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Experimental and Computational Thermochemistry of 2- and 3-Thiophenecarboxylic Acids

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The enthalpies of combustion and sublimation of 2- and 3-thiophenecarboxylic acids were measured and the gas-phase enthalpies of formation at 298.15 K were determined. Standard ab initio molecular orbital calculations at the G2(MP2) and G2 levels were performed, and a theoretical study on molecular and electronic structures of the studied compounds has been carried out. Calculated enthalpies of formation using atomization and isodesmic bond separation reactions are compared with the experimental data. From experimental and theoretical results it seems that 3-thiophenecarboxylic acid is slightly more stable than the 2-isomer. A comparison of substituent effect of the carboxylic group in benzene and thiophene rings has been made.

1. Introduction

The family of the five-membered heterocycles is of basic importance in chemistry[1] and included among them is the family of the thiophene derivatives. If benzenes are the paradigm of aromatic molecules,[2] thiophenes are the simplest representatives of stable aromatic structures bearing sulfur. Their structure can be assumed to be derived from benzene by replacement of two annular CH groups with sulfur. The sulfur atom in this five-membered ring acts as an electron donating heteroatom by contributing two electrons to the aromatic sextet, and thiophene is thus considered to be an electron-rich heterocycle. The chemistry of thiophene derivatives is consequently dominated by this effect. The fact that the lone pair on sulfur contributes to the aromaticity is seen in the lower dipole moment of thiophene as compared to its saturated analogue tetrahydrothiophene.[3] Thiophene derivatives represent a portion of the sulfur-containing constituents of many of the light oils from carbonaceous deposits. It can be stated that all types of thiophene homologues have been found in products obtained from natural sources. The large number of reports pertaining to the synthesis of thiophene and its derivatives corroborates the continuing interest and importance of these compounds in biology,[4] chemistry,[1] industry,[5] and medicine.[6] Interest in thiophenes has also been extended to the study of oligomers of thiophene and their derivatives. Interest in oligomers arises from their wide range of photobiological effects[7−10] and as alternatives to inorganic materials in the synthesis of a class of organic conducting polymers.[8] These electron-rich conjugated oligomers have π-electron systems similar to the linear *cis,trans*-polyenes. Polythiophenes are attractive because they are stable in air, and when some of the hydrogens are substituted by alkyl or phenyl groups, they are soluble in most organic solvents.[11]

In general, it can be considered that the −COOH group in thiophenecarboxylic acids acts much the same as in any organic compounds. It undergoes esterification to give yields almost identical to those with benzoic acids. Amide formation is carried out in a manner similar to the preparation of benzamide. However, unlike benzamide, 2-thiophenecarboxamide cannot be pyrolyzed to 2-thiophenenitrile in yields above 10%, and the thiophenecarboxylic acids have specific reactions. Methods for the determination of isomers formed during nitration of 2-thiophenecarboxylic acid were studied by Rinkes.[12] He established irrevocably that the influence of a normally meta-directing group such as the carboxyl group is not influencial in the thiophene series and that, as a result of such substitution reactions, the major product is a 5-substituted-2-thiophenecarboxylic acid rather than a 4-substituted-2-thiophenecarboxylic acid.

In the context of a systematic study of the thermodynamic properties of thiophene derivatives, reliable experimental thermochemical studies of 2- and 3-substituted derivatives are still very scarce. Kharasch, in his critically revised compilation,[13] reports values for the heat of combustion of thiophene and 2-thiophenecarboxylic acid. Experimental enthalpy of formation values in the gas phase have only been reported for thiophene[14,15] and for 2- and 3-methylthiophene.[15] The purpose of this work is to study the energetics of 2- and 3-thiophenecarboxylic acids and their relationship with thiophene in comparison to benzoic acid and its relationship to benzene.

The approach selected is a combination of experimental determinations and high-level ab initio calculations of enthalpies of formation.

2. Experimental Section

Material and Purity Control. 2- and 3-thiophenecarboxylic acid were purified by crystallization twice from an ethanol−water mixture. The samples were carefully dried under vacuum at 50 °C. Determination of purities, assessed by DSC by the fractional fusion technique[16] indicated that the mole fraction of impurities in the compounds were less than 0.001. The samples were studied by DSC over the temperature range between $T = 258$ K and their fusion melting points, $T = 400.9$ K and $T = 412.9$ K for 2- and 3-thiophenecarboxylic acids, respectively; no transitions in the solid state were observed in these temperature ranges.

Procedure for Thermochemical Measurements. *Calorimetry*. An isoperibol calorimeter equipped with a rotary bomb and an isothermal water jacket was used for the measurements of the energies of combustion. Apparatus and procedure have

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TABLE 1: Physical Properties at $T = 298.15$ K (Estimated Values in Parentheses)

compound	M/g mol^{-1}	ρ/g cm^{-3}	$10^{-7}(\delta V/\delta T)_P$/dm^3 g^{-1} K^{-1}	c_P/J K^{-1} g^{-1}
polyethene	13.5582	0.918	7.650	1.99
Vaseline	14.0266	0.870[a]	8.374[b]	2.22[c]
cotton	27.700	1.5	9.69[d]	1.48
2-thiophenecarboxylic acid	128.15006	1.49	(3.354)	1.203
3-thiophenecarboxylic acid	128.15006	1.47	(3.354)	1.047

[a] Value taken from ref 19. [b] Value taken from ref 20. [c] Value taken from ref 21. [d] Value taken from ref 22.

been described in refs 17a and 17b. The initial temperature of the combustion experiments was chosen so that the final calorimeter temperature would be near 298.15 K. The energy of the reaction was always referred to the final temperature of 298.15 K. The value of the energy equivalent determined and used in computing the results of the combustion experiments was $\epsilon(\text{calor}) = 28.8709 \pm 0.0010$ kJ K^{-1}.

The energies of combustion of 2- and 3-thiophenecaboxylic acids were determined by burning the solid samples in pellet form. The pelleted compound was enclosed in polyethene bags. Vaseline was used as auxiliary material to have only around 8 mmol of sulfur in the samples. The bomb was filled with oxygen to a pressure of $p = 3.04$ MPa. Under these conditions no carbon, CO, or SO_2 was found. The empirical formula and massic energy of combustion of our polyethene,[18] $C_{0.960}H_{2.000}$ and $-46\,371 \pm 4$ J g^{-1}, and cotton-thread fuse, $C_{1.000}H_{1.740}O_{0.871}$ and $17\,410 \pm 37$ J g^{-1}, were determined in our laboratory. The massic energy of combustion of Vaseline used was $-46\,086 \pm 5$ J g^{-1}.[17] After disassembly of the calorimeter, the bomb gases were slowly let out and the absence of CO and SO_2 was confirmed with Dräger tubes (sensitivity level $\approx 1 \times 10^{-6}$ and 1×10^{-7} mass fractions, respectively). Analysis of the liquid phase in the bomb was performed as described in refs 17a and 17b. The absence of SO_3^{2-} and NO_2^- was checked by calibrated ionic chromatography. The quantity of nitric acid was taken as the difference between the total acid and the theoretical quantity of sulfuric acid calculated from the mass of sample. The corrections for nitric acid were based on the value of -59.7 kJ mol^{-1} for the molar energy of formation of 0.1 mol dm^{-3} HNO_3(aq) from N_2(g), O_2(g), and H_2O(l). All weighings were performed with a Mettler AT-21 microbalance. For the correction of apparent mass to mass, conversion of the energy of the actual bomb process to that of the isothermal process, and the correction to standard states, we have used the values of density, ρ, massic heat capacity, c_p, and $(\delta V/\delta T)_p$, for polyethene, Vaseline, cotton, and the two compounds given in Table 1. Heat capacities were determined by DSC. Corrections to the standard states were made according to Hubbard et al.[23] The atomic weights of the elements were those recommended by IUPAC in 2000.[24]

A differential scanning calorimeter (Perkin-Elmer, Pyris 1) equipped with an Intracooler unit was used in this research to measure the heat capacities of the compounds, to control the purity, and to study the phase transitions of the samples. Its temperature scale was calibrated by measuring the melting temperature of the recommended high-purity reference materials: benzoic acid, tin, and indium.[25] The power scale was calibrated with high-purity indium (mass fraction: >0.999 99) as a reference material.[25] Heat capacities were determined following the method described in ref 26. Synthetic sapphire and benzoic acid were used as standard materials[27] for checking all the process.

Knudsen-Effusion Method. The vapor pressure as a function of temperature of the 2- and 3-thiophenecarboxylic acids were measured by a mass-loss Knudsen-effusion method, using the procedure described in ref 28. The apparatus consists, essentially, of a stainless steel sublimation chamber immersed in a thermoregulated water jacket and connected to a high-vacuum system ($p = 1 \times 10^{-4}$ Pa). The Knudsen cell was weighed before and after each experiment to determine the mass of sublimed material. The weighings were reproducible to within ±0.000 002 g. The vapor pressure, p, for each temperature, T, was calculated by means of the equation

$$p = (\Delta m/W_a at)\,(2\pi RT/M)^{1/2} \qquad (1)$$

where a is the area of the effusion orifice, t is the time, and W_a is the corresponding Clausing[29] coefficient. The membrane for the effusion measurements of vapor pressure was a tantalum foil $l = 0.021 \pm 0.004$ mm. The area of the effusion orifice was $a = 0.347 \pm 0.002$ mm^2, and the Clausing[29] coefficient $W_a = 0.980 \pm 0.004$.

Computational Details. Standard ab initio molecular orbital calculations[30] were performed with the Gaussian98 series of programs.[31] The energies of the studied compounds were calculated using Gaussian-2 theory, at the G2(MP2)[32] and G2[33] levels.

G2(MP2) and G2 correspond effectively to calculations at the QCISD(T)/6-311+G(3df,2p) level on MP2(full)/6-31G(d) optimized geometries, incorporating scaled HF/6-31G(d) zero-point vibrational energies and a so-called higher-level correction to accommodate remaining deficiencies.

We have also reoptimized the geometries at the MP2(full)/6-31G(3df,2p) level to obtain more reliable molecular structures for the compounds studied.

The bonding characteristics of the compounds studied have been investigated using a population partition technique, the natural bond orbital (NBO) analysis of Reed and Weinhold.[34,35] The NBO formalism provides values for the atomic natural total charges and describes the bonding in terms of the natural hybrids centered on each atom. The NBO analysis has been performed using the NBO program,[36] implemented in the Gaussian98 package. Calculations were carried out on the MP2 charge densities to explicitly include electron correlation effects.

Theoretical Determination of Heats of Formation. In standard Gaussian-n theories, theoretical enthalpies of formation are calculated through atomization reactions. We have detailed this method in previous studies.[37,38]

$$C_5H_4O_2S(g) \rightarrow 5C(g) + 4H(g) + 2O(g) + S(g) \qquad (2)$$

Raghavachari et al.[39] have proposed to use a standard set of isodesmic reactions, the "bond separation reactions",[30] to derive the theoretical enthalpies of formation. This method has been detailed in previous studies.[37,38]

In the case of thiophenecarboxylic acids, the bond separation reaction using their effective valence bond structures, is

$$C_5H_4O_2S(g) + 7CH_4(g) + H_2S(g) \rightarrow 2CH_3CH_3(g) + 2CH_2{=}CH_2(g) + 2CH_3SH(g) + CH_3OH(g) + H_2CO(g) \qquad (3)$$

TABLE 2: Results of Combustion Experiments of the Two Isomers of Thiophenecarboxylic Acid at $T = 298.15$ K[a]

	2-Thiophenecarboxylic Acid					
m'(compound)/g[b]	1.03230	1.02882	1.02744	1.03080	1.02663	1.02824
m''(polyethene)/g[b]	0.08297	0.07487	0.08412	0.07949	0.08206	0.08329
m'''(Vaseline)/g[b]	0.17252	0.20054	0.19339	0.18676	0.16221	0.21149
m''''(fuse)/g[b]	0.00234	0.00230	0.00253	0.00227	0.00231	0.00244
$\Delta T_c/\mathrm{K} = (T_f - T_i + \Delta T_{corr})/\mathrm{K}$	−1.1884	−1.2178	−1.2202	−1.2045	−1.1661	−1.2485
ϵ(calor)($-\Delta T_c$)/kJ[c]	−34.3090	−35.1592	−35.2281	−34.7758	−33.6670	−36.0458
ϵ(cont)($-\Delta T_c$)/kJ[d]	−0.0602	−0.0622	−0.0620	−0.0611	−0.0590	−0.0636
ΔU_{ign}/kJ[e]	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$\Delta U_{dec}(HNO_3)$/kJ[f]	0.0551	0.0554	0.0450	0.0565	0.0574	0.0618
$\Delta U_{diln}(H_2SO_4)$/kJ[g]	−0.00395	−0.00390	−0.00388	−0.00393	−0.00390	−0.00387
ΔU(corr to std states)/kJ[h]	0.0339	0.0347	0.0349	0.0343	0.0333	0.0354
$-m''\Delta_c u^o$(polyethene)/kJ	3.8477	3.4717	3.9010	3.6861	3.8052	3.8622
$-m'''\Delta_c u^o$(Vaseline)/kJ	7.9509	9.2423	8.9130	8.6071	7.4760	9.7470
$-m''''\Delta_c u^o$(fuse)/kJ	0.0408	0.0401	0.0442	0.0396	0.0404	0.0425
$\Delta_c u^o$(compound)/kJ g^{-1}	−21.7425	−21.7542	−21.7590	−21.7473	−21.7387	−21.7500
$\langle\Delta_c u^o$(298.15 K)$\rangle$/kJ g^{-1}	−21.7486 ± 0.003					
	3-Thiophenecarboxylic Acid					
m'(compound)/g[b]	1.01724	1.01353	1.02986	1.02832	1.02376	1.03268
m''(polyethene)/g[b]	0.08456	0.09241	0.09599	0.08760	0.08929	0.08269
m'''(Vaseline)/g[b]	0.18611	0.17123	0.18988	0.19671	0.15030	0.16675
m''''(fuse)/g[b]	0.00247	0.00243	0.00244	0.00214	0.00220	0.00216
$\Delta T_c/\mathrm{K} = (T_f - T_i + \Delta T_{corr})/\mathrm{K}$	−1.2004	−1.1872	−1.2349	−1.2305	−1.1560	−1.1784
ϵ(calor)($-\Delta T_c$)/kJ[c]	−34.6560	−34.2741	−35.6515	−35.5259	−33.3758	−34.0203
ϵ(cont)($-\Delta T_c$)/kJ[d]	−0.0607	−0.600	−0.0626	−0.0624	−0.0582	−0.0595
ΔU_{ign}/kJ[e]	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$\Delta U_{dec}(HNO_3)$/kJ[f]	0.0573	0.0636	0.0574	0.0588	0.0571	0.0636
$\Delta U_{diln}(H_2SO_4)$/kJ[h]	−0.00377	−0.00374	−0.00390	−0.00388	−0.00387	−0.00396
ΔU(corr to std states)/kJ[i]	0.0342	0.0338	0.0351	0.0350	0.0331	0.0336
$-m''\Delta_c u^o$(polyethene)/kJ	3.9212	4.2851	4.4514	4.0622	4.1404	3.8344
$-m'''\Delta_c u^o$(Vaseline)/kJ	8.5772	7.8913	8.7511	9.0660	6.9270	7.6848
$-m''''\Delta_c u^o$(fuse)/kJ	0.0431	0.0424	0.0426	0.0374	0.0383	0.0376
$\Delta_c u^o$(compound)/kJ g^{-1}	−21.7131	−21.7277	−21.7315	−21.7179	−21.7259	−21.7199
$\langle\Delta_c u^o$(298.15 K)$\rangle$/kJ g^{-1}	−21.7227 ± 0.003					

[a] For a definition of the symbols see refs 23 and 40. $T_{th} = 298.15$ K; $V_{bomb} = 0.260$ dm^3; $p^i_{gas} = 3.04$ MPa; $m^i_{water} = 10.00$ g. [b] Masses obtained from apparent mass. [c] ϵ(calor), energy equivalent of the whole system less the content of the bomb. [d] ϵ(cont), energy equivalent of the contents of the bomb ϵ (cont)($-\Delta T_c$) = ϵ^i(cont)(T^i − 298.15 K) + ϵ^i(cont)(298.15 K − T^f+ ΔT_{corr}). [e] Experimental energy of ignition. [f] Experimental energy of formation of nitric acid. [g] Experimental energy of formation of sulfuric acid. [h] ΔU(corr to std states) is the sum of items 81−85, 87−90, 93, and 94 in ref 23.

TABLE 3: Standard Molar Energy of Combustion and Enthalpies of Combustion and Formation at $T = 298.15$ K

compound	$\Delta_c U^0_m$/kJ mol^{-1}	$\Delta_c H^\circ_m$/kJ mol^{-1}	$\Delta_f H^\circ_m$/kJ mol^{-1}
2-thiophenecarboxylic acid	−2787.1 ± 1.3	−2790.8 ± 1.3	−350.4 ± 1.4
3-thiophenecarboxylic acid	−2783.8 ± 1.2	−2787.5 ± 1.2	−353.7 ± 1.4

At it is evident, the 2- and 3-isomers have the same products whether it be from atomization or bond separation reactions, and so many errors are expected to cancel if one looks at the isomerization reaction as well:

$$\text{2-}C_4H_3SCOOH \rightleftarrows \text{3-}C_4H_3SCOOH \tag{4}$$

3. Results and Discussion

The results of combustion experiments for the 2- and 3-thiophenecarboxylic acids are given in Table 2.

The symbols in this table have the same meaning as in ref 40. The experimental values have been derived as in ref 23. The massic energy of combustion is referred to the final temperature of the experiments, $T = 298.15$ K. The energy of solution of carbon dioxide in water at 298.15 K, $\Delta_{sol}U(CO_2)$, was taken as −17.09 kJ mol^{-1}, and the solubility constant, $K(CO_2)$, as 0.034 40 mol dm^{-3} atm^{-1} at 298.15 K.[41]

Table 3 gives the derived molar energies and enthalpies of combustion referred to the combustion reaction of 2- and 3-thiophenecarboxylic acids, in the crystalline state at $T = 298.15$ K, and correspond to the reaction

$$C_5H_4O_2S(c) + {}^{13}/_2O_2 + 114H_2O(l) = 5CO_2 + [H_2SO_4{\bullet}115H_2O](l) \tag{5}$$

In accordance with normal thermochemical practice, the uncertainties assigned are, in each case, twice the overall standard deviation of the mean and include the uncertainties in calibration and in the values of the auxiliary quantities.[42] To derive $\Delta_f H^\circ_m$(cr) from $\Delta_c H^\circ_m$(cr), the standard molar enthalpies of formation of H_2O(l) and CO_2(g), at $T = 298.15$ K, −285.839 ± 0.042 and −393.51 ± 0.13 kJ mol^{-1}, respectively, were used.[43]

The results of our Knudsen-effusion experiments for the 2- and 3-thiophenecarboxylic acids are summarized in Table 4.

An equation of the type

$$\log(p/\mathrm{Pa}) = -B(T/\mathrm{K})^{-1} + A \tag{6}$$

was fitted to the results of Table 4 by the least-squares method. The quantities $\delta p/p$ are the fractional deviations of the experimental vapor pressures from those computed using eq 6. The highest error for the vapor pressure, p, in Table 4 is $5 \times 10^{-3}p$, computed as the sum of the estimated errors of all quantities in eq 1. The parameters A and B for 2- and 3-thiophenecarboxylic acids are given in Table 5. The enthalpies of sublimation at the mean temperature θ of their experimental range, have been calculated from the corresponding B values and are also listed in Table 5. The uncertainties assigned to the values of $\Delta_{sub}H^\circ_m(\theta)$ are based on the standard deviations of B values.

Sublimation enthalpy at the temperature $T = 298.15$ K was derived using the same equation as in ref 44. $C_{p,m}{}^\circ$(g) has been calculated by using the group contribution scheme of Rihani,[45] and $C_{p,m}{}^\circ$(cr) has been taken from the experimental results determined in our laboratory and given in ref 46.

TABLE 4: Vapor Pressures of the Thiophenecarboxylic Acids

T/K	t/s[a]	Δm/mg[b]	p/Pa[c]	$10^2(\delta p/p)$[d]	T/K	t/s[a]	Δm/mg[b]	p/Pa[c]	$10^2(\delta p/p)$[d]
				2-Thiophenecarboxylic Acid					
306.8	26 100	3.62	0.144	1.12	315.6	13 200	4.70	0.375	−2.47
309.8	18 000	3.53	0.205	1.57	318.6	16 500	8.42	0.541	0.82
312.5	20 400	5.23	0.269	−1.75	321.8	14 400	10.26	0.759	1.39
				3-Thiophenecarboxylic Acid					
307.8	21 420	3.52	0.171	0.194	319.7	20 400	12.14	0.631	−2.52
310.8	26 100	6.08	0.244	1.21	322.4	22 020	18.15	0.879	1.38
313.6	25 200	7.99	0.333	0.796	325.4	18 000	20.23	1.200	0.941
316.7	26 580	11.54	0.459	−1.49					

[a] Time for the experiment. [b] Mass of sublimed substance. [c] Vapor pressure. [d] δp denotes deviation of the experimental vapor pressures from the values computed using eq 5.

TABLE 5: Molar Enthalpies of Sublimation

compound	θ/K	A	B	$\Delta_{\mathrm{sub}}H^\circ_{\mathrm{m}}(\theta)$
2-thiophenecarboxylic acid	314.26	33.7 ± 0.5	−10921.4 ± 154.6	90.8 ± 1.3
3-thiophenecarboxylic acid	316.61	34.0 ± 0.3	−10996.0 ± 104.9	91.4 ± 0.9

The standard molar enthalpies of sublimation and formation in crystalline and gaseous states for 2- and 3-thiophenecarboxylic acids at $T = 298$ K are given in Table 6.

No combustion enthalpies for the two thiophenecarboxylic acids isomers have been found for comparison with our results. The enthalpy of sublimation of 2-thiophenecarboxylic acid was determined previously by Bradley.[47] The result obtained with a sample of unknown purity, in the temperature interval from 314.97 to 323.17 K, $\Delta_{\mathrm{sub}}H(319\ \mathrm{K}) = 96.94$ kJ mol^{-1} corrected at $T = 298.15$ K is $\Delta_{\mathrm{sub}}H = 97.45$ kJ mol^{-1}. This result is in poor agreement with our value.

Molecular and Electronic Structures. Structural data, measured by X-ray diffraction, for 2- and 3-thiophenecarboxylic acids have been described in the literature.[48−50] In the crystal,[48] 2-thiophenecarboxylic acid is almost planar except that the sulfur atom is displaced by 0.03 Å from the molecular plane. The authors obtain a dihedral angle between the planes SC_2C_3 and SC_5C_4 of 178°. A lack of planarity in the ring of 2-thiophenecarboxylic acid was also observed in a study at −170 °C by Hudson and Robertson,[51] who find the sulfur atom lying 0.02 Å out of the plane of the four carbon atoms of the ring.

In the case of 3-thiophenecarboxylic acid, the molecular structure was determined by means of X-ray diffraction by Hudson and Robertson.[50] They conclude that the molecule is nonplanar in two respects: the thiophene ring is slightly buckled, with the sulfur atom out of the plane by 0.02 Å, like in 2-thiophenecarboxylic acid; and the carboxylic acid group is twisted with respect to the thiophene ring by 4.4°. This behavior is not observed in the calculated structures. Visser and coworkers[52] carried out a refinement of the structure of 3-thiophenecarboxylic acid with Hudson and Robertson's data because they observed the same anomalies as in the structure obtained for 3,3′-dithienyl when no disorder was assumed. In 3-thiophenecarboxylic acid one of the "double" bonds in the thiophene ring is long, which suggests that disorder may also occur in its crystals. The changes in the bonds lengths obtained by taking disorder into consideration are significant (see Table S2 of the Supporting Information).

The calculated molecular structures, optimized at the MP2(full)/6-31G(3df,2p) level of theory, are planar for the two compounds studied. They are shown in Figure 1. Bond distances and bond angles are collected in Tables S1 and S2 of the Supporting Information and compared with the available experimental data.

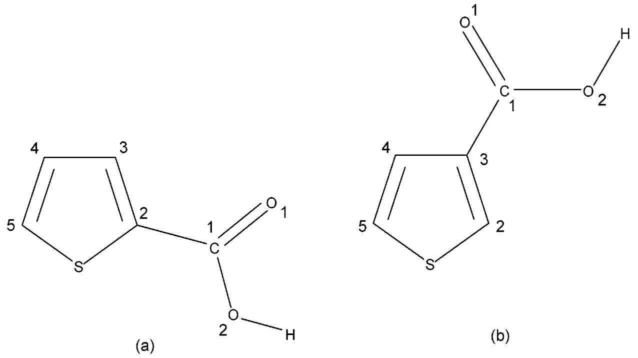

Figure 1. Molecular conformations of the two studied compounds: (a) 2-thiophenecarboxylic acid; (b) 3-thiophenecarboxylic acid.

In both optimized structures, the oxygen of the OH group is facing the sulfur of the ring (see Figure 1), in agreement with the experimental data. The corresponding structures with the oxygen of the carbonyl group facing the sulfur of the ring are very close in energy. At the G2(MP2) level, the differences between both types of structures are only 0.25 and 1.0 kJ mol^{-1}, for 2- and 3-thiophenecarboxylic acids, respectively.

It is interesting to note that the valency angle on the sulfur atom, C_2SC_5, is intermediate between the tetrahedral angle and a right angle. This fact is in line with the three 2-compounds, furoic, thenoic, and selenophenecarboxylic acids, where the experimental angles at O, S, and Se, are 107°,[53] 92°,[48] and 87°,[48] respectively. These angles follow the same pattern that the HXH angles in the simple hydrides, 103.4°, 92.3°, and 91.3°, for X = O, S, and Se, respectively.[54]

On the basis of the single bond distance $C(sp^2){-}S$ in divinyl sulfide calculated to be 1.74 Å,[54] the two experimental C−S distances, $C_2{-}S$ and $C_5{-}S$ in 2- and 3-thiophenecarboxylic acid, average as 1.71 ± 0.03 and 1.70 ± 0.03 Å, the same two bond distances obtained by calculation, average to a bond length of 1.69 Å. Both experiment and calculation suggest considerable double bond character. The $C(sp^3){-}S$ distances calculated[54] for methanethiol and dimethyl sulfide are larger, 1.80 and 1.79 Å, respectively. The C−C bonds are all shorter than single bonds and indicate considerable conjugation, including the exocyclic C−C bonds.

The whole carboxyl group appears to be attracted by the S atom in 2-thiophenecarboxylic acid, the angle $C_1C_2C_3$ being larger than C_1C_2S. The oxygen of the OH group is facing the

TABLE 6: Standard Molar Enthalpies at $T = 298.15$ K

compound	$\Delta_{\mathrm{f}}H^\circ_{\mathrm{m}}(\mathrm{cr})$/kJ mol^{-1}	$\Delta_{\mathrm{sub}}H^\circ_{\mathrm{m}}$/kJ mol^{-1}	$\Delta_{\mathrm{f}}H^\circ_{\mathrm{m}}(\mathrm{g})$/kJ mol^{-1}
2-thiophenecarboxylic acid	−350.4 ± 1.4	91.2 ± 1.3	−259.2 ± 1.9
3-thiophenecarboxylic acid	−353.7 ± 1.4	91.9 ± 0.9	−261.8 ± 1.7

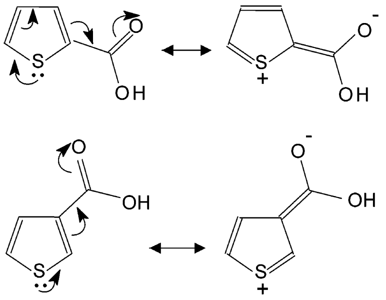

Figure 2. Resonance structures of 2- and 3-thiophenecarboxylic acids.

heteroatom of the ring, the inverse situation occurs in 2-furancarboxylic acid.[53] The distance O_2-S, 2.948 Å, is slightly shorter than the sum of the van der Waals radii, 3.00 Å.

Both the thiophene ring and the carboxyl group have electrons with orbitals of π-symmetry and it would thus be expected that conjugation would take place provided the groups were coplanar. A planar molecule is therefore favored. Resonance between the S atom and the COOH group through the ring[55] is represented for both compounds in Figure 2. As can be seen in the figure, the resonance structures suggest a longer C_2-S bond length in 2-thiophenecarboxylic acid and a longer C_3-C_4 bond length in the corresponding 3-isomer if resonance with the carboxyl group is important. If this hypothesis is correct, the bond between C atoms 3 and 4 in 2-thiophenecarboxylic acid would have more double-bond character than the same bond in 3-thiophenecarboxylic acid. This fact is observed in the calculated values, the C_3-C_4 bond length being slightly shorter in 2-thiophenecarboxylic acid. However, the experimental bond distances measured by different workers cited in Tables S1 and S2 are totally inconclusive (1.414 and 1.413 Å in 2-thiophenecarboxylic acid, 1.41 and 1.437 Å in 3-thiophenecarboxylic acid). Similarly, C_5-S should be shorter in the 2-isomer and C_2-S should be shorter in the 3-isomer. The calculated values follow this pattern but the experimental results remain inconclusive at best (C_5-S: 1.695 and 1.701 Å in 2-thiophenecarboxylic acid, 1.699 and 1.70 Å in 3-thiophenecarboxylic acid; C_2-S: 1.693 and 1.707 Å in 2-thiophenecarboxylic acid, 1.708 and 1.73 Å in 3-thiophenecarboxylic acid).

We have calculated the Wiberg bond indices,[56] B_i. The bond index between two atoms is a measure of the bond order and, hence, of the bond strength between these two atoms. They are shown in Figure 3. As can be seen, the bond orders accord with the previous hypothesis, and the C_3-C_4 bond has more double-bond character in 2-thiophenecarboxylic acid. Bond orders for C−S bonds also indicate a great π-delocalization in the ring.

The length of the bond C_1-C_2 (or C_1-C_3) linking the carboxyl group to the thiophene ring indicates that conjugation takes place between the two parts of the molecule. One result of this would be to shorten still further one or both of the C−S bonds, and the C_3-C_4 bond, in the thiophene ring of thiophenecarboxylic acids from the lengths observed in thiophene itself ($C-S = 1.714$ Å,[57] measured by microwave spectroscopy, and 1.714,[58] 1.717,[59] and 1.74 Å,[60] measured by electron diffraction; $C_3-C_4 = 1.424$ Å,[57] measured by microwave spectroscopy, and 1.419,[58] 1.442,[59] and 1.44 Å,[60] measured by electron diffraction). Again, this shortening is observed in the calculated values but some of the experimental results are inconclusive. It is interesting to note that a high electron concentration in these bonds of thiophenecarboxylic acids is suggested by the relatively large dissociation constants (pK_a values in aqueous solution of 2- and 3-thiophenecarboxylic acids: 3.49 (at 25 °C)[61] and 4.08 (at 20 °C),[62] respectively) as compared with that of benzoic acid ($pK_a = 4.19$, at 25 °C).[63]

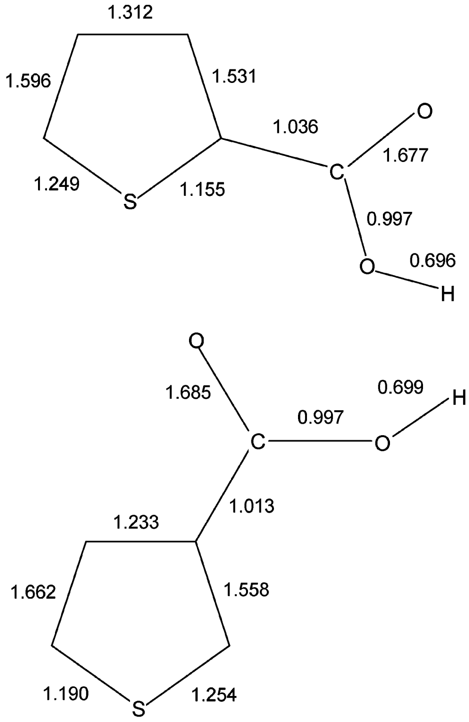

Figure 3. Wiberg bond indices calculated for 2- and 3-thiophenecarboxylic acids, calculated at the MP2(full)/6-31G(3df,2p) level.

To our knowledge there is only one experimental determination of the infrared spectra of 3-thiophenecarboxylic acid.[64] In the case of 2-thiophenecarboxylic acid there are three experimental studies[64−66] of its IR spectrum, but in one of them,[65] the author did not show all the experimental frequencies and only mentioned some of the bands.

The computed vibrational frequencies at the HF/6-31G(d) level, scaled by the factor 0.8953 recommended by Scott and Radom,[67] for both studied compounds are collected in Table S3 of the Supporting Information and compared with the available experimental data. An assignation of the frequencies to the different normal vibrational modes of the molecules is beyond the scope of this work.

In the investigation of the electronic structure of the five-membered ring heterocycles, understanding of the π-system is of basic importance. The rings are aromatic according to Hückel's rule. The π-system can be built up from four electrons provided by the π-MOs of the *cis*-butadiene fragment and two electrons originating from the p_z lone pair orbital of the heteroatom.[68] The other heteroatom lone pair incorporates into the σ-system.

We have carried out a population analysis using the natural bond orbital, NBO, analysis[34,35] to obtain the natural atomic charges (the nuclear charges minus summed natural populations of the natural atomic orbitals on the atoms) that characterize the ground electronic state of the thiophenecarboxylic acids. The calculated charges located at the heavy atoms for both compounds are reported in Figure 4.

As can be seen, the negative charge is located at the oxygen atoms of the carboxylic group and at the C atoms of the thiophene ring, being more negative in the last case when the C atoms are directly bonded to the S atom, whereas the positive charge is located at the sulfur atom, and at the C atom of the COOH group. The charge distribution does not appreciably change with the position of the carboxylic group, only a small charge redistribution takes place on the atoms of the thiophene ring.

TABLE 7: G2(MP2)- and G2-Calculated Energies at 0 K and Enthalpies at 298 K for the Compounds Studied

	G2(MP2)		G2	
compound	E_0	H_{298}	E_0	H_{298}
2-thiophenecarboxylic acid	−740.597843	−740.589923	−740.611082	−740.603162
3-thiophenecarboxylic acid	−740.598656	−740.590754	−740.611862	−740.603960

TABLE 8: G2(MP2)- and G2-Calculated Enthalpies of Formation of the Compounds Studied, Both from Atomization and from Bond Separation Isodesmic Reactions (All Values in kJ mol^{-1})

	G2(MP2)		G2		
compound	atomization	bond separation	atomization	bond separation	exp
2-thiophenecarboxylic acid	−271.4	−263.5	−262.0	−266.1	−259.2 ± 1.9
3-thiophenecarboxylic acid	−273.5	−265.6	−264.1	−268.2	−261.8 ± 1.7

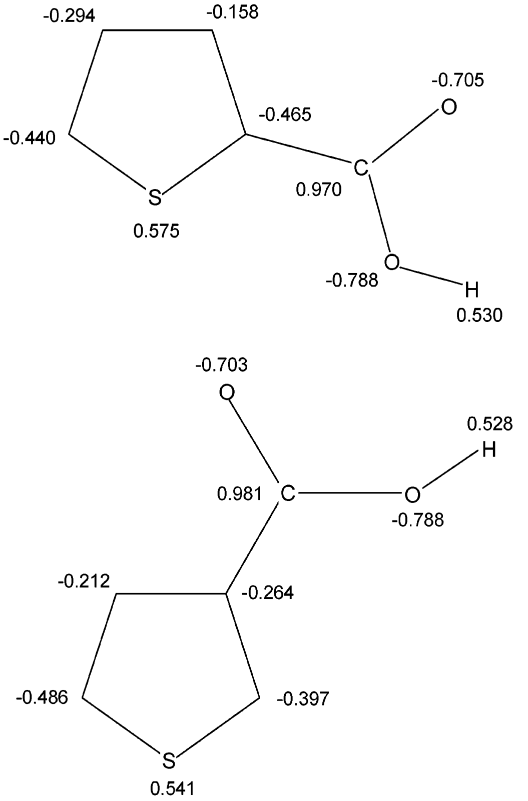

Figure 4. NBO atomic charges calculated for 2- and 3-thiophenecarboxylic acids, calculated at the MP2(full)/6-31G(3df,2p) level.

The NBO analysis also describes the bonding in terms of the natural hybrid orbitals. In the compounds studied, the hybridization of sulfur atoms is sp^4, with more than 78% of p character, whereas the hybridization of carbonyl oxygen atoms is sp$^{1.4}$ with only 57% p character, and that of the hydroxylic oxygen atoms is close to sp^2 to form the C−O bonds and sp$^{3.4}$ to form the O−H bonds. Sulfur and oxygen have sp (sp$^{0.7}$ in the case of S, and sp$^{0.7}$ and sp$^{1.3}$ in the case of O_1 and O_2, respectively) and p lone pairs that may delocalize into the vicinal antibonding orbitals. Through orbital occupancies and second-order perturbation energy lowering, ΔE^2, due to the interaction of the donor and acceptor orbitals, one can fix the exact orbitals that are involved in the charge-transfer process. Occupancies and energy lowerings of the orbitals involved in the delocalization of the lone pairs of S and O in 2- and 3-thiophenecarboxylic acids are shown in Table S4 of the Supporting Information.

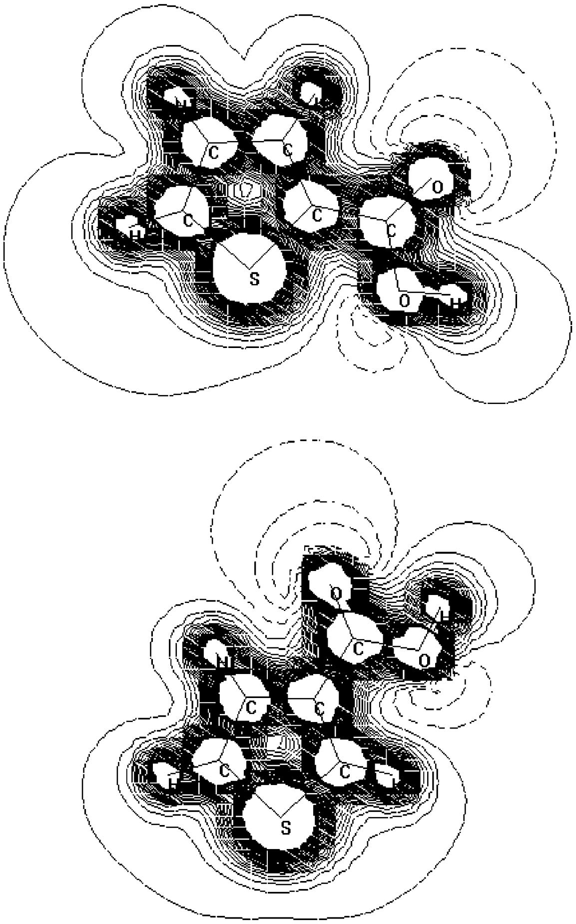

Figure 5. Electrostatic potential contours obtained for 2- and 3-thiophenecarboxylic acids.

Several studies on compounds involving atoms with different types of lone pairs (O, S, Se) have shown that the effect of the charge delocalization should not be analyzed only in the basis of $p_X \rightarrow \sigma^*_{CX}$ hyperconjugations because orbital interactions involving sp lone pairs, that is, $sp_X \rightarrow \sigma^*_{CX}$, are not negligible.[69] This behavior is observed in the compounds studied.

Figure 5 presents the electrostatic potential contours for the compounds studied. Most relevant, the regions of highest electron density (V_{min}) are easily located and assigned to the lone electron pairs on oxygen atoms. These are the regions in the molecules studied that are subject to electrophilic attack.

An important characteristic of the ground electronic state of a molecule is the ionization potential, IP. The first ionization potential for 2-thiophenecarboxylic acid has been experimentally determined[70] by means of photoelectron spectroscopy, the value being 9.14 eV.

We have calculated the IP values for the compounds studied according to Koopmans' theorem.[71,72] The ionization potentials, IP, and the electron affinities, EA, correspond approximately to the negatives of the energies of the highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO, respectively.

$$\mathrm{IP} = -E_{\mathrm{HOMO}} \qquad \mathrm{EA} = -E_{\mathrm{LUMO}} \tag{7}$$

The calculated IP value for 2-thiophenecarboxylic acid is 9.24 eV, obtained at the MP2(full)/6-31G(3df,2p) level, and it is in very good agreement with the experimental value. For 3-thiophenecarboxylic acid, we have obtained an IP value of 9.22 eV, indicating a very slight HOMO stabilization when the COOH group is in position ortho with respect to the S atom of the thiophene ring.

Electron affinities of −2.08 and −2.48 eV have been obtained for 2- and 3-thiophenecarboxylic acids, respectively.

Theoretical Enthalpies of Formation. G2(MP2)[32] and G2[33] calculated energies, at 0 K, for 2- and 3-thiophenecarboxylic acids are given in Table 7.

To calculate enthalpy values at 298 K, the difference between the enthalpy at temperature T and 0 K can be evaluated according to standard thermodynamics.[73] The thermal correction in Gaussian-*n* theories is made by using scaled (0.8929) HF/6-31G(d) frequencies for the vibrations in the harmonic approximation for vibrational energy,[74] the classical approximation for translation ($^3/_2RT$) and rotation ($^3/_2RT$ for nonlinear molecules, and RT for linear molecules), and an additional RT for converting energy to enthalpy (the PV term).

G2(MP2) and G2 enthalpies at 298 K, for the compounds studied, are also collected in Table 7.

It has been reported[39,75−77] that the G2 family of computational methods (notably G2(MP2)[32] and G2[33] itself) allows the reliable estimation of the standard enthalpies of formation in the gas phase of a variety of compounds. In many cases, the computed magnitudes agree with the experimental data within about 7.5 kJ mol^{-1}.[77] The standard procedure to obtain enthalpies of formation in Gaussian-*n* theories is through atomization reactions, but there has been some evidence in recent years that there is an accumulation of errors in the application of G2 theory (or similar approaches) to larger molecules.[75−79] Glukhovtsev and Laiter[78] have shown that more accurate heats of formation can be derived using isodesmic or homodesmotic reactions rather than atomization energies as in standard G2 theory.

As Raghavachari et al.[39] have pointed out, one of the deficiencies of the isodesmic reaction approach is that many different isodesmic reactions can be set up for the same molecule yielding different results. These authors have proposed to use simpler, but better defined, reactions to assess the performance of theoretical methods in a more systematic manner. A standard set of isodesmic reactions is “bond separation reactions”,[30] where all formal bonds between nonhydrogen atoms are separated into the simplest parent molecules containing these same kinds of linkages.

We have obtained in this study theoretical values of the enthalpy of formation of both compounds studied at G2(MP2) and G2 levels of theory, using both methods above-mentioned. The values obtained are shown in Table 8.

As can be seen in that table, the $\Delta_f H°_m$ values for 2- and 3-thiophenecarboxylic acids, calculated from G2(MP2) energies using the atomization reaction scheme are not in agreement with the experimental values, being 12.2 and 11.7 kJ mol^{-1} lower, respectively.

Calculations at the more expensive G2 level of theory should be more reliable because the electron correlation effect higher than those of second order could be very important for the sulfur compounds. The heats of formation of both compounds studied, calculated at the G2 level from atomization reactions, are very close to the experimental values, being only 2.8 and 2.3 kJ mol^{-1} lower than the experimental ones for 2- and 3-thiophenecarboxylic acids, respectively.

When a bond separation isodesmic reaction scheme is used to calculate the heats of formation of the molecules studied, the comparison of the calculated $\Delta_f H°$ values, both at G2(MP2) and G2 levels, with the experimental values is good, but the values obtained at the G2(MP2) level are closer to the experimental ones.

Comparison of our experimental and theoretical results for the enthalpies of formation of the two isomers of thiophenecarboxylic acids shows that the 3-thiophenecarboxylic acid is slightly more stable, thermodynamically, than the 2-isomer. The isomerization enthalpy obtained from eq 4 gives a value of 2.6 kJ mol^{-1} from experimental results. From theoretical calculations at both G2(MP2) and G2 levels a value of 2.1 kJ mol^{-1} is obtained. The agreement between both values is excellent.

Our experimental results allow us to make a comparative analysis with analogous substituted benzenes. This can be done by the evaluation of the energetic of

$$C_6H_5COOH + C_4H_4S \rightarrow C_4H_3SCOOH + C_6H_6 \tag{8}$$

Using the experimental enthalpies of formation of benzene,[15] thiophene,[15] and benzoic acid,[14] we can conclude that 2-thiophenecarboxylic acid is destabilized by 4.1 ± 2.2 kJ mol^{-1}. The value obtained for the 2-isomer can be a result of the through-space interaction between the oxygen of hydroxyl group with the sulfur atom. From the result obtained with 3-thiophenecarboxylic acid, 1.5 ± 2.0 kJ mol^{-1}, we can conclude that there are not significant differences between the substituent effect produced by a carboxylic group in benzene and the thiophene ring in the 3-position.

4. Conclusions

The experimental enthalpies of formation of 2- and 3-thiophenecarboxylic acids have been determined. Theoretical calculations of the enthalpies of formation at the G2 level, using the atomization reaction method, agree well with the experimental values. From experimental and theoretical results it seems that 3-thiophenecarboxylic acid is slightly more stable than the 2-isomer.

Molecular and electronic structures for the compounds studied have been obtained from theoretical calculations. The whole carboxyl group appears to be attracted by the S atom in 2-thiophenecarboxylic acid. The oxygen of the OH group is facing the heteroatom of the ring. The distance O−S is slightly shorter than the sum of the van der Waals radii. This attraction does not take place in the 3-isomer.

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Supporting Information Available: Tables S1 and S2 with the calculated and experimental bond distances and bond angles; Table S3 with the calculated and experimental vibrational frequencies, and Table S4 with the results of the NBO analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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