COH in-plane bending mode^{12,15} is not supported by the present study. The calculations indicate that this band should have a predominant contribution of the CO stretching oscillator (see table 9), and that the COH in-plane bending mode should correspond to the i.r. band at 1160 cm^{-1} . It is important to note that this band was previously assigned to the C=S stretching mode.¹²⁻¹⁵ This mode is now calculated to occur at a much lower frequency. Considering the effects that determine the electronic density on the C=X double bond, it is expected that the C=S stretching vibration occurs at a higher frequency in dithioformic acid than in thionformic acid. Thus, an upper value of 1048 cm^{-1} (the experimental value for the C=S stretching mode of HCSSH^{45,46}) can be established *a priori* for the frequency of this mode in thionformic acid. The 6-31G* calculated frequency is 1027 cm^{-1} . Considering the usual overestimation of frequencies by *ab initio* calculations, this result suggests that the C=S vibration of the *s-cis* thionformic acid should be ascribed to a band below 950 cm^{-1} , probably overlapping with the 946 cm^{-1} i.r. band observed in ref. (12) (the calculated 6-31G*/scaled frequency is 935 cm^{-1} ; see table 9).

The higher degree of vibrational coupling in thione forms of thioformic acid as compared with thiol conformers has been previously predicted¹⁵ and is clearly confirmed by our results.

Dithioformic Acid

Vibrational spectra of dithioformic acid have not attracted much attention in the past. In a short communication,⁴⁵ the i.r. spectrum of this molecule was reported but band assignments were not performed. More recently, a molecular-mechanical calculation using the PF2 force field was carried out and an assignment of the i.r. spectrum proposed.⁴⁶

The present study confirms the assignments based on molecular mechanics and shows that a high degree of vibrational mixing occurs, as in thione forms of thioformic acid. It should be pointed out that the extent of vibrational coupling draws a line between the carbonyl and thiocarbonyl molecules.^{3,4,51}

Table 16. Values of P_{ZZ}^x/e^a for the C=X \rightarrow z stretching (X = O or S), obtained from a 6-31G* calculation [see eqn. (3)]

P_{ZZ}^x/e^a molecule	total		static		dynamic	
	O	S	O	S	O	S
H ₂ C(=X)	-1.072	-0.660	-0.406	-0.173	-0.666	-0.487
<i>s-cis</i> HC(=X)OH	-1.326	-1.137	-0.479	-0.306	-0.847	-0.831
<i>s-trans</i> HC(=X)OH	-1.355	-1.156	-0.468	-0.273	-0.887	-0.883
<i>s-cis</i> HC(=X)SH	-1.426	-1.164	-0.364	-0.183	-1.062	-0.981
<i>s-trans</i> HC(=X)SH	-1.436	-1.178	-0.381	-0.173	-1.055	-1.005

$$^a e = 1.602\ 189\ 2 \times 10^{-19} \text{ C.}$$

Infrared Intensity Parameters for C=X Stretching Vibrations

In order to better understand the electronic effect of the substituent on the C=X stretching mode (X = O or S) we have focused our attention on the $\partial p_z/\partial z_x$ element of APT and the X atom, which is directly associated with the C=X \rightarrow z stretching intensity. Considering the definition of ζ_x^{corr} within the CCFO framework,²³ the element $\partial p_z/\partial z_x$ can be partitioned into two contributions,

$$(P_{ZZ}^x)_{\text{total}} = (P_{ZZ}^x)_{\text{static}} + (P_{ZZ}^x)_{\text{dynamic}} \quad (3)$$

where

$$(P_{ZZ}^x)_{\text{total}} = \partial p_z/\partial z_x \quad (3a)$$

$$(P_{ZZ}^x)_{\text{static}} = \zeta_x^{\text{corr}} \quad (3b)$$

and

$$(P_{ZZ}^x)_{\text{dynamic}} = \sum_{\alpha} (\partial \zeta_{\alpha}^M/\partial z_x) Z_x^{\circ} + \Delta_{\text{ov},x}^{\text{zz-xx}} \quad (3c)$$

with

$$\Delta_{\text{ov},x}^{\text{zz-xx}} = \Delta_{\text{ov},x}^{\text{zz}} - \Delta_{\text{ov},x}^{\text{xx}} \quad (3d)$$

This partition procedure has been previously used successfully to analyse experimental and calculated values for both the static and dynamic contributions of the $\partial p_z/\partial z_x$ element in other molecules.⁵²

Table 16 shows the values of $(P_{ZZ}^x)_{\text{total}}$ and its static and dynamic contributions for the molecules studied in this work. The absolute values of $(P_{ZZ}^o)_{\text{total}}$ are always greater than $(P_{ZZ}^s)_{\text{total}}$. This is mainly due to the static contributions.

For the HC(=O)R compounds, with R = H, OH or SH, the substituent effect affects mainly the dynamic contribution. In addition, the *s-cis*/*s-trans* conformational effect does not significantly alter the $(P_{ZZ}^o)_{\text{total}}$ element (see table 16). Indeed, the similarity between intensity parameters of rotational isomers of carbonyl compounds has already been pointed out before.⁵³

For the HC(=S)R compounds, with R = H, OH or SH, the effect of the substituent on the static contribution of $\partial p_z/\partial z_s$ is relatively greater than that observed in the case of the carbonyl compounds. However, in both kinds of molecule, the dynamic contribution is more affected by the R substituent than the static contribution (table 16). Again, rotational isomers present similar values for both $(P_{ZZ}^s)_{\text{static}}$ and $(P_{ZZ}^s)_{\text{dynamic}}$, thus suggesting the transferability of intensity parameters between rotational isomers also in thiocarbonyl compounds.

It should be pointed out that, while the C=X bond stretching affects also $(P_{YZ}^x)_{\text{total}}$, this contribution is negligible with respect to $(P_{ZZ}^x)_{\text{total}}$.

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