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Thermochemistry of 2,5-Thiophenedicarboxylic Acid

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The enthalpies of combustion and sublimation of 2,5-thiophenedicarboxylic acid [CASRN 4282-31-9] were measured by rotary-bomb combustion calorimetry and the method of transference in a saturated stream of nitrogen, and the gas-phase enthalpy of formation was determined, $\Delta_f H^o_m(g) = -(632.6 \pm 2.2)$ kJ·mol^{-1}. Standard ab initio molecular orbital calculations at the G2(MP2) and G3(MP2) levels were performed, and a theoretical study on the molecular and electronic structure of the compound has been carried out. The three most stable conformers have been explicitly taken into account. The calculated enthalpy of formation averaged using three different isodesmic reactions, -631.1 kJ·mol^{-1}, is in very good agreement with the experimental value. A comparison of the substituent effect of the carboxylic groups in benzene and thiophene ring has been made. The relative stability obtained for the substitution of two H atoms by COOH in position 2,5- for thiophene and 1,4- for benzene involve the same energetic effects, $\Delta\Delta_f H^o_m = -747.6 \pm 2.4$ and -748.2 ± 2.7 kJ·mol^{-1}, respectively.

Introduction

Over the past years, we have been involved in a thermochemical study of the energetic effects of sulfur compounds,[1−18] among them thiophene derivatives.[6,9,16,17] The fundamental interest in this work is the understanding of structural effects on thermodynamic stabilities that are reflected on the enthalpies of formation for the compounds studied. If benzenes are the paradigm of aromatic molecules,[19] thiophenes are the simplest representatives of stable aromatic structures bearing sulfur.[20] Thiophene obeys the $4n + 2\pi$ electron rule, and it is generally considered to be aromatic.[21] Its structure can be assumed to be derived from benzene by the replacement of two annular CH groups by 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.

In the context of a systematic study of the thermodynamic properties of thiophene derivatives, reliable experimental thermochemical studies are still scarce. Kharasch, in his almost 80-year-old compendium of critically evaluated data[22] reports values for the heat of combustion of thiophene and 2-thiophenecarboxylic acid. Furthermore, experimental enthalpies of formation in the gas phase have only been reported for thiophene,[23−27] 2- and 3-methylthiophene,[28,29] 2- and 3-thiophenecarboxylic acids,[6] benzo[*b*]thiophene,[30] dibenzothiophene,[30−32] and 1,2,3,4-tetrahydrodibenzothiophene.[33]

In a previous paper, we studied the thermochemistry of 2- and 3-thiophenecarboxylic acids.[6] In general, it can be considered that the −COOH group on thiophenecarboxylic acids acts much the same way as in other organic compounds. In our work, we showed that 3-thiophenecarboxylic acid is slightly more stable, thermodynamically, than 2-thiophenecarboxylic acid with an isomerization enthalpy of 2.6 kJ·mol^{-1}. In the comparison with benzene and its analogous substituted benzene, benzoic acid, we showed that the 2-isomer is destabilized by 2.4 kJ·mol^{-1} as a result of the through-space interaction between the oxygen of the hydroxyl group with the sulfur atom,[16] as opposed to stabilization because of an S···H···O hydrogen bond. With the result obtained with 3-thiophenecarboxylic acid, −0.2 kJ·mol^{-1}, we concluded that there are not significant differences between the substituent effects produced by a carboxyl group in benzene and the 3-position in thiophene.[16]

The purpose of this work is to study the energetic effects of 2,5-thiophenedicarboxylic acid (2,5-dicarboxythiophene) and its relationship with thiophene and 2-thiophenecarboxylic acid. Furthermore, a comparison with the analogous benzene derivatives (benzene, benzoic acid, and 1,4-benzenedicarboxylic acid) has been carried out. The approach selected is a combination of experimental determinations of the enthalpy of formation and high-level ab initio calculations.

Experimental Section

Material and Purity Control. 2,5-Thiophenedicarboxylic acid was commercially available from Aldrich (mass fraction 0.99). The commercial off-white powdered product was purified by crystallization twice from water, and then it was carefully dried under vacuum at 100 °C. Determination of purity by HPLC indicated that the mole fraction of impurities in the compound was less than 0.001. An elemental analysis of the purified sample gave the following results: Anal. Calcd for $C_6H_4O_4S$: C, 41.86%; H, 2.34%; S, 18.63%. Found: C, 41.80%; H, 2.26%; S, 18.33%.

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TABLE 1: Physical Properties at $T = 298.15$ K

compound	M $g{\cdot}mol^{-1}$	ρ $g{\cdot}cm^{-3}$	$(\delta V/\delta T)P \times 10^{-7}$ $dm^3{\cdot}g^{-1}{\cdot}K^{-1}$	$C_p(298.15\ K)$ $J{\cdot}K^{-1}{\cdot}g^{-1}$
vaseline	14.0266	0.870[a]	8.374[b]	2.22[c]
cotton	27.700	1.5	9.69[d]	1.48
2,5-thiophenedicarboxylic acid	140.1598	1.60[e]	3.354[f]	1.19[g]

[a] Value taken from ref 40. [b] Value taken from ref 41. [c] Value taken from ref 42. [d] Value taken from ref 43. [e] Determined in our lab. [f] Value estimated. [g] Value taken from ref 17.

Procedure for Thermochemical Measurements. *Combustion Calorimetry*. The enthalpy of formation in the crystalline state was determined from combustion calorimetry using an isoperibol combustion calorimeter equipped with a rotary bomb. Details of the technique and procedure used have been previously described.[2] The energy equivalent of the calorimeter, ϵ(calor), was determined from the combustion of benzoic acid, NIST Standard Reference Sample 39j, having a specific energy of combustion, $\Delta_c u = -(26\,434 \pm 3)$ $J{\cdot}g^{-1}$, under certificate conditions. From nine calibration experiments $\epsilon(\text{calor}) = (28\,871.08 \pm 0.90)$ $J{\cdot}K^{-1}$, where the uncertainty quoted is the standard deviation of the mean. Frequent calibration experiments were made throughout the series of combustion experiments. Thianthrene was used as a secondary reference material[34] to confirm the chemistry of the combustion process and the accuracy of the energy corrections involved in the analysis of results. The standard molar energy obtained, $\Delta_c u° = -(33\,465.3 \pm 5.9)$ $J{\cdot}g^{-1}$ is in good agreement with the recommended value,[34] $\Delta_c u° = -(33\,468 \pm 4)$ $J{\cdot}g^{-1}$.

The energy of combustion of 2,5-thiophenedicarboxylic acid was determined by burning the solid samples in pellet form in oxygen using Vaseline as auxiliary material so as to have around 8 mmol of sulfur in the samples.[35] The empirical formula and specific energy of combustion of our cotton-thread fuse, $C_{1.000}H_{1.740}O_{0.870}$ and $-(17410 \pm 37)$ $J{\cdot}g^{-1}$, were determined in our laboratory. The specific energy of combustion of Vaseline used was $-(46086 \pm 5)$ $J{\cdot}g^{-1}$.[2]

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 $\approx 1{\cdot}10^{-6}$ and $1{\cdot}10^{-7}$ mass fractions, respectively). 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 formation[36] were based on the value of -59.7 $kJ{\cdot}mol^{-1}$ for the standard molar energy of formation of 0.1 $mol{\cdot}dm^{-3}$ HNO_3(aq) from N_2(g), O_2(g), and H_2O(l). All samples were weighed with a Mettler AT-21 microbalance, sensitivity $\pm 1 \times 10^{-6}$ g. 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 given in Table 1. Corrections to the standard states were made according to Hubbard et al.[37] The atomic weights of the elements were those recommended by IUPAC in 2000.[38] The energy of solution of carbon dioxide in water at 298.15 K, $\Delta_{sol}U(CO_2)$, was taken as -17.09 $kJ{\cdot}mol^{-1}$, and the solubility constant, $K(CO_2)$ was taken as 0.03440 $mol{\cdot}dm^{-3}{\cdot}atm^{-1}$ at 298.15 K.[39] From the combustion energy, the enthalpy of formation in the condensed state at 298.15 K was calculated.

Vapor Pressure Measurements. The vapor pressures and enthalpy of sublimation, $\Delta_{cr}^{g}H_m$, of 2,5-thiophenedicarboxylic acid were determined using the method of transference in a saturated stream of nitrogen. The method has been described in detail before[44,45] and has proven to give results in agreement with other established techniques.[46] The temperature dependence of the vapor pressures was used to determine the enthalpies of vaporization of the pure substances. A sample of approximately 0.5 g of the sample was mixed with glass beads and placed in a thermostated U-tube of length 10 cm and diameter 0.5 cm. Preheated nitrogen stream was passed through the U-tube at constant temperature ($\pm$0.1 K). The flow rate of the nitrogen stream was measured using a soap film bubble flowmeter ($\pm$0.2−0.3%) and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. We tested our apparatus at different flow rates of the carrier gas in order to check the lower boundary of the flow, below which, the contribution of the vapor condensed in the trap by diffusion becomes comparable to the transpired one. In our apparatus the contribution due to diffusion was negligible at flow rates down to 0.5 $dm^3{\cdot}h^{-1}$. The upper limit for our apparatus was a flow rate of 10.5 $dm^3{\cdot}h^{-1}$. Thus, we carried out the experiments in the using flow rates ranging from 8 to 9 $dm^3{\cdot}h^{-1}$, which ensured that the transporting gas was in saturated equilibrium with the coexisting solid phase in the saturation tube. The material transported was condensed in a cold trap. The amount of condensed product was determined by weighing ($\pm$0.0001 g).

The saturated vapor pressure, p_i^{sat}, at each temperature, T_i, was calculated from the amount of product collected within a definite period of time. Assuming that Dalton's law of partial pressures when applied to the nitrogen stream saturated with the substance i of interest is valid, values of p_i^{sat} were calculated:

$$p_i^{sat} = m_i R T_a / V M_i; \quad V = V_{N2} + V_i; \quad (V_{N2} \gg V_i) \qquad (1)$$

where $R = 8.31447$ J $K^{-1}{\cdot}mol^{-1}$, m_i is the mass of the transported compound, M_i is the molar mass of the compound, and V_i is its volume contribution to the gaseous phase. V_{N2} is the volume of transporting gas, and T_a is the temperature of the soap film bubble flowmeter. The volume of transporting gas V_{N2} was determined from the flow rate and time measurements.

Computational Details. Standard ab initio molecular orbital calculations[47] were performed with the Gaussian 03 series of programs.[48] The energy of the studied compound was calculated using Gaussian-n theories, at the G2(MP2)[49] and G3(MP2)[50] levels.

G2(MP2) and G3(MP2) correspond effectively to calculations at the QCISD(T)/6-311+G(3df,2p) and QCISD(T)/G3MP2large levels, respectively, G3MP2large being a modification of the 6-311+G(3df,2p) basis set used in G2(MP2) theory. The G3MP2large basis set differs from the 6-311+G(3df,2p) basis set in three ways:[50] (a) 2df polarization functions on the first-row atoms (Li−Ne) and 3d2f polarization functions on second-row atoms (Na−Ar); (b) a new 6-311G basis for S, Cl, and Ar that is optimized for the neutral atoms; and (c) diffuse functions on hydrogens.

In both methods, single-point energy calculations are carried out 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. G3(MP2) also incorporates a spin−orbit correction for atomic species only.[50] We have also reoptimized the geometries at the MP2(full)/6-31G(3df,2p) level to obtain more reliable molecular structures for the studied compound.

The charge distribution has been analyzed using a population partition technique, the natural bond orbital (NBO) analysis of

TABLE 2: Results of Combustion Experiments of 2,5-Thiophenedicarboxylic Acid at T = 298.15 K[a]

m'(compound)/g [b]	1.260632	1.604812	1.602409	1.611630	1.599238
m''(vaseline)/g [b]	0.000000	0.064247	0.196777	0.176951	0.153898
m'''(fuse)/g[b]	0.002715	0.002569	0.002542	0.002565	0.002424
$\Delta T_c/\mathrm{K} = (T_f - T_i + \Delta T_{corr})/\mathrm{K}$	0.7026	0.9952	1.2065	1.1790	1.1363
ϵ(calor) $(-\Delta T_c)$/kJ[c]	−20.2840	−28.7320	−34.8328	−34.0390	−32.8067
ϵ(cont.) $(-\Delta T_c)$/kJ[d]	−0.0339	−0.0503	−0.0610	−0.0598	−0.0574
ΔU_{ign}/kJ[e]	0.0005	0.0005	0.0005	0.0005	0.0005
$\Delta U_{dec}(HNO_3)$/kJ[f]	0.0141	0.0199	0.0362	0.0358	0.0203
$\Delta U_{diln}(H_2SO_4)$/kJ[g]	−0.0032	−0.0059	−0.0058	−0.0059	−0.0058
ΔU(corr. to std. States)/kJ[h]	0.0306	0.0410	0.0463	0.0457	0.0444
$-m''\Delta_c u°$(vaseline)/kJ	0.0000	2.9610	9.0689	8.1551	7.0927
$-m'''\Delta_c u°$(fuse)/kJ	0.0473	0.0448	0.0443	0.0447	0.0423
$\Delta_c u°$(compound)/kJ·g^{-1}	−16.0464	−16.0274	−16.0405	−16.0228	−16.0512
$\langle\Delta_c u°(298.15\ \mathrm{K})\rangle$/kJ·g^{-1}	−16.0377 ± 0.0054				

[a] For a definition of the symbols see refs 37 and 55. 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 but the content of the bomb. [d] ϵ(cont.), energy equivalent of the contents of the bomb. [e] Experimental energy of ignition. [f] Experimental energy of formation of nitric acid. [g] Experimental energy of formation of sulfuric acid. [h] Energy of correction to standard states.

Reed and Weinhold.[51−53] The NBO analysis has been performed using the NBO program[54] implemented in the Gaussian 03 package.[48]

Results and Discussion

Experimental Results. The enthalpy of formation in the gas state of 2,5-thiophenedicarboxylic acid at T = 298.15 K, $\Delta_f H^o_m$(g, 298.15 K) was determined from the experimental values of the standard enthalpy of formation in the crystalline state, $\Delta_f H^o_m$(cr) and the standard enthalpy of sublimation, $\Delta^g_{cr} H_m$, both referred at T = 298.15 K.

The experimental value for the enthalpy of formation in the crystalline state was determined from combustion experimental results given in Table 2 corresponding to the reaction:

$$C_6H_4O_4S(cr) + {}^{13}/{}_2O_2\ (g) + 114H_2O(l) = 6CO_2(g) + [H_2SO_4{\cdot}115H_2O](l) \quad (2)$$

In accordance with the normal thermochemical practice, the uncertainty assigned is twice the overall standard deviation of the mean and included the uncertainties in calibration and in the values of the auxiliary quantities.[56] To derive $\Delta_f H^o_m$(cr) from $\Delta_c H^o_m$(cr), the standard molar enthalpies of formation at T = 298.15 K of H_2O(l),[57] CO_2(g),[57] and [$H_2SO_4{\cdot}115\ H_2O$](l),[36] −(285.839 ± 0.042), −(393.51 ± 0.13), and −(887.811 ± 0.042) kJ·mol^{-1}, respectively, were used.

The enthalpy of sublimation, $\Delta^g_{cr} H_m$, was obtained from vapor pressure measurements by the method of transference in a saturated stream of nitrogen (Table 3). Our experimental vapor pressures have been measured between 425 and 498 K (see Table 3). The following equation

$$R \ln p_i^{sat} = a + \frac{b}{T} + \Delta^g_{cr} C_p \ln\left(\frac{T}{T_0}\right) \quad (3)$$

was fitted to the experimental p,T data using a and b as adjustable parameters. T_0 appearing in eq 3 is an arbitrarily chosen reference temperature (which in this case is 298.15 K). Consequently, from eq 3 the expression for the vaporization enthalpy at temperature T is

$$\Delta^g_{cr} H_m(T) = -b + \Delta^g_{cr} C_p T \quad (4)$$

The value of $\Delta^g_{cr} C_p$ has been chosen as 32 J·mol^{-1}·K^{-1} according to the recommendation by Chickos et al.[58] Experimental results and parameters a and b are listed in Table 3.

TABLE 3: Results from Measurements of the Vapor Pressure p of 2,5-Thiophenedicarboxylic Acid Using the Transpiration Method

T[a]	m[b]	$V_{(N2)}$[c]	gas flow	p[d]	$(p_{exp} - p_{calc})$	$\Delta^g_{cr} H_m$
K	mg	dm^3	dm^3/h	Pa	Pa	kJ·mol^{-1}
2,5-Thiophenedicarboxylic Acid; $\Delta^g_{cr} H_m(298.15\ \mathrm{K}) = (139.79 \pm 0.44)$ kJ·mol^{-1}						
$\ln(p/\mathrm{Pa}) = \frac{352.9}{R} - \frac{149333.7}{R(T/\mathrm{K})} - \frac{32.0}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$						
424.6	4.1	197.5	9.08	0.295	0.00	135.75
435.4	18.2	340.6	9.08	0.760	0.00	135.40
442.1	14.8	158.2	8.82	1.33	−0.01	135.19
447.8	19.2	128.7	8.82	2.13	−0.03	135.00
454.8	8.6	32.5	9.08	3.78	0.03	134.78
458.5	14.3	40.7	8.82	5.00	0.01	134.66
463.4	15.6	31.1	8.82	7.15	−0.10	134.51
468.1	13.5	18.5	8.82	10.4	0.1	134.36
474.3	16.5	14.7	8.82	16.0	−0.2	134.16
480.1	13.3	7.65	8.82	24.8	0.4	133.97
484.1	15.2	6.69	8.82	32.4	0.2	133.84
489.0	15.5	4.71	8.82	46.9	2.1	133.69
493.3	16.1	3.90	8.82	58.9	−0.9	133.55
498.4	13.3	2.35	8.82	80.6	−2.8	133.39

[a] Temperature of saturation. [b] Mass of transferred sample, condensed at T = 273 K. [c] Volume of nitrogen, used to transfer mass m of sample. [d] Vapor pressure at temperature T, calculated from m and the residual vapor pressure at the cooling temperature T = 273 K.

TABLE 4: Experimentally Determined Standard Molar Energy of Combustion and Standard Molar Enthalpies of Combustion, Sublimation, and Formation in the Crystalline and Gaseous State at T = 298.15 K for 2,5-Thiophenedicarboxylic Acid

thermodynamic properties	experimental values[a]
$\Delta_c U^o_m$(cr)	−2761.0 ± 2.1
$\Delta_c H^o_m$(cr)	−2762.3 ± 2.1
$\Delta_f H^o_m$(cr)	−772.4 ± 2.2
$\Delta^g_{cr} H_m$	139.8 ± 0.4
$\Delta_f H^o_m$(g)	−632.6 ± 2.2

[a] All values in kJ·mol^{-1}.

Table 4 collects the determined values for the standard molar energy of combustion, $\Delta_c U^o_m$, and the standard molar enthalpy of combustion, $\Delta_c H^o_m$, sublimation, $\Delta^g_{cr} H_m$, and formation in the crystalline, $\Delta_f H^o_m$(cr), and gaseous state, $\Delta_f H^o_m$(g), at T = 298.15 K of 2,5-thiophenedicarboxylic acid. No experimental results for the energies and enthalpies of combustion, sublima-

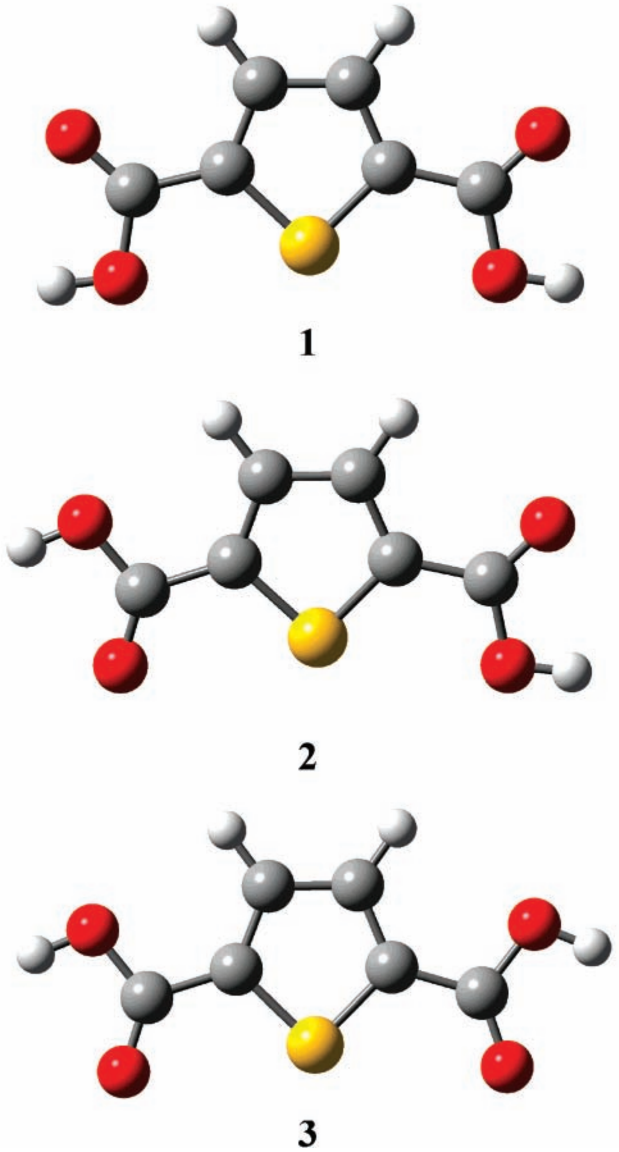


Figure 1. Three most stable conformers of 2,5-thiophenedicarboxylic acid, optimized at the MP2(full)/6-31G(3df,2p) level of theory.

tion and formation have been found in the literature for comparison with our results.

Molecular and Electronic Structures. To our knowledge, there is not any experimental determination of the molecular structure of 2,5-thiophenedicarboxylic acid, neither in the gaseous nor in the solid state (Cambridge Structural Database, version 5.27 of November 2005).[59] However, the crystal structures of two molecular complexes[60,61] and a salt, in which the neutral 2,5-thiophenedicarboxylic acid molecule is included,[62] were retrieved from the CSD (CSD refcodes: ODEHIO, BIHZAU, and LAPPAU, respectively). There are three possible conformers regarding the disposition of the hydroxyl group with respect to the S atom of the ring: syn−syn, syn−anti, and anti−anti (Figure 1), each of them is present in each of the reported structures (Figure 2a). In all of them, the carboxylic group is almost coplanar with the thiophene ring, and the hydroxyl group is involved in hydrogen bonds.

The calculations indicate that the three possible structures are very close in energy. As in the crystal structures, all conformers are planar, and the bond distances and angles optimized at the MP2(full)/6-31G(3df,2p) level of theory (Figure 2b) are in good agreement with the X-ray results.

The relative energies obtained at different calculational levels are shown in Table 5. As it can be observed, at the MP2(full)/6-31G(d) and G2(MP2) levels, the most stable structure is that with the two hydroxylic oxygen atoms facing the sulfur atom of the ring, whereas at the HF/6-31G(d), MP2(full)/6-31G(3df,-2p), and G3(MP2) levels, the most stable structure has the hydroxylic oxygen atom facing the sulfur atom at one side, and at the other side, the carbonyl oxygen atom, but the differences in energy are very small. The third structure, with the two carbonyl oxygen atoms facing the sulfur atom, is close in energy too. For 2-thiophenecarboxylic acid the energy difference of the two conformers calculated at the G2(MP2) level[6] is 0.25 kJ·mol^{-1}, with the oxygen of the OH group facing the sulfur of the ring being the more stable structure

Comparing these structures with that calculated at the same level for 2-thiophenecarboxylic acid,[6] we can see that the bond distances are all similar whereas in the bond angles there are small differences. So, the CSC angle of the ring is 92.2° for 2-thiophenecarboxylic acid. When the second carboxylic group is added at position 5, the angle decreases to 91.3−91.6° while the SCC angles of the ring, 111.6° and 111.9° in the monosubstituted thiophene, increase to 112.2−112.6° when there are two carboxylic groups in positions 2 and 5.

As in 2-thiophenecarboxylic acid,[6] the whole carboxyl groups appear to be attracted by the S atom of the ring, with the CCC angles being larger than the CCS ones. This attraction is stronger in conformer **3**, where the carbonyl O atoms are facing S atom (CCS angles of 119.0°), than in conformer **1**, where the hydroxylic O atoms are facing S atom of the ring (CCS angles of 122.9°). The O−S non-bonded distances, 2.89 Å in **1** and 3.01 Å in **3**, are shorter than the sum of the van der Waals radii, 3.32 Å.[63]

We have carried out a population analysis using the natural bond orbital (NBO) analysis[51−53] 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 conformers of 2,5-thiophenedicarboxylic acid. The results are very similar to those obtained in the study of 2-thiophenecarboxylic acid.[6]

The negative charge is located at the oxygen atoms of the carboxylic groups (−0.70 at the carbonyl oxygen and −0.79 at the hydroxyl one) and at the C atoms of the thiophene ring (−0.19), whereas the positive charge is located at the sulfur atom and at the C atoms of the COOH groups. The positive charge on the S atom slightly increases going to conformer **1** (+0.64) to conformer **3** (+0.67). It is higher than the one located at the S atom in 2-thiophenecarboxylic acid, (+0.58).[6]

The NBO analysis also describes the bonding in terms of the natural hybrid orbitals. In the compound studied, the hybridization of sulfur atom is sp^4, with more than 79% of p character, whereas the hybridization of carbonyl oxygen atom is sp$^{1.4}$ (ca. 58% of p character), and that of the hydroxyl oxygen atom is close to sp^2 with ca. 66% of p character to form the C−O bonds. Sulfur and oxygen atoms have sp and p lone pairs that may delocalize into the vicinal antibonding orbitals.

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 on the basis of $p_X \rightarrow \sigma^*_{CX}$ hyperconjugation because orbital interactions involving sp lone pairs, that is, $sp_X \rightarrow \sigma^*_{CX}$ is not negligible.[64] This behavior is observed in the compound studied and it was observed in our previous study on 2- and 3-thiophenecarboxylic acids.[6]

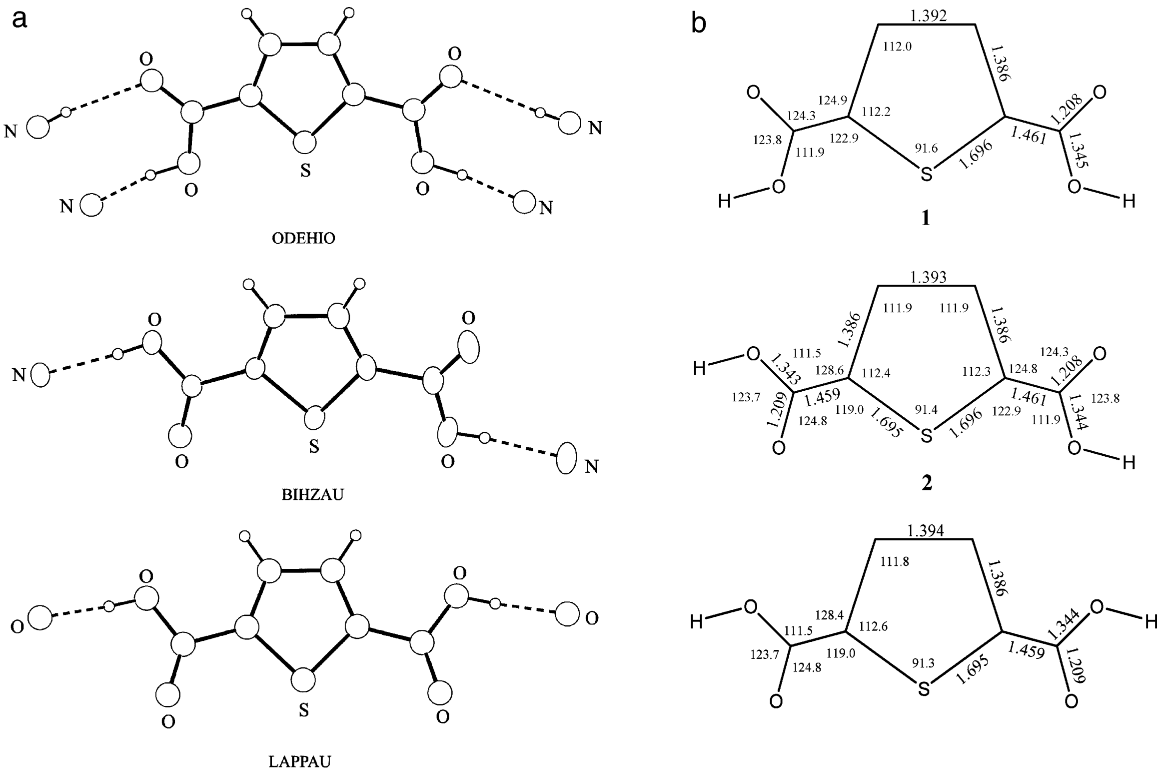


Figure 2. (a) 2,5-Thiophenedicarboxylic acid molecule showing the hydroxyl hydrogen interactions: molecular complexes with 2,4-di-*n*-propylamino-6-methyl-*s*-triazine (CSD refcode ODEHIO), with 4,4′-bipyridine (BIHZAU) and in the 2-amino-5-picolinium salt (LAPPAU), where the neutral and the anion molecules are linked by OH···O$^-$ hydrogen bonds. (b) Bond distances and angles optimized at the MP2(full)/6-31G(3df,2p) level of theory for the three studied conformers of 2,5-thiophenedicarboxylic acid.

TABLE 5: Relative Energy Values at Different Computational Levels among the Three Most Stable Conformers of 2,5-Thiophenedicarboxylic Acid[a]

conformer	HF/ 6-31G(d)	MP2(full)/ 6-31G(d)	MP2(full)/ 6-31G(3df,2p)	G2(MP2)	G3(MP2)
1	0.23	0.00	0.06	0.00	0.02
2	0.00	0.01	0.00	0.40	0.00
3	0.39	0.35	0.33	1.28	0.67

[a] All values in kJ·mol^{-1}.

TABLE 6: G2(MP2) and G3(MP2) Calculated Energies at 0 K and Enthalpies at 0 K for the Three Most Stable Conformers of 2,5-Thiophenedicarboxylic Acid[a]

	G2(MP2)		G3(MP2)	
conformer	E_0	H_{298}	E_0	H_{298}
1	−928.944198	−928.933289	−929.039643	−929.028734
2	−928.944046	−928.933140	−929.039651	−929.028744
3	−928.943710	−928.932803	−929.039396	−929.028489

[a] All values in Hartrees.

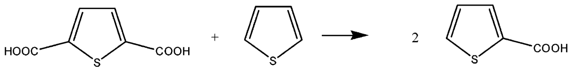
Theoretical Determination of the Enthalpy of Formation. G2(MP2) and G3(MP2) calculated energies at 0 K and enthalpies at 298 K for the three most-stable conformers of 2,5-thiophenedicarboxylic acid are given in Table 6.

The standard procedure to obtain enthalpies of formation in Gaussian-n theories is through atomization reactions,[65,66] but there has been some suggestion[67−71] that there is an accumulation of errors in the application of this method to larger molecules. Glukhovtsev and Laiter[67] have shown that more accurate heats of formation can be derived using isodesmic or homodesmotic reactions[72] rather than atomization energies. As Raghavachari et al.[73] 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 a standard set of isodesmic reactions, the “bond separation reactions”,[47] where all formal bonds between non-hydrogen atoms are separated into the simplest parent molecules containing these same kinds of linkages to derive the theoretical enthalpies of formation.

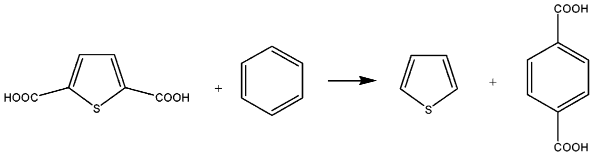
In this work, we have obtained the enthalpies of formation of three different conformers of 2,5-thiophenedicarboxylic acid, $C_6H_4O_4S$, using the bond separation isodesmic reaction 5:

$$C_6H_4O_4S(g) + 10CH_4(g) + H_2S(g) \rightarrow 3CH_3CH_3(g) + 2CH_2{=}CH_2(g) + 2CH_3SH(g) + 2CH_3OH(g) + 2H_2CO(g) \quad (5)$$

and another two isodesmic reactions (eqs 6 and 7) using 2-thiophenecarboxylic acid and 1,4-benzenedicarboxylic acid as references, respectively:



(6)



(7)

The G2(MP2) and G3(MP2) calculated enthalpies of formation are shown in Table 7.[74] Also in Table 7 are the mean values calculated using all six values obtained at the two computational levels.

To obtain the conformational composition in the gas phase at 298 K, we need the $\Delta_f G^\circ_m$ values. They can be calculated

TABLE 7: G2(MP2) and G3(MP2) Calculated Enthalpies of Formation, Using Isodesmic Reactions 5−7, for the Three Most Stable Conformers of 2,5-Thiophenedicarboxylic Acid[a]

	G2(MP2)			G3(MP2)			
conformer	eq 5	eq 6	eq 7	eq 5	eq 6	eq 7	mean value
1	−638.2	−627.2	−629.6	−635.3	−628.3	−629.2	−631.3
2	−637.8	−626.8	−629.2	−635.3	−628.3	−629.2	−631.1
3	−636.9	−625.9	−628.3	−634.7	−627.7	−628.5	−630.3

[a] All values in kJ·mol^{-1}.

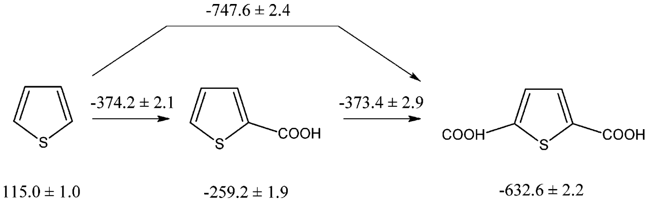


Figure 3. Enthalpies of formation ($\Delta_f H^o_m$ in kJ·mol^{-1}) of the gaseous compounds thiophene, 2-thiophenecarboxylic acid, and 2,5-thiophenedicarboxylic acid. Differences in the enthalpies of formation ($\Delta\Delta_f H^o_m$ in kJ·mol^{-1}) are shown on the arrows.

through

$$\Delta_f G^\circ_m(i) = \Delta_f H^\circ_m(i) - T[S^\circ(i) - \sum S^\circ(\mathrm{el})] \tag{8}$$

where the sum of the entropy of the elements, in the case of the compound studied, is calculated as

$$\sum S^\circ(\mathrm{el}) = 6S^\circ(\mathrm{C,s}) + 2S^\circ(\mathrm{H_2,g}) + 2S^\circ(\mathrm{O_2,g}) + S^\circ(\mathrm{S,s}) \tag{9}$$

Using for the elements the entropy values, at 298 K, taken from ref 73, $\Delta_f G^o_m$ values of −532.0, −531.7, and −529.2 kJ·mol^{-1} have been obtained for the conformers **1**, **2**, and **3**, respectively.

Using

$$x_i = \frac{e^{-[\Delta_f G^\circ_m(i)/RT]}}{\sum_{i=1}^{n} e^{-[\Delta_f G^\circ_m(i)/RT]}} \tag{10}$$

we have obtained that in the gas phase at 298 K, there are 32.31% of isomer **1**, 57.25% of the two symmetry-related forms of isomer **2**, and 10.44% of isomer **3**. Using

$$\Delta_f H^\circ_m(X) = \sum_{i=1}^{n} x_i \Delta_f H^\circ_m(i) \tag{11}$$

the final value obtained for the enthalpy of formation of 2,5-thiophenedicarboxylic acid is −631.1 kJ·mol^{-1}, in very good agreement with the experimental one, −(632.6 ± 2.2) kJ·mol^{-1}.

Comparison of the experimental results for the enthalpies of formation of thiophene,[74] 2-thiophenecarboxylic acid,[6] and 2,5-thiophenedicarboxylic acid (Figure 3) shows that there is not any significant energetic difference between the introduction of a second carboxylic group in 2-thiophenecarboxylic acid to give 2,5-thiophenedicarboxylic acid, −(373.4 ± 2.9) kJ·mol^{-1}, and that when a H atom is replaced by COOH in thiophene to give 2-thiophenecarboxylic acid, −(374.2 ± 2.1) kJ·mol^{-1}.

Furthermore, a comparative analysis with the analogous substituted benzenes has been made. This can be done by the evaluation of the energetic differences obtained from the scheme shown in Figure 4 in comparison with that in Figure 3.

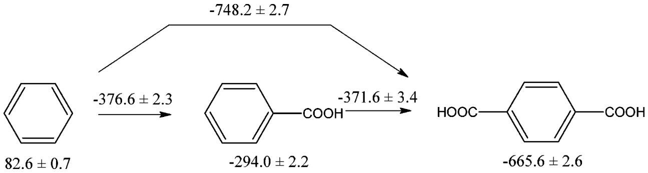


Figure 4. Enthalpies of formation ($\Delta_f H^o_m$ in kJ·mol^{-1}) of the gaseous compounds benzene, benzoic acid, and 1,4-benzenedicarboxylic acid. Differences in the enthalpies of formation ($\Delta\Delta_f H^o_m$ in kJ·mol^{-1}) are shown on the arrows.

Using the enthalpies of formation taken from the literature for benzene,[74] benzoic acid,[75] and 1,4-benzenedicarboxylic acid,[74] we obtain the $\Delta\Delta_f H^o_m$ values given in Figure 4. This figure shows the energetic effects observed in the conversion from benzene to benzoic acid and to 1,4-benzenedicarboxylic acid.

In all cases, the introduction of a carboxylic group in the ring is a highly exothermic change. The conversion of thiophene to 2-thiophenecarboxylic acid, $\Delta\Delta_f H^o_m = -(374.2 \pm 2.1)$ kJ·mol^{-1}, is approximately of the same magnitude as the analogous substitution in the benzene ring, $\Delta\Delta_f H^o_m = -(376.6 \pm 2.3)$ kJ·mol^{-1}. Interestingly, the introduction of a second acid group has the same consequences in thiophene and benzene rings, $\Delta\Delta_f H^o_m = -(373.4 \pm 2.9)$ kJ·mol^{-1} in 2-thiophenecarboxylic acid versus $\Delta\Delta_f H^o_m = -(371.6 \pm 3.4)$ kJ·mol^{-1} in benzoic acid. The differences found among all of these values are inside their corresponding uncertainty intervals. Taking these results into account, we can conclude that the relative stability obtained for the substitution of two H atoms by two COOH groups in position 2,5 for thiophene and 1,4 for benzene involves the same energetic effects, $\Delta\Delta_f H^o_m = -(747.6 \pm 2.4)$ and −(748.2 ± 2.7) kJ·mol^{-1} in thiophene and benzene, respectively.

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