# Thermochemistry of 2- and 3-Thiopheneacetic Acids: Calorimetric and Computational Study

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The enthalpies of formation in the condensed and gas states, $\Delta_f H_m°(cd)$ and $\Delta_f H_m°(g)$, of 2- and 3-thiopheneacetic acids were derived from their respective enthalpies of combustion in oxygen, measured by a rotating bomb calorimeter, and the variation of vapor pressure with temperature determined by the Knudsen effusion technique. Theoretical calculations at the G3 level were performed, and a study on molecular and electronic structure of the compounds has been carried out. Calculated $\Delta_f H_m°(g)$ values using atomization and isodesmic reactions are compared with the experimental data. Experimental and theoretical results show that the 3-thiopheneacetic acid is thermodynamically more stable than the 2-isomer.

## 1. Introduction

Thiophene is a chemically stable compound and is easy to process, and its applications have been a constant matter of investigation. Several books and reviews are available on the chemistry of thiophenes.[1−3] It is the simplest representative of an aromatic structure bearing sulfur. Thiophene obeys the $4n + 2$ $\pi$ electron rule, and it is generally considered to be aromatic.[4] 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.

Thiophene-based compounds have been investigated extensively and have also found widespread use in modern drug design,[5,6] biodiagnostics,[7] electronic and optoelectronic devices,[8,9] and conductive polymers.[10−14] Moreover, condensed thiophenes comprise a significant portion of the organosulfur compounds in petroleum and in other products from fossil fuels, being obtainable as byproducts of petroleum distillation.[15] Thus, different studies related to their biodegradation,[16] catalytic dehydrodesulfuration,[17−19] and oxidative desulfurization[20−22] have been carried out.

Over the past few years, we have been involved in a thermochemical study of the energetics of thiophene derivatives.[23−29] A development of an understanding of the structural effects on thermodynamic stabilities reflected in the gas-phase enthalpies of formation of the compounds studied has been of fundamental interest to us. Substituents on the five-membered ring of thiophene have a relationship to one another different from that of similar substituents in benzene. Our work has focused mainly on the energetic differences between isomers containing different functional groups in positions 2 and 3 and the substituent effects in thiophene relative to benzene analogues. We showed previously that 3-thiophenecarboxylic acid is slightly more stable, thermodynamically, than 2-thiophenecarboxylic acid with an isomerization enthalpy of 2.6 ± 1.7 kJ mol$^{-1}$. This can be interpreted as a result of the through-space interaction between the oxygen of the hydroxyl group and the sulfur atom in the 2-isomer.[25] However, this behavior is reversed in the case of the acetylthiophenes where the 2-isomer is more stable than the corresponding 3-isomer by 4.7 ± 2.8 kJ mol$^{-1}$.[29] This observation is interpreted in terms of the resonance interaction between the CO group and the S atom through the ring and a possible attractive interaction between the negative carbonyl oxygen and the positive ring sulfur.[29] Moreover, the experimental difference between the enthalpies of formation of 2- and 3-thiopheacetic acid, methyl esters, 0.9 ± 2.1 kJ mol$^{-1}$, is too close to call.[28] These results are consistent with the expectation that, in the absence of substantial steric effects, alkyl substituents, less capable of resonance interactions, are likely to have a smaller effect on relative stabilities than observed for carboxyl groups.

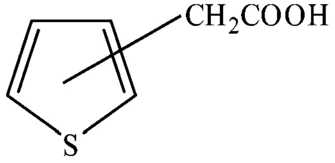

**Figure 1.** Structural formula of thiopheneacetic acids.

Very recently, the thermochemistry of several alkyl-substituted thiophenes,[30] 2-thiophenecarboxamide and 2-thiopheneacetamide,[31] several thiophenecarbonitrile derivatives,[32] thiophenecarboxaldehydes and some of their alkyl derivatives,[33] the three methyl-substituted 2-acetylthiophene isomers,[34] 2,5-dimethylthiophene and its acetyl derivative,[35] and 2-thiophenecarboxylic acid derivatives[36] has also been studied by Ribeiro da Silva and Santos.

The purpose of the present work is to study the energy−structure relationship of the 2- and 3-thiopheneacetic acids (thienylacetic acids) whose formula is presented in Figure 1. The approach selected is a combination of experimental determinations of the enthalpy of formation, molecular structure and high-level ab initio calculations.

## 2. Experimental Section

**2.1. Materials and Purity Control.** 2- and 3-thiopheneacetic acids were commercially available from Lancaster (mass fraction

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0.98). Both acids were purified by crystallization twice from *n*-hexane and then from petroleum ether. The samples were carefully dried under vacuum. The determination of the purities, assessed by DSC by the fractional fusion technique,[37] indicated that the mole fraction of impurities in the compounds was less than 0.001. The samples were studied by DSC over the temperature range between $T = 258$ K and their fusion melting points, $T = 337.4$ K and $T = 353.3$ K for the 2- and 3-isomers, respectively, and no transitions in the solid state were observed.[26]

**2.2. Procedure for Thermochemical Measurements.** ***2.2.1. 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. The details of the technique and procedure used have been previously described.[38] The energy equivalent of the calorimeter, $\varepsilon$(calor), was determined from the combustion of benzoic acid, NIST standard reference sample 39j, having a specific energy of combustion $\Delta_c u = -26434 \pm 3$ J g$^{-1}$, under certificate conditions. From nine calibration experiments $\varepsilon$(calor) $= 28871.08 \pm 0.90$ J 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[39] to confirm the chemistry of the combustion process and the accuracy of the energy corrections involved in the analysis of the results. The standard molar energy obtained, $\Delta_c u° = -33465.3 \pm 5.9$ J g$^{-1}$ is in good agreement with the recommended value,[39] $\Delta_c u° = -33468 \pm 4$ J g$^{-1}$.

The energies of combustion of both isomers of thiopheneacetic acid were determined by burning the solid samples in pellet form in oxygen. The pelleted samples were enclosed in polyethene bags. Vaseline was used as an auxiliary material to have around 8 mmol of sulfur in the samples.[40] The empirical formula and massic energy of combustion of our polyethene, $C_{0.960}H_{2.000}$ and $-46371 \pm 4$ J g$^{-1}$, and cotton-thread fuse, $C_{1.000}H_{1.740}O_{0.871}$ and $17410 \pm 37$ J g$^{-1}$, were determined in our laboratory. The specific energy of combustion of the Vaseline used was $-46086 \pm 5$ J g$^{-1}$.[41]

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 $\sim 1 \times 10^{-6}$ and $1 \times 10^{-7}$ 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 the sample. The corrections for nitric acid formation[42] were based on the value of $-59.7$ kJ mol$^{-1}$ for the standard 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 samples were weighed with a Mettler AT-21 microbalance, sensitivity $\pm 1 \times 10^{-6}$ g. For the correction of the 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.[46] The atomic weights of the elements were those recommended by IUPAC in 2005.[47] The energy of a 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 0.03440 mol dm$^{-3}$ atm$^{-1}$ at 298.15 K.[48]

From the combustion energy, the enthalpy of formation in the condensed state at 298.15 K was calculated.

***2.2.2. Knudsen-Effusion Method.*** The vapor pressures as a function of temperature were measured by a mass-loss Knudsen-effusion method,[49] using the procedure described in ref 50. 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 $\pm 0.000002$ g. The vapor pressure, $p$, for each temperature, $T$, was calculated by means of the equation

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

where $a$ is the area of the effusion orifice and $W_a$ the corresponding Clausing coefficient.[51] 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 coefficient $W_a = 0.980 \pm 0.004$.

**TABLE 1: Physical Properties at $T = 298.15$ K[a]**

| compd | $M$/g mol$^{-1}$ | $\rho$/g cm$^{-3}$ | $(\delta V/\delta T)_p \times 10^{-7}$/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[b] | 8.374[c] | 2.22[d] |
| cotton | 27.700 | 1.5 | 9.69[e] | 1.48 |
| 2-thiopheneacetic acid | 142.1766 | 1.392[f] | (3.354) | 1.12[f] |
| 3-thiopheneacetic acid | 142.1766 | 1.398[f] | (3.354) | 1.18[f] |

[a] Values in parentheses were estimated. [b] Value taken from ref 41. [c] Value taken from ref 43. [d] Value taken from ref 44. [e] Value taken from ref 45. [f] Value taken from ref 26.

**2.3. Computational Details.** Standard ab initio molecular orbital calculations[52] were performed with the Gaussian 03 series of programs.[53] The energy of the compounds studied was calculated using Gaussian-*n* theory at the G3 level.[54]

G3 corresponds effectively to calculations at the QCISD(T)/G3large level, G3large being a modification of the 6-311+G(3df,2p) basis set, including more polarization functions for the second row (3d2f) and less on the first row (2df) and other changes to improve uniformity. In addition, some core polarization functions are added.[54] 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, a so-called higher level correction to accommodate the remaining deficiencies, and spin–orbit correction for atomic species only.[54]

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 charge distribution has been analyzed using a population partition technique, the natural bond orbital (NBO) analysis of Reed and Weinhold.[55–57] The NBO analysis has been performed using the NBO program[58] implemented in the Gaussian 03 package.[53]

## 3. Results and Discussion

**3.1. Experimental Results.** The enthalpy of formation in the gas state of 2- and 3-thiopheneacetic acids at $T = 298.15$ K, $\Delta_f H_m°$(g, 298.15 K) was determined from the experimental values of the standard enthalpy of formation in the crystalline state, $\Delta_f H_m°$(cr) and the standard enthalpy of sublimation, $\Delta_{cr}^{g} H_m$, 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

$$C_6H_6O_2S(cr) + 8O_2 + 113H_2O(l) \rightleftarrows 6CO_2 + [H_2SO_4 \cdot 115H_2O](l) \quad (2)$$

In accordance with the normal thermochemical practice, the uncertainty assigned is twice the overall standard deviation of the mean and includes the uncertainties in calibration and in the values of the auxiliary quantities.[60] To derive $\Delta_f H_m°(cr)$ from $\Delta_c H_m°(cr)$, the standard molar enthalpies of formation at $T = 298.15$ K of $H_2O(l)$,[61] $CO_2(g)$,[61] and $[H_2SO_4 \cdot 115H_2O](l)$,[42] $-285.839 \pm 0.042$, $-393.51 \pm 0.13$, and $-887.811 \pm 0.042$ kJ mol$^{-1}$, respectively, were used.

The results of our Knudsen-effusion experiments for both thiopheneacetic acids are summarized in Table 3. An equation of the type

$$\log(p/\mathrm{Pa}) = -B(T/\mathrm{K})^{-1} + A \quad (3)$$

was fitted to the results of Table 3 by the least-squares method. The quantities $\delta p/p$ are the fractional deviations of the experimental vapor pressures from those computed using eq 3. The highest error for the vapor pressure, $p$, in Table 3 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-thiopheneacetic acids

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

| parameter | | | | | |
|---|---|---|---|---|---|
| | | | 2-Thiopheneacetic Acid | | |
| $m'(\mathrm{compd})^b/\mathrm{g}$ | 1.099505 | 1.048217 | 1.093625 | 1.103328 | 1.094347 |
| $m''(\mathrm{polyethene})^b/\mathrm{g}$ | 0.077864 | 0.078439 | 0.084826 | 0.073612 | 0.083937 |
| $m'''(\mathrm{Vaseline})^b/\mathrm{g}$ | 0.091014 | 0.096721 | 0.081351 | 0.088292 | 0.084477 |
| $m''''(\mathrm{fuse})^b/\mathrm{g}$ | 0.002312 | 0.002668 | 0.002408 | 0.002232 | 0.002152 |
| $\Delta T_c/\mathrm{K} = (T_f - T_i + \Delta T_{corr})/\mathrm{K}$ | 1.1965 | 1.1635 | 1.1874 | 1.1885 | 1.1912 |
| $\varepsilon(\mathrm{calor})^c/\mathrm{kJ}\ (-\Delta T_c)$ | −34.5428 | −33.5923 | −34.2822 | −34.3127 | −34.3920 |
| $\varepsilon(\mathrm{cont})^d/\mathrm{kJ}\ (-\Delta T_c)$ | −0.0604 | −0.0586 | −0.0599 | −0.0600 | −0.0601 |
| $\Delta U_{ign}{}^e/\mathrm{kJ}$ | 0.0005 | 0.0005 | 0.0005 | 0.0005 | 0.0005 |
| $\Delta U_{dec}(HNO_3)^f/\mathrm{kJ}$ | 0.0158 | 0.0318 | 0.0383 | 0.0273 | 0.0230 |
| $\Delta U_{diln}(H_2SO_4)^g/\mathrm{kJ}$ | −0.00348 | −0.00303 | −0.00343 | −0.00352 | −0.00343 |
| $\Delta U(\mathrm{corr\ to\ std\ states})^h/\mathrm{kJ}$ | 0.0344 | 0.0333 | 0.0339 | 0.0341 | 0.0342 |
| $-m''\Delta_c u°(\mathrm{polyethene})/\mathrm{kJ}$ | 3.6107 | 3.6374 | 3.9335 | 3.4135 | 3.8923 |
| $-m'''\Delta_c u°(\mathrm{Vaseline})/\mathrm{kJ}$ | 4.1946 | 4.4576 | 3.7492 | 4.0691 | 3.8933 |
| $-m''''\Delta_c u°(\mathrm{fuse})/\mathrm{kJ}$ | 0.0403 | 0.0465 | 0.0420 | 0.0389 | 0.0375 |
| $\Delta_c u°(\mathrm{compd})/\mathrm{kJ\ g^{-1}}$ | −24.2931 | −24.2763 | −24.2754 | −24.2836 | −24.2836 |
| $\langle\Delta_c u°(298.15\ \mathrm{K})\rangle/\mathrm{kJ\ g^{-1}}$ | | | −24.2824 ± 0.0032 | | |
| | | | 3-Thiopheneacetic Acid | | |
| $m'\ (\mathrm{compd})^b/\mathrm{g}$ | 1.103337 | 1.099236 | 1.087205 | 1.086919 | 1.093374 |
| $m''(\mathrm{polyethene})^b/\mathrm{g}$ | 0.084807 | 0.077557 | 0.078660 | 0.075524 | 0.083269 |
| $m'''(\mathrm{Vaseline})^b/\mathrm{g}$ | 0.000000 | 0.109489 | 0.078184 | 0.081451 | 0.084561 |
| $m''''(\mathrm{fuse})^b/\mathrm{g}$ | 0.002223 | 0.002682 | 0.002397 | 0.002496 | 0.002315 |
| $\Delta T_c/\mathrm{K} = (T_f - T_i + \Delta T_{corr})/\mathrm{K}$ | 1.0624 | 1.2224 | 1.1637 | 1.1641 | 1.1869 |
| $\varepsilon(\mathrm{calor})/\mathrm{kJ}\ (-\Delta T_c)^c$ | −30.6723 | −35.2908 | −33.5982 | −33.6084 | −34.2661 |
| $\varepsilon\ (\mathrm{cont})/\mathrm{kJ}\ (-\Delta T_c)^d$ | −0.0531 | −0.0619 | −0.0587 | −0.0587 | −0.0600 |
| $\Delta U_{ign}{}^e/\mathrm{kJ}$ | 0.0005 | 0.0005 | 0.0005 | 0.0005 | 0.0005 |
| $\Delta U_{dec}(HNO_3)^f/\mathrm{kJ}$ | 0.0361 | 0.0424 | 0.0406 | 0.0438 | 0.0444 |
| $\Delta U_{diln}(H_2SO_4)^g/\mathrm{kJ}$ | −0.00359 | −0.00347 | −0.00338 | −0.00338 | −0.00343 |
| $\Delta U(\mathrm{corr\ to\ std\ states})^h/\mathrm{kJ}$ | 0.0308 | 0.0349 | 0.0334 | 0.0333 | 0.0339 |
| $-m''\Delta_c u°(\mathrm{polyethene})/\mathrm{kJ}$ | 3.9327 | 3.5965 | 3.6476 | 3.5022 | 3.8613 |
| $-m'''\Delta_c u°(\mathrm{Vaseline})/\mathrm{kJ}$ | 0.0000 | 5.0460 | 3.6033 | 3.7538 | 3.8972 |
| $-m''''\Delta_c u°(\mathrm{fuse})/\mathrm{kJ}$ | 0.0388 | 0.0468 | 0.0418 | 0.0435 | 0.0404 |
| $\Delta_c u°(\mathrm{compd})/\mathrm{kJ\ g^{-1}}$ | −24.1903 | −24.1887 | −24.1841 | −24.1907 | −24.1928 |
| $\langle\Delta_c u°(298.15\ \mathrm{K})\rangle/\mathrm{kJ\ g^{-1}}$ | | | −24.1893 ± 0.0015 | | |

[a] For a definition of the symbols see refs 46 and 59. $T_{th} = 298.15$ K, $V_{bomb} = 0.260$ dm$^3$, $p^i_{gas} = 3.04$ MPa, and $m^i_{water} = 10.00$ g. [b] Masses obtained from the apparent mass. [c] $\varepsilon$(calor) = energy equivalent of the whole system but the contents of the bomb. [d] $\varepsilon$(cont) = energy equivalent of the contents of the bomb. $\varepsilon(\mathrm{cont})(-\Delta T_c) = \varepsilon^i(\mathrm{cont})(T_i - 298.15\ \mathrm{K}) + \varepsilon^i(\mathrm{cont})(298.15\ \mathrm{K} - T_f + \Delta T_{corr})$. [e] Experimental energy of ignition. [f] Experimental energy of formation of nitric acid. [g] Experimental energy of formation of sulfuric acid. [h] $\Delta U$ (corr to std states) is the standard state correction.

**TABLE 3: Vapor Pressures of Thiopheneacetic Acids**

| $T$/K | $t^a$/s | $\Delta m^b$/mg | $p^c$/Pa | $10^2(\delta p/p)^d$ | $T$/K | $t^a$/s | $\Delta m^b$/mg | $p^c$/Pa | $10^2(\delta p/p)^d$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 2-Thiopheneacetic Acid | | | | | |
| 291.55 | 27000 | 1.45 | 0.0267 | −2.47 | 303.26 | 29820 | 3.88 | 0.128 | −1.08 |
| 294.82 | 33060 | 1.50 | 0.0439 | 2.62 | 306.42 | 19380 | 3.72 | 0.189 | −2.02 |
| 298.11 | 31200 | 3.87 | 0.0664 | 0.120 | 307.21 | 21900 | 4.75 | 0.214 | 0.579 |
| 300.56 | 26040 | 2.54 | 0.0952 | 3.99 | | | | | |
| | | | | 3-Thiopheneacetic Acid | | | | | |
| 293.95 | 36000 | 0.695 | 0.0187 | 1.28 | 306.20 | 21000 | 2.11 | 0.0989 | 2.70 |
| 297.57 | 17460 | 0.574 | 0.0320 | 4.69 | 309.62 | 14460 | 2.16 | 0.148 | −0.725 |
| 300.47 | 31200 | 3.87 | 0.596 | −6.11 | 311.81 | 16860 | 3.39 | 0.200 | 1.85 |
| 302.97 | 30600 | 1.93 | 0.619 | −1.90 | | | | | |

[a] Time for the experiment. [b] Mass of the sublimed substance. [c] Vapor pressure. [d] $\delta p$ denotes the deviation of the experimental vapor pressures from the values computed using eq 3.

**TABLE 4: Molar Enthalpies of Sublimation**

| compd | $\Theta$/K | $A$ | $B$ | $\Delta_{sub}H_m°(\Theta)$/kJ mol$^{-1}$ |
|---|---|---|---|---|
| 2-thiopheneacetic acid | 299.38 | 36.6 ± 0.5 | 11718.2 ± 164.5 | 97.4 ± 1.4 |
| 3-thiopheneacetic acid | 302.88 | 37.2 ± 0.7 | 12118.5 ± 224.1 | 100.8 ± 1.9 |

**TABLE 5: Experimentally Determined Thermodynamic Magnitudes at $T = 298.15$ K[a]**

| | $\Delta_cU_m°$ | $\Delta_cH_m°$ | $\Delta_fH_m°$(cr) | $\Delta_{sub}H_m°$ | $\Delta_fH_m°$(g) |
|---|---|---|---|---|---|
| 2-thiopheneacetic acid | −3452.4 ± 1.5 | −3457.3 ± 1.5 | −363.2 ± 1.7 | 97.5 ± 1.4 | −265.7 ± 2.2 |
| 3-thiopheneacetic acid | −3439.2 ± 1.3 | −3444.1 ± 1.3 | −376.4 ± 1.5 | 100.9 ± 1.9 | −275.5 ± 2.4 |

[a] All values in kilojoules per mole.

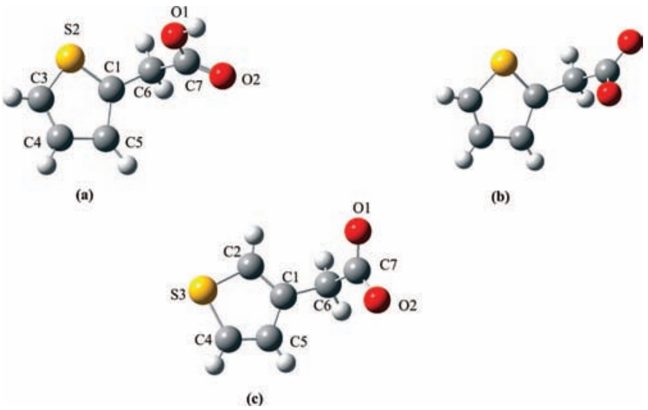

**Figure 2.** Molecular structure of the thiopheneacetic acid derivatives: (a) 2-thiopheneacetic acid in the molecular complex with acridine (CSD refcode RAHGUC, ref 65), (b) 2-thiopheneacetate anion in the ammonium salt of tryptamine (LACPUA, ref 66), (c) 3-thiopheneacetate anion in the dicyclohexylammonium salt (QIJBIU, ref 67).

are given in Table 4. The enthalpies of sublimation to the mean temperature $\Theta$ of their experimental ranges have been calculated from the corresponding $B$ values and are also listed in Table 4. The uncertainties assigned to the values of $\Delta_{sub}H_m°(\Theta)$ are based on the standard deviations of the $B$ values.

The sublimation enthalpy at $T = 298.15$ K was derived using the same equation as in ref 62. $C_{p,m}°$(g) has been calculated by using the group contribution scheme of Rihani,[63] and $C_{p,m}°$(cr) has been taken from the experimental results determined in our laboratory and given in ref 26.

Table 5 collects the determined values for the standard molar energy of combustion, $\Delta_cU_m°$, and the standard molar enthalpy of combustion, $\Delta_cH_m°$, sublimation, $\Delta_{cr}^{g}H_m$, and formation in the crystalline, $\Delta_fH_m°$(cr), and gaseous, $\Delta_fH_m°$(g), states at $T = 298.15$ K of both thiopheneacetic acids.

No experimental results for the energies and enthalpies of combustion, sublimation, and formation have been found in the literature for comparison with our results.

**3.2. Molecular and Electronic Structures.** To our knowledge, there has been no experimental determination of the molecular structure of 2- and 3-thiopheneacetic acids, in either the gas or solid state. A search of the Cambridge Crystallographic Database[64] (CSD version 5.29, January 2008 update; in the following, refcodes in the CSD are given in capitals) gives no crystal structures for the 2- and 3-thiopheneacetic acids, although it yields one molecular complex (CSD refcode RAHGUC)[65] and one salt (LACPUA)[66] for the former and only one salt (QIJBIU)[67] for the latter. Figure 2 displays the molecular structure of the neutral molecule and the anions, and the geometrical parameters are reported in Table 6. The main differences between them concern the bond distances, bond angles, and thiophene C−C−C−O torsion angles (Table 6), showing similar C−O distances and C−C−O angles in the anions. Furthermore, the differences in bond distances and angles between the 2-thiopheneacetic acid derivatives are due to the disorder of the thiophene ring over two positions.[65] In 75% of the cells the S atom is located at position 2 (Figure 2 and Table 6), while in the remaining 25% it is at position 5.

The calculated molecular structures of 2- and 3-thiopheneacetic acids, optimized at the MP2(Full)/6-31G(3df,2p) level of theory, are shown in Figure 3. Calculated bond distances and angles are also collected in Table 6. As can be seen, the optimized structure of 3-thiopheneacetic acid agrees well with the experimental structure of the anion in the dicyclohexylammonium salt (QIJBIU). In the case of 2-thiopheneacetic acid there are some differences between the optimized structure and the available experimental data, overall in the relative position of the carboxylic group.

The thiophene ring is planar in both derivatives. The valency angle of the sulfur atom in the ring, CSC, is calculated as 93.0° and 92.6° in 2- and 3-thiopheneacetic acid, respectively, intermediate between the tetrahedral angle and a right angle, and in line with the values calculated previously for other thiophene derivatives.[23,27−29]

A population analysis using the NBO analysis[55−57] to obtain the natural atomic charges (the nuclear minus summed populations of the natural atomic orbitals on the atoms) that characterize the ground electronic state of the compounds studied has also been carried out. The calculated charges located at the heavy atoms for both compounds are reported in Figure 4.

Partial negative charges are located at the oxygen atoms of the carboxylic group, at the C atoms of the thiophene ring, and at the C atom of the methylene group, whereas partial positive charges are located at the sulfur atom of the ring and at the C atom of the carboxylic group. The charge distribution does not appreciably change with the position of the substituent; only a small charge redistribution takes place on the atoms of the thiophene ring.

The NBO analysis also describes the bonding in terms of the natural hybrid orbitals. In the compounds studied, the hybridization of the sulfur atom is sp$^4$, with 78% p character, whereas the hybridization of the carbonyl oxygen atom is sp$^{1.3}$ (56% p character) and that of the hydroxyl oxygen atom is close to sp$^2$, with 65% 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, $sp_X \rightarrow \sigma^*_{CX}$, are not negligible.[68] This behavior is observed in the compounds studied and was also observed in our previous studies on 2- and 3-thiophen-

**TABLE 6: Selected Geometrical Parameters (Bond Distances, Å; Angles, deg)**[a]

| | | 2-derivative | | | 3-derivative | |
|---|---|---|---|---|---|---|
| | | LACPUA[d] | | | | |
| | RAHGUC[b,c] | molecule 1 | molecule 2 | calcd[e] | QIJBIU[b,f] | calcd[e] |
| C1−X2 | 1.667(4) | 1.701(7) | 1.676(9) | 1.698 | 1.375(3) | 1.376 |
| X2−X3 | 1.638(4) | 1.705(5) | 1.670(11) | 1.694 | 1.688(2) | 1.693 |
| X3−C4 | 1.333(6) | 1.318(14) | 1.325(22) | 1.375 | 1.707(7) | 1.695 |
| C4−C5 | 1.554(5) | 1.503(15) | 1.462(9) | 1.406 | 1.353(5) | 1.374 |
| C5−C1 | 1.550(4) | 1.470(3) | 1.463(13) | 1.377 | 1.406(4) | 1.411 |
| C1−C6 | 1.498(5) | 1.513(8) | 1.488(8) | 1.481 | 1.498(2) | 1.496 |
| C6−C7 | 1.514(4) | 1.518(10) | 1.501(12) | 1.506 | 1.539(3) | 1.499 |
| C7−O1 | 1.297(4) | 1.252(8) | 1.245(6) | 1.345 | 1.248(3) | 1.344 |
| C7−O2 | 1.196(5) | 1.255(6) | 1.233(7) | 1.203 | 1.249(3) | 1.206 |
| X2−C1−C5 | 114.6(2) | 115.4(1) | 112.0(5) | 110.7 | 111.1(2) | 112.0 |
| C1−X2−X3 | 95.0(2) | 91.0(2) | 95.1(2) | 93.0 | 112.6(2) | 111.6 |
| X2−X3−C4 | 113.9(3) | 114.2(2) | 110.2(3) | 111.2 | 91.4(2) | 92.6 |
| X3−C4−C5 | 117.2(4) | 116.0(7) | 118.1(2) | 112.2 | 111.8(1) | 111.4 |
| C4−C5−C1 | 99.3(2) | 103.3(1) | 104.6(1) | 112.8 | 113.1(4) | 112.4 |
| X2−C1−C6 | 122.1(3) | 117.7(4) | 121.1(2) | 121.7 | 124.0(2) | 124.4 |
| C5−C1−C6 | 123.2(3) | 126.9(1) | 126.7(1) | 127.5 | 124.9(2) | 123.4 |
| C1−C6−C7 | 112.7(3) | 115.2(1) | 116.8(2) | 112.4 | 110.9(2) | 107.3 |
| C6−C7−O1 | 113.8(3) | 118.0(3) | 118.0(3) | 125.9 | 116.7(2) | 111.2 |
| C6−C7−O2 | 122.9(3) | 116.7(3) | 118.0(3) | 110.4 | 117.3(2) | 125.2 |
| O1−C7−O2 | 123.3(3) | 125.3(4) | 124.0(3) | 123.7 | 125.9(2) | 123.5 |
| X2−C1−C6−C7 | 91.8(3) | 76.6(7) | −79.3(9) | 84.4 | −101.4(2) | −108.3 |
| C1−C6−C7−O1 | −57.4(4) | 33.9(9) | −16.5(10) | 179.4 | 87.7(2) | 83.0 |
| C1−C6−C7−O2 | 124.5(4) | −145.3(6) | 164.7(7) | −0.5 | −91.3(2) | −94.4 |

[a] X2 = S and X3 = C for 2-thiopheneacetic/acetate and X2 = C and X3 = S for the 3-thiopheneacetate compounds. [b] The S2, C5 and S3, C4 atoms in the 2-thiophene and 3-thiophene derivatives are disordered over two sites with 0.75:0.25 occupancy factors. [c] Reference 65. [d] Reference 66. [e] Parameters optimized at the MP2(Full)/6-31G(3df,2p) level of theory. [f] Reference 67.

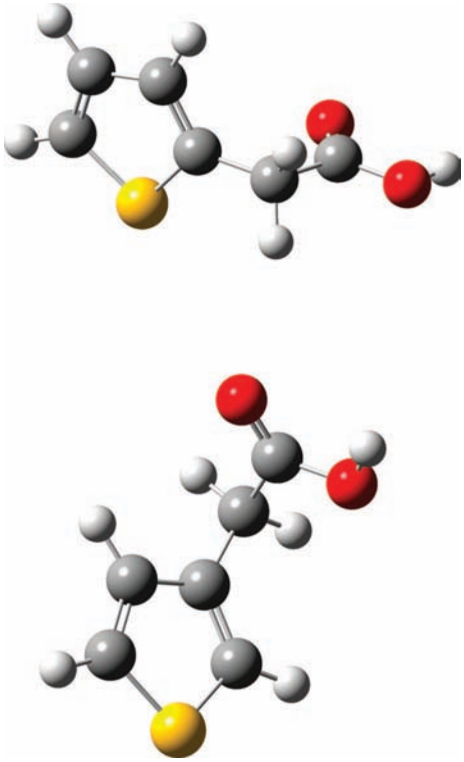

**Figure 3.** MP2(Full)/6-31G(3df,2p)-optimized structures of 2- and 3-thiopheneacetic acids.

ecarboxylic acids,[23] 2,5-thiophenedicarboxylic acid,[27] 2- and 3-thiopheneacetic acid methyl esters,[28] and 2- and 3-acetylthiophenes.[29]

**3.3. Theoretical Determination of the Enthalpies of Formation.** G3-calculated energies at 0 K, and enthalpies at 298 K, for the two compounds studied are given in Table 7.

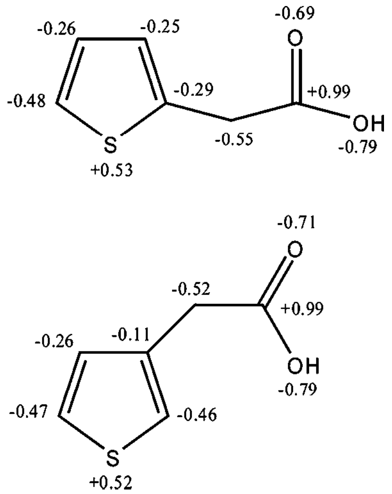

**Figure 4.** NBO atomic charges for 2- and 3-thiopheneacetic acids calculated at the MP2(Full)/6-31G(3df,2p) level.

**TABLE 7: G3-Calculated Energies at 0 K, and Enthalpies at 298 K, for 2- and 3-Thiopheneacetic Acids and Phenylacetic Acid**[a]

| | G3 | |
|---|---|---|
| compd | $E_0$ | $H_{298}$ |
| 2-thiopheneacetic acid | −780.505188 | −780.495723 |
| 3-thiopheneacetic acid | −780.506866 | −780.497450 |
| phenylacetic acid | −459.814588 | −459.804813 |

[a] All values in hartrees.

The standard procedure in obtaining enthalpies of formation in Gaussian-*n* theories is through atomization reactions,[69,70] but there have been some suggestions[71−75] that there is an accumulation of errors in the application of this method to larger molecules. Glukhovtsev and Laiter[71] have shown that more accurate heats of formation can be derived using isodesmic or homodesmotic reactions[76] rather than atomization energies. As Raghavachari et al.[77] 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",[52] 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 calculated the enthalpies of formation of 2- and 3-thiopheneacetic acids, $C_6H_6O_2S$, using the atomization reactions and the bond separation isodesmic reaction (4):

$$C_6H_6O_2S(g) + 8CH_4(g) + H_2S(g) \rightarrow 3CH_3CH_3(g) + 2CH_2{=}CH_2(g) + 2CH_3SH(g) + H_2CO(g) + CH_3OH(g) \quad (4)$$

Another two isodesmic reactions (5 and 6), using phenylacetic acid and methylthiophenes as references, respectively, have been used:

$$C_6H_6O_2S(g) + \text{benzene}(g) \rightarrow \text{thiophene}(g) + \text{phenylacetic acid}(g) \quad (5)$$

$$C_6H_6O_2S(g) + \text{methane}(g) \rightarrow \text{2- or 3-methylthiophene}(g) + \text{acetic acid}(g) \quad (6)$$

The condition for using an isodesmic reaction is to have reference molecules with reliable experimental values of their enthalpy of formation in the gas phase. We have recently determined[78] the enthalpy of formation of a reference molecule in reaction 5, phenylacetic acid, and a value of −314.7 ± 3.1 kJ mol$^{-1}$ was obtained. More recently, Ribeiro da Silva et al.[79] have remeasured the enthalpy of formation of the same compound, obtaining a value of −302.3 ± 2.0 kJ mol$^{-1}$. The discrepancy between both values has prompted us to carry out a theoretical study at the G3 level.

The G3-calculated energy at 0 K, and enthalpy at 298 K, for phenylacetic acid is given in Table 7. Three reactions have been used to calculate the enthalpy of formation value: the atomization reaction, the bond separation isodesmic reaction (7), and another isodesmic reaction (8) using toluene as the reference.

$$C_8H_8O_2(g) + 10CH_4(g) \rightarrow 5CH_3CH_3(g) + 3CH_2{=}CH_2(g) + H_2CO(g) + CH_3OH(g) \quad (7)$$

$$C_8H_8O_2(g) + \text{methane}(g) \rightarrow \text{toluene}(g) + \text{acetic acid}(g) \quad (8)$$

Using the G3-calculated enthalpies of reaction and the experimental enthalpies of formation, $\Delta_f H_m°(g)$, for the species involved[80] in these reactions, the enthalpy of formation of phenylacetic acid has been calculated as −312.7 k J mol$^{-1}$ (from the atomization reaction), −315.1 kJ mol$^{-1}$ (from reaction 7), and −316.3 kJ mol$^{-1}$ (from reaction 8). A mean theoretical value of −314.7 kJ mol$^{-1}$ is derived. This value matches our experimental value,[78] so it is the value used in reaction 5 for calculating the enthalpy of formation of thiopheneacetic acids.

The G3-calculated[80] enthalpies of formation of 2- and 3-thiopheneacetic acids are shown in Table 8. There is a reasonable agreement between experimental and theoretical results.

From the literature value[81] of the enthalpy of formation in the gas phase of thiophene, and the values reported in this work, we can calculate the enthalpic increments for the introduction of a $-CH_2COOH$ group in positions 2 and 3 of the thiophene ring, the values being −380.7 ± 2.4 and −390.5 ± 2.6 kJ mol$^{-1}$, respectively (see Figure 5). If we make a comparison with the stabilization in the benzenic ring (see Figure 6), we can see that the introduction of a $-CH_2COOH$ group into benzene yields an enthalpic increment of −397.3 ± 3.2 kJ mol$^{-1}$, higher than that of the introduction of the same group into the 2- and 3-positions of the thiophene ring.

**TABLE 8: A Comparison of G3-Calculated Enthalpies of Formation, Using the Atomization Reaction and Isodesmic Reactions (4−6), for 2- and 3-Thiopheneacetic Acids with Experimental Values**[a]

| | G3 | | | | |
|---|---|---|---|---|---|
| compd | atomization reaction | isodesmic reaction (4) | isodesmic reaction (5) | isodesmic reaction (6) | experimental value |
| 2-thiopheneacetic acid | −277.6 | −282.1 | −277.7 | −278.2 | −265.7 ± 2.2 |
| 3-thiopheneacetic acid | −282.1 | −286.6 | −282.3 | −283.7 | −275.5 ± 2.4 |

[a] All values in kJ mol$^{-1}$.

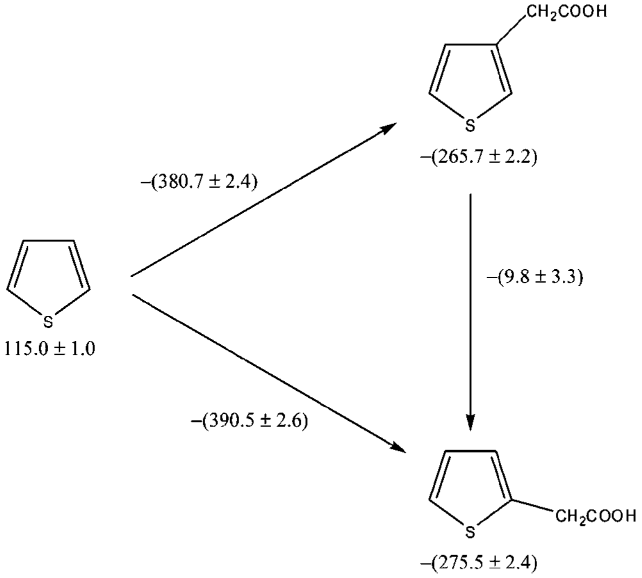

**Figure 5.** Enthalpic increments for the introduction of a $-CH_2COOH$ group into positions 2 and 3 of the thiophene ring.

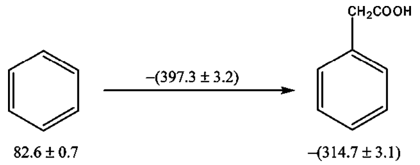

**Figure 6.** Enthalpic increment for the introduction of a $-CH_2COOH$ group into benzene.

The stabilization enthalpic increment of the substitution of a hydrogen atom in the thiophene ring by a $-CH_2COOH$ group is higher in the 3-position of the ring. The isomerization enthalpy is calculated as −9.8 ± 3.3 kJ mol$^{-1}$. The G3-calculated value, −4.5 kJ mol$^{-1}$, is in reasonable agreement with the experimental difference. This experimental isomerization enthalpy value, obtained when a hydrogen atom is substituted by a $-CH_2COOH$ group, is higher than the isomerization enthalpy, 0.9 ± 2.1 kJ mol$^{-1}$, obtained[28] when a hydrogen atom is substituted by a $-CH_2COOCH_3$ group.

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2007-60895/BQU is gratefully acknowledged. M.T. thanks MEC/SEUI, Grant FPU AP2002-0603, Spain, for financial support.

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