Thermochemistry of 2- and 3-Acetylthiophenes: Calorimetric and Computational Study

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The relative stabilities of 2- and 3-acetylthiophenes have been evaluated by experimental thermochemistry and the results compared to high-level ab initio calculations. The enthalpies of combustion, vaporization, and sublimation were measured by rotating-bomb combustion calorimetry, Calvet microcalorimetry, correlation gas chromatography, and Knudsen effusion techniques and the gas-phase enthalpies of formation, at $T = 298.15$ K, were determined. Standard ab initio molecular orbital calculations at the G2 and G3 levels were performed, and a theoretical study on the molecular and electronic structures of the compounds studied has been conducted. Calculated enthalpies of formation using atomization and isodesmic reactions are compared with the experimental data. Experimental and theoretical results show that 2-acetylthiophene is thermodynamically more stable than the 3-isomer. A comparison of the substituent effect of the acetyl group in benzene and thiophene rings has been carried out.

1. Introduction

Thiophene is a chemically stable compound, readily available, and the chemistry of thiophene and its derivatives has been a constant matter of investigation. Several books and reviews are available on the chemistry of thiophenes.[1] 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.[2] 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 derivatives comprise a significant portion of the organosulfur compounds in petroleum and in other products from fossil fuels, being obtainable as byproducts of petroleum distillation.[3] Different studies related to their biodegradation[4] and catalytic dehydrodesulfuration[5] have been carried out. Thiophene-based compounds have also found widespread use in modern drug design,[6] biodiagnostics,[7] electronic and optoelectronic devices,[8] and conductive and electroluminescent polymers.[9] Also, several reviews of various aspects of thiophene coordination and reactivity in transition metal complexes have been reported.[10]

In recent years, we have been involved in a thermochemical study of the energetics of thiophene derivatives.[11−16] 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 different relationship to one another than 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 corresponding benzene analogues. In a previous article, we reported the thermochemistry of 2- and 3-thiophenecarboxylic acids.[11] In general, the −COOH group of thiophenecarboxylic acids acts much the same way as in other organic compounds. We showed previously that 3-thiophenecarboxylic acid is slightly more thermodynamically stable than 2-thiophenecarboxylic acid with an isomerization enthalpy of 2.6 kJ·mol^{-1}. In comparison with benzene and its analogous substituted derivative, benzoic acid, we found 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 and the sulfur atom.[13] On the basis of a similar comparison with the result obtained for 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.[13] Similarly, comparing the relative stability obtained by substituting two H atoms by COOH groups in the 2,5-position of thiophene and at the 1,4-positions of benzene results in similar energetic effects.[15] Moreover, the experimental difference between the enthalpies of formation of 2- and 3-thiopheneacetic acid methyl esters, 0.9 ± 2.1 kJ·mol^{-1}, is too close to call.[16] These results are consistent with the expectation that, in the absence of substantial steric and

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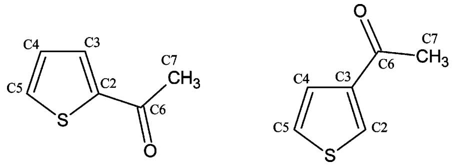


Figure 1. Structural formula of 2- and 3-acetylthiophenes.

electronic effects (the through-space interaction observed in 2-thiophenecarboxylic acid), alkyl substituents, less capable of resonance interactions, are likely to have a smaller effect on relative stabilities than observed for carboxyl groups.

The purpose of the present work is to study the energetics of the 2- and 3-acetylthiophenes whose formula is presented in Figure 1. The approach selected is a combination of experimental determination of the enthalpies of formation and high-level ab initio calculations.

2. Experimental Section

2.1. Material and Purity Control. Commercial samples of 2- and 3-acetylthiophene were obtained from Lancaster at a stated mass fraction of 0.99 and 0.98, respectively. To obtain a dry and pure sample of 2-acetylthiophene, the commercial compound was dried over 4A molecular sieves before and after fractional distillation in a packed column under reduced pressure. This procedure was repeated three times. 3-Acetylthiophene was purified by crystallization twice from petroleum ether and then it was carefully dried under vacuum.

To assess the purity of the compounds, a standard gas chromatograph with a 60 m BPX70 fused silica SGE capillary column was used. The purity of 3-acetylthiophene was also assessed by DSC by the fractional fusion technique.[17]

The water content of liquid 2-acetylthiophene was determined using a Karl Fisher instrument (Metron 682) and by GC-MS. The purified 2-acetylthiophene had 0.396% of the 3-isomer present as an impurity and a water content of 0.009%. No other impurities were detected. The mole fraction of 3-acetylthiophene was better than 0.999.

2.2. Experimental Determination of the Enthalpies of Formation in the Gas Phase. The enthalpies of formation in the gas phase of 2- and 3-acetylthiophene, $\Delta_f H_m^o$ (g), at T = 298.15 K, were determined from the experimental values of their standard enthalpies of formation in the condensed state, $\Delta_f H_m^o$ (cd), and the standard phase change enthalpies, $\Delta_l^g H_m^o$ and $\Delta_{cr}^g H_m^o$, the 2-isomer being a liquid and the 3-isomer being a solid at this temperature.

2.2.1. Combustion Calorimetry. The enthalpies of formation in the condensed state were determined from combustion calorimetry using two isoperibol combustion calorimeters equipped with rotating bombs. The enthalpy of combustion of 2-acetylthiophene was measured at the University of Porto and the enthalpy of combustion of 3-acetylthiophene at the Instituto de Química Física Rocasolano in Madrid. Details of the techniques and procedures used have been previously described.[18,19]

The samples of 2-acetylthiophene were contained in sealed polyester bags made of Melinex (0.025 mm of thickness) with massic energy of combustion $\Delta_c u^\circ = -(22902 \pm 5)$ J·g^{-1},[20] a value which was confirmed in the Porto laboratory. The mass of Melinex used in each experiment was corrected for the mass fraction of water ($w = 0.0032$), and the mass of carbon dioxide produced from its combustion was calculated using the factor previously reported.[20] The energy of combustion of the 3-isomer was determined by burning the solid samples in pellet form enclosed in polyethylene bags. The empirical formula and massic energies of combustion of the polyethylene were $C_{0.968}H_{2.000}$ and $-(46339.3 \pm 6.6)$ J·g^{-1}, respectively, and were determined in Madrid.

The energy equivalent of the Spanish calorimeter, ϵ(calor), was determined under the same conditions in which the experiments were performed using the combustion of benzoic acid, NIST standard reference sample 39j. The value of the energy equivalent of the calorimeter (ϵ(calor, Madrid) = {28871.08 ± 0.90 (0.003%)} J·K^{-1}) was determined from 10 calibration experiments, and this value was used in computing the results of the combustion experiments performed in Madrid. The energy equivalent of the calorimeter of the Portuguese system, ϵ(calor, Porto) = {20369.0 ± 2.3 (0.011%)} J·K^{-1}, was determined without rotation of the bomb, as previously described[21] from an average of 10 calibration experiments.[18] The calorimeter was calibrated using benzoic acid, NBS thermochemical standard 39i, having a massic energy of combustion under bomb conditions of $-(26434 \pm 3)$ J·g^{-1} (using an average mass of 3965.0 g of water added to the calorimeter); the quoted uncertainty is the standard deviation of the mean.

Under the conditions of the experiments (T_{th} = 298.15 K; V_{bomb} (Madrid) = 0.260 dm^3; V_{bomb} (Porto) = 0.329 dm^3; p_{gas}^i = 3.04 MPa; and 10.00 (Madrid) or 15.00 cm^3 (Porto) of water added to the bomb), no carbon (soot), CO, or SO_2 were detected.

Corrections for nitric acid formation, from traces of N_2 remaining inside the bomb, were based on -59.7 kJ·mol^{-1} for the molar energy of formation of 0.1 mol·dm^{-3} HNO_3 (aq) from O_2, N_2, and H_2O (l).[22] 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, the values of density, ρ, massic heat capacity, C_p, and $(\partial V/\partial T)_p$ used, are given in Table S1 of the Supporting Information for cotton, the different auxiliary substances used, and for 2- and 3-acetylthiophene.

The energy of solution of carbon dioxide in water at T = 298.15 K, $\Delta_{sol}U(CO_2)$, was taken as -17.09 kJ·mol^{-1}, and the solubility constant, $K(CO_2)$ at T = 298.15 K, as 0.03440 mol·dm^{-3}·atm^{-1}.[23] The standard state corrections were calculated by the procedures given by Hubbard et al.[24] and by Good and Scott.[25] All samples were weighed on a Mettler AT-21 microbalance, sensitivity ±1 × 10^{-6} g (Madrid), and on a Mettler AG 245 balance with a sensitivity of ±1 × 10^{-5} g (Porto).

The derived molar energies of combustion of both isomers in the condensed state at T = 298.15 K correspond to the following reaction:

$$C_6H_6OS\ (cd) + 17/2O_2\ (g) + 113H_2O\ (l) = 6CO_2\ (g) + [H_2SO_4 \cdot 115H_2O]\ (l) \quad (1)$$

The atomic masses used for the elements were those recommended by the IUPAC Commission in 2005,[26] yielding molar masses for 2- and 3-acetylthiophene of 126.179 g·mol^{-1}.

2.2.2. Calvet Microcalorimetric Measurements. The enthalpy of vaporization of 2-acetylthiophene was measured by the "vacuum vaporization" drop microcalorimetric method,[27,28] using a high-temperature Calvet microcalorimeter (SETARAM HT 1000 D) with a sensitivity of 3 μV·mW, held at T = 350 K. Samples, about 7−10 mg, contained in a thin glass capillary tube sealed at one end, were dropped, at room temperature, into the hot reaction vessel, and then removed from the hot zone by vacuum vaporization. From the observed enthalpy of vaporization, $\Delta_{l,298.15K}^{g,T} H_m$, the standard molar enthalpy of vaporization, at $T = 298.15$ K, was calculated using a value for $\Delta_{298.15\mathrm{K}}^{350\mathrm{K}} H_\mathrm{m}^\mathrm{o}$ (g) estimated by the Benson's group method[29] using values from Stull et al.[30] The microcalorimeter was calibrated in situ for these measurements by using the reported enthalpy of vaporization, at $T = 298.15$ K, of *n*-undecane:[31] $\Delta_\mathrm{l}^\mathrm{g} H_\mathrm{m}^\mathrm{o}$ ($C_{11}H_{24}$) = (56.580 ± 0.566) kJ·mol^{-1}. The compound and the glass capillary tubes were weighed on a Mettler CH-8608 analytical balance, with a sensitivity of (1×10^{-6}) g. The thermal corrections for the glass capillary tubes were determined in separate experiments and were minimized as far as possible by dropping tubes of nearly equal mass (within ± 10 mg), into each of the twin calorimeter cells.

2.2.3. Knudsen Effusion Technique. The enthalpy of sublimation of 3-acetylthiophene was determined by measurement of the vapor pressure over a 16 K temperature interval using the Knudsen-effusion technique, and the enthalpy of sublimation was derived from the temperature dependence of the vapor pressure (Clausius−Clapeyron equation). The technique and procedure used have been previously described.[32] The Knudsen cell was weighed before and after each experiment to determine the mass of sublimed material (Δm). The vapor pressure, p, at each temperature, T, was calculated by means of the equation:

$$p = (\Delta m / W_\mathrm{a} a\, t)(2\pi\, RT/M)^{1/2} \qquad (2)$$

where a is the area of the effusion orifice, t is time, R is the gas constant, M is the molecular weight of the effusing species, and W_a is the corresponding Clausing coefficient.[33] The membrane for the effusion measurements was a tantalum foil, $l = (0.021 \pm 0.004)$ mm. The area of the effusion orifice was $a = (0.0444 \pm 0.0002)$ mm^2, and the Clausing coefficient $W_\mathrm{a} = (0.943 \pm 0.012)$.

2.2.4. Correlation-Gas Chromatography. The enthalpies of vaporization of 2- and 3-acetylthiophene were also measured by correlation-gas chromatography using the procedure previously described.[34] A Hewlett-Packard model 5890 Series II gas chromatograph equipped with a split/splitless capillary injection port, a flame ionization detector (FID), and a 30 m SPB-5 capillary column was used. The retention times were recorded to three significant figures following the decimal point on an HP 3356 Series II integrator. The solvent used was methylene chloride. Methane was bubbled into the solution just prior to injection and was used as the nonretained reference to determine the dead volume of the column. Column temperatures were controlled by the instrument and monitored using a Fluke 51 K/J thermometer. All correlation-gas chromatography experiments were performed in duplicate to confirm reproducibility. The results of only one experiment are reported.

2.3. Computational Details. Standard ab initio molecular orbital calculations[35] were performed with the Gaussian 03 series of programs.[36] The energy of the compounds studied was calculated using Gaussian-n theories at the G2[37] and G3[38] levels.

G2 corresponds effectively to calculations at the QCISD(T)/6-311+G(3df,2p) level. In this method, 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 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), less on the first row (2df), and other changes to improve uniformity. In addition, some core polarization functions are added.[38] 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 remaining deficiencies, and spin−orbit correction for atomic species only.[38]

TABLE 1: Individual Results of the Massic Energies of Combustion at $T = 298.15$ K ($p° = 0.1$ MPa), for the 2- and 3-Acetylthiophene Isomers

expt no.	$-\Delta_\mathrm{c}u°$, J·g^{-1} (exptl)	correction, J·g^{-1}	$-\Delta_\mathrm{c}u°$, J·g^{-1} (corrected)
	2-Acetylthiophene		
1	29298.81	−0.37	29299.17
2	29297.56	−0.36	29297.92
3	29296.53	−0.36	29296.89
4	29283.74	−0.31	29284.05
5	29289.05	−0.33	29289.38
6	29295.96	−0.36	29296.32
$-\langle\Delta_\mathrm{c}u°\rangle$/(J·g^{-1})	(29293.6 ± 2.4)		(29294.0 ± 2.4)
	3-Acetylthiophene		
1	29216.1		
2	29211.8		
3	29200.8		
4	29208.0		
5	29199.0		
$-\langle\Delta_\mathrm{c}u°\rangle$/(J·g^{-1})	(29207.1 ± 3.2)		

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.[39−41] The NBO analysis has been performed using the NBO program[42] implemented in the Gaussian 03 package.[36]

3. Results and Discussion

3.1. Experimental Results. The results of combustion experiments for 2- and 3-acetylthiophenes are given in Tables S2 and S3 of the Supporting Information. The experimental values have been derived as in ref 24, and the symbols in these tables have the same meaning as in refs 24 and 43. The results for all the combustion experiments of both 2- and 3-acetylthiophene, together with the mean value of their massic energy of combustion, $\Delta_\mathrm{c}u^\mathrm{o}$, and its standard deviation, are given in Table 1.

As noted above, the sample of 2-acetylthiophene was contaminated by a water content of 0.009% and by 0.396% of 3-acetylthiophene, which could not be removed during purification. The massic energy of combustion of 2-acetylthiophene reported is based on the mass of this compound that was burnt in each experiment after the masses of water and of 3-acetylthiophene present as contaminants were subtracted. Because the massic energy of combustion of crystalline 3-acetylthiophene was determined in this work, the individual experimental massic energies of combustion of the contaminated samples have been corrected for the contribution of 3-acetylthiophene to the massic energy of combustion of the 2-acetylthiophene isomer. The corrections are also given in Table 1. These corrections were made by subtracting the contribution of liquid 3-acetylthiophene (calculated by adding its fusion enthalpy at $T = 298.15$ K[14] to its combustion enthalpy and adjusting its contribution on the basis of its composition in the sample) and by assuming that the enthalpy of mixing of the two liquid isomers is negligible.

TABLE 2: Standard Molar Energies of Combustion and Enthalpies of Combustion and Formation at $T = 298.15$ K

compound	$\Delta_c U^\circ_m$, kJ·mol^{-1}	$\Delta_c H^\circ_m$, kJ·mol^{-1}	$\Delta_f H^\circ_m$ (cd), kJ·mol^{-1}
2-acetylthiophene (l)	−3696.3 ± 1.6	−3702.5 ± 1.6	−118.0 ±1.7
3-acetylthiophene (cr)	−3685.3 ± 1.2	−3691.5 ± 1.2	−129.1 ± 1.4

TABLE 3: Standard ($p^\circ = 0.1$ MPa) Molar Enthalpy of Vaporization of 2-Acetylthiophene at $T = 298.15$ K Determined by Calvet Microcalorimetry[a]

expt no.	m, 10^{-3}g	T, K	$\Delta^{g,T}_{l,298.15K} H_m$, kJ · mol^{-1}	$\Delta^{T}_{298.15K} H^\circ_m$ (g), kJ·mol^{-1}	$\Delta^g_l H^\circ_m(T = 298.15\text{K})$, kJ·mol^{-1}
1	8.502	349.9	65.95	7.29	58.66
2	8.200	349.8	65.96	7.28	58.68
3	9.465	349.9	66.44	7.29	59.15
4	7.776	349.8	65.59	7.28	58.31
5	6.822	349.8	66.26	7.28	58.98

[a] $\langle \Delta^g_l H^o_m(T = 298.15\text{K})\rangle = 58.8 \pm 1.2$ kJ·mol^{-1}.

TABLE 4: Vapor Pressures of 3-Acetylthiophene Determined by the Knudsen Effusion Technique

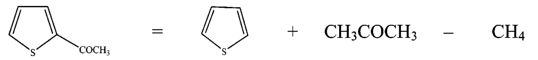
T, K	t, s[a]	Δm, mg[b]	p, Pa[c]	10^2·$(\delta p/p)$[d]	T, K	t, s[a]	Δm, mg[b]	p, Pa[c]	10^2·$(\delta p/p)$[d]
268.51	29160	1.15	0.315	3.04	279.08	17100	2.29	1.09	−0.544
271.46	27120	1.47	0.435	−1.30	282.44	16380	3.23	1.61	−0.150
274.02	25200	1.89	0.602	0.0253	284.27	15960	3.95	2.03	2.36
276.36	27900	2.66	0.770	−3.41					

[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 3.

Table 2 gives the molar energies and enthalpies of combustion derived from the combustion reaction of both isomers in the condensed state at $T = 298.15$ K.

In accordance with normal thermochemical practice,[44] the uncertainty assigned to the standard molar enthalpy of combustion is twice the overall standard deviation of the mean and include the uncertainties in calibration and in the values of auxiliary quantities used. To derive $\Delta_f H^\circ_m$ (cd), at $T = 298.15$ K, from $\Delta_c H^\circ_m$ (cd), the standard molar enthalpy of formation of H_2SO_4 in 115 H_2O(l), −(887.81 ± 0.01) kJ·mol^{-1},[45] and the CODATA values[46] of the standard molar enthalpies of formation, at $T = 298.15$ K, $\Delta_f H^\circ_m$ (H_2O, l) = −(285.830 ± 0.042) kJ·mol^{-1} and $\Delta_f H^o_m$ (CO_2, g) = −(393.51 ± 0.13) kJ·mol^{-1}, were used.

The individual values of the standard molar enthalpies of vaporization determined by Calvet microcalorimetry, at the experimental temperature $T = 350$ K are given in Table 3. These values were corrected to $T = 298.15$ K, using $\Delta^T_{298K} H^\circ_m$ (g) estimated by a group scheme based on values Stull et al.[47] The scheme applied for 2-acetylthiophene was:



which yielded the $\Delta^T_{298K} H^\circ_m$ corrections registered in Table 3. The standard molar enthalpy of vaporization, at $T = 298.15$ K, is also reported in Table 3, where the uncertainty associated is twice the overall standard deviation of the mean and includes the uncertainties in calibration.

The results of our Knudsen-effusion experiments for 3-acetylthiophene are summarized in Table 4.

The vapor pressures of Table 4 were fit to an equation of the type

$$\ln(p/\text{Pa}) = -B(T/\text{K})^{-1} + A \qquad (3)$$

by the method of least-squares. The enthalpy of sublimation at the mean temperature of its experimental range, $T_m = 276.39$ K, was calculated by multiplying the corresponding B value by the gas constant R, $\Delta^g_{cr} H^\circ_m$ (276.39 K) = 75.2 ± 1.1 kJ·mol^{-1}. The uncertainty assigned to this magnitude is based on the standard deviation of the B value.

The sublimation enthalpy at the temperature $T = 298.15$ K was derived using the same procedure as in ref 48 using the equation:

$$\Delta^g_{cr} H^\circ_m (298.15\text{ K}) = (\Delta^g_{cr} H^\circ_m (T_m)\text{ J·mol}^{-1}) + [0.75 + 0.15 C^o_{p,m}\text{ (cr) J·mol}^{-1}\cdot\text{K}^{-1}][T_m/\text{K} - 298.15] \qquad (4)$$

Using the estimated value, $C^o_{p,m}$ (cr) = 135.2 J·mol^{-1}·K^{-1}, calculated by the method given in ref 49, a value $\Delta^g_{cr} H^\circ_m$ (298.15 K) = (74.6 ± 1.1) kJ·mol^{-1} was obtained.

The vaporization enthalpies of both 2- and 3-acetylthiophene were also measured by correlation-gas chromatography. A plot of $\ln(1/t_a)$, where t_a represents the time each analyte spends on the column, against reciprocal temperature, T^{-1}, results in a straight line whose slope is $\Delta^g_{sln} H_m/R$. Multiplication of the slope by the gas constant results in the enthalpy of transfer from the stationary phase of the column to the gas phase. Enthalpies of transfer measured experimentally are then correlated to known vaporization enthalpies measured by some other means. The vaporization enthalpy of the target is obtained from the correlation equation. Selection of the reference compounds is crucial in the evaluation. Generally, reference compounds are chosen with the same type and number of functional groups as the target compound. Some flexibility is possible in certain cases where it has been demonstrated empirically that substitution of a different functional group still provides suitable correlations.[50] In this case, we could not find any reference compounds in the literature with the same functional group combination as found in 2-acetylthiophene. Therefore, we used as standard compounds with functional groups that have similar numerical contributions as those present in the target compound in accordance with the group contribution scheme of ref 51. Chloroesters and chloroketones were chosen as reference compounds. This substitution has been previously proven useful in the determination of the enthalpies of vaporization of 2- and 3-thiopheneacetic acid methyl esters.[16]

The analysis of the values used as standards and further details in the correlation-gas chromatography calculations are given as Table S4 of the Supporting Information. The correlations involving 2-acetylthiophene as the target compound also included using the vaporization enthalpy of 3-acetylthiophene and 2- and 3-thiopheneacetic acid methyl esters as reference compounds.

The retention times for only one of a duplicate set of runs are reported in Table S5 of the Supporting Information. Plots of $\ln(1/t_a)$ versus $1/T$ resulted in straight lines characterized by the slopes and intercepts reported in Table 5. The correlation coefficient, r^2, exceeded 0.99 in all cases. The correlation between enthalpies of transfer $\Delta^g_{sln} H_m(T_m)$ measured at the mean temperature, T_m, and vaporization enthalpies at $T = 298.15$ K resulted in eq 5 (given beneath Table 5). This resulted in the vaporization enthalpies reported in the last column of this table. The uncertainty reported in this column reflects 2 standard deviations associated with the slope of the correlation equation.

As can be seen by comparison of the values in Tables 3 and 5, the experimental values of the enthalpy of vaporization obtained by correlation-gas chromatography[34] and by the adaptation to vaporization of the vacuum sublimation drop

TABLE 5: Summary of Calculated Values Obtained by Correlation-Gas Chromatography[a]

compound	slope	intercept	$\Delta_{sln}^{g}H_{m}^{\circ}$ (364 K), kJ· mol^{-1}	$\Delta_{l}^{g}H_{m}^{\circ}$ (298.15 K), kJ·mol^{-1} (literature)	$\Delta_{l}^{g}H_{m}^{\circ}$ (298.15 K), kJ·mol^{-1} (this work)
3-chloro-2-butanone	−3350.0	10.002	27.9	40.5	39.0
ethyl 2-chloropropionate	−4136.2	11.189	34.4	46.2	47.1
isopropyl chloroacetate	−4275.9	11.479	35.5	46.0	48.5
3-acetylthiophene	−4923.9	11.811	40.9	57.2	55.2
2-acetylthiophene	−4948.2	11.831	41.1		55.4 ± 5.4
2-thiopheneacetic acid, methyl ester	−5545.0	12.854	46.1	61.9	61.5
3- thiopheneacetic acid, methyl ester	−5586.5	12.907	46.4	60.9	62.0
4-chloroacetophenone	−5591.8	12.661	46.5	62.7	62.0

[a] Equation 5: $\Delta_{l}^{g}H_{m}^{o}$ (298.15K)/kJ·mol^{-1} = (1.23 ± 0.10) $\Delta_{sln}^{g}H_{m}$ (364 K) + (4.6 ± 1.7).

TABLE 6: Standard Molar Enthalpies at T = 298.15 K

compound	$\Delta_{f}H_{m}^{\circ}$ (cd), kJ·mol^{-1}	$\Delta_{l}^{g}H_{m}^{\circ}$, kJ·mol^{-1}	$\Delta_{cr}^{g}H_{m}^{\circ}$, kJ·mol^{-1}	$\Delta_{f}H_{m}^{\circ}$ (g), kJ·mol^{-1}
2-acetylthiophene	−118.0 ± 1.7	58.8 ± 1.2		−59.2 ± 2.1
3-acetylthiophene	−129.1 ± 1.4		74.6 ± 1.1	−54.5 ± 1.8

microcalorimetric technique[27,28] agree well within the uncertainty associated with the combined results. However, because the data calculated by correlation gas chromatography are strongly dependent on the quality of the standards used, larger uncertainties have been obtained in this instance. Therefore, in the present study, we have used the values determined by Calvet microcalorimetry to derive the enthalpy of formation in the gas phase of 2-acetylthiophene.

Combining the derived standard molar enthalpies of formation in the condensed phase with the standard molar enthalpies of vaporization and sublimation yield the standard molar enthalpies of formation in the gaseous phase of 2- and 3-acetylthiophene summarized in Table 6.

To our knowledge, there are no experimental results for the energies and enthalpies of combustion and formation in the literature of the title compounds for comparison with our results. There is one study of some physical properties of 2-acetylthiophene that calculated a value for its vaporization enthalpy[52] of 90 cal·g^{-1} with an uncertainty about 5% at the normal boiling point (487.1 K). This corresponds to a value of $\Delta_{l}^{g}H_{m}$ (298.15 K) = (60.6 ± 8.7) kJ·mol^{-1}, (the uncertainty includes the uncertainty associated with the temperature adjustment). The estimated value is in good agreement with the experimental value determined in this work.

3.2. Molecular and Electronic Structures. To our knowledge, there has been no experimental determination of the molecular structure of 2- and 3-acetylthiophenes, either in the gas or solid state. However, the X-ray crystal structures of several derivatives of 2-acetylthiophene have been reported: 2-thionyltrifluoroacetone isonicotinyl hydrazone,[53] 2-acetylthiophene thiosemicarbazone and 2-acetylthiophene-4-phenyl thiosemicarbazone,[54] the ligand 2-acetylthiophene-*o*-aminobenzoylhydrazone,[55] and an *ortho*-manganated derivative.[56]

The calculated molecular structures of 2- and 3-acetylthiophenes, optimized at the MP2(full)/6-31G(3df,2p) level of theory, are shown in Figure 2. Bond distances and bond angles are collected in Table 7. Both molecules are planar, pertaining to the symmetry point group C_s. S,O-*syn* is the preferred conformation in 2-acetylthiophene, S,O-*anti* conformation being 4.0 and 4.1 kJ·mol^{-1} less stable than the S,O-*syn*, calculated at the HF/6-31G(d) and B3LYP/6-31G(d) levels, respectively. Although the energy difference between the two rotamers is small, the free rotation is not likely because the rotational barrier is very high, values of 32.5 and 34.0 kJ·mol^{-1} have been calculated.[57,58]

The thiophene ring is planar in both derivatives. The valency angle of the sulfur atom in the ring, CSC, is calculated as 92.2° and 92.7° in 2- and 3-acetylthiophene, respectively, intermediate between the tetrahedral angle and a right angle and in line with the values calculated previously for other thiophene derivatives.[11,15,16] Calculated C−S distances suggest a considerable double-bond character, and the C−C bonds in the ring are all shorter than single bonds, indicating considerable conjugation, including the exocyclic C−C bonds.

The entire $COCH_3$ group appears to be attracted by the S atom in 2-acetylthiophene, the angle $C_3C_2C_6$ being larger than SC_2C_6 (129.2° and 119.4°, respectively). The nonbonded O−S distance, 2.968 Å, is shorter than the sum of the Van der Waals radii, 3.32 Å.[59]

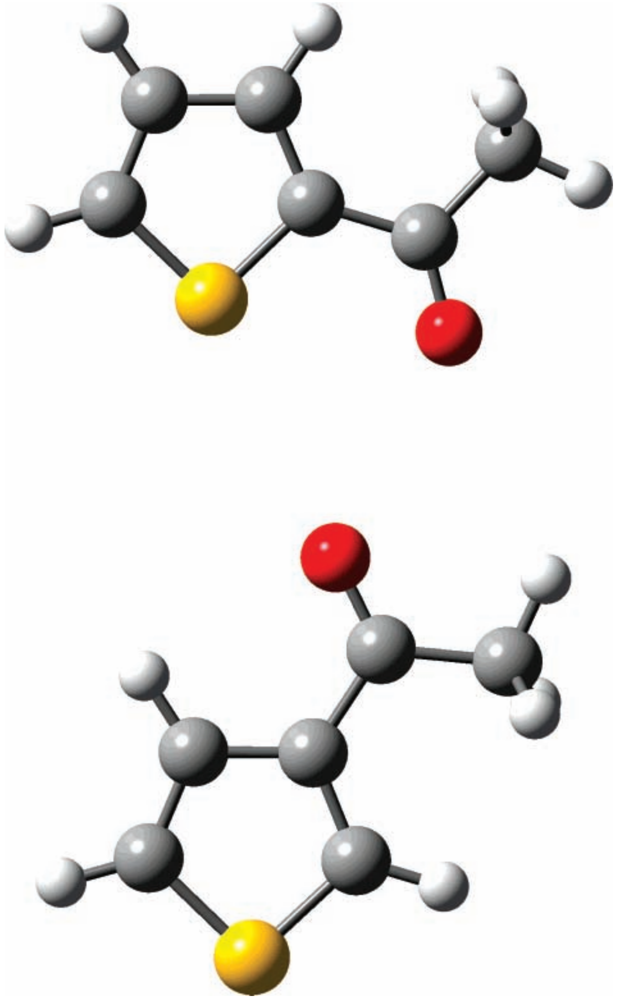


Figure 2. Molecular structures of 2- and 3-acetylthiophenes, optimized at the MP2(full)/6-31G(3df,2p) level.

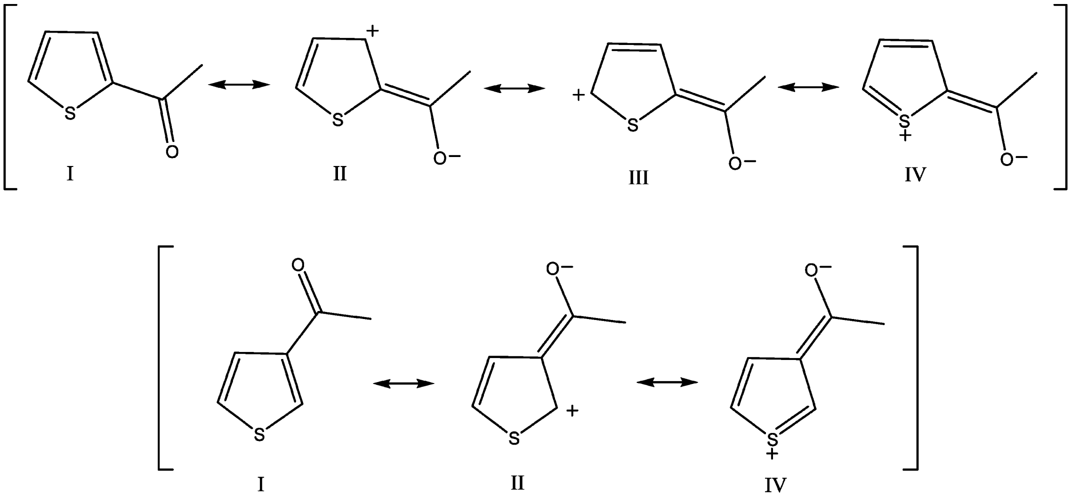


Figure 3. Resonance structures of 2- and 3-acetylthiophenes.

TABLE 7: Molecular Structures Optimized at the MP2(full)/6-31G(3df,2p) Level for the Studied Compounds[a]

	2-acetylthiophene	3-acetylthiophene
S−C2	1.701	1.689
C2−C3	1.385	1.383
C3−C4	1.401	1.412
C4−C5	1.379	1.370
C5−S	1.691	1.699
C2−C6	1.462	
C3−C6		1.472
C6−O	1.221	1.219
C6−C7	1.502	1.502
S−C2−C3	111.3	111.4
C2−C3−C4	112.4	112.1
C3−C4−C5	111.9	112.2
C4−C5−S	112.2	111.5
C5−S−C2	92.2	92.7
S−C2−C6	119.4	
C3−C2−C6	129.2	
C4−C3−C6		122.7
C2−C3−C6		125.2
C2−C6−C7	116.8	
C3−C6−C7		117.6
C7−C6−O	122.0	121.7
S−C2−C6−O	0.0	
C4−C3−C6−O		0.0

[a] Bond distances in Å and bond angles in deg.

Both the thiophene ring and the carbonyl 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 CO group through the ring is represented for both compounds in Figure 3. The contribution of forms II and III should be favorable because the p orbital of the S atom can overlap with the π orbital of the conjugated system. It has been reported, however, that the contribution of form IV should be very unlikely because of the difference in sizes of C and S atoms.[60] Furthermore, the resonance structures suggest a longer $C_2{-}S$ bond length in 2-acetylthiophene and a longer $C_3{-}C_4$ bond length in 3-acetylthiophene if resonance with the CO group is important. If this hypothesis is correct, the $C_3{-}C_4$ bond in 2-acetylthiophene would have more double-bond character than the same bond in 3-acetylthiophene. This fact is observed in the calculated values, the $C_3{-}C_4$ bond length being slightly shorter in 2-acetylthiophene (1.401 versus 1.412 Å). Similarly, the $C_5{-}S$ bond should be shorter in the 2-isomer and the $C_2{-}S$ bond should be shorter in the 3-isomer. The calculated values follow this pattern (see Table 7).

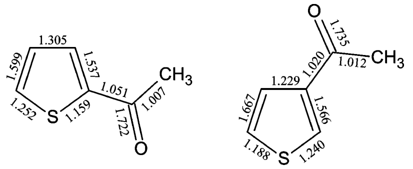


Figure 4. Wiberg bond indices for 2- and 3-acetylthiophenes, calculated at the MP2(full)/6-31G(3df,2p) level.

TABLE 8: G2 and G3 Calculated Energies at 0 K, and Enthalpies at 0 K, for 2- and 3-Acetylthiophenes[a]

	G2		G3	
compound	E_0	H_{298}	E_0	H_{298}
2-acetylthiophene	−704.673992	−704.665289	−705.298163	−705.289460
3-acetylthiophene	−704.673049	−704.664361	−705.297112	−705.288424

[a] All values in hartrees.

We have also calculated the Wiberg bond indices,[61] 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 4. As can be seen, the bond orders are according to the previous hypothesis, and the $C_3{-}C_4$ bond has more double-bond character in 2-acetylthiophene. Bond orders for C−S bonds also indicate significant π delocalization in the ring.

Previous spectroscopic studies by IR[62] and UV[63,64] suggested more effective conjugation in the 2-isomer than in the 3-isomer based on the larger bathochromic shift of the UV primary band for the 2-isomer[63,64] and on the higher carbonyl frequency for the 3-isomer (1662 and 1666 cm^{-1} for the 2- and 3-isomers, respectively).[62] This can also be observed in the frequencies calculated at the HF/6-31G(d) level (1776.6 and 1781 cm^{-1} for the 2- and 3-isomers, respectively, where the values have been scaled[65] by the factor 0.8953). Similarly, the bond lengths between the carbonyl carbon and the ring carbon are 1.462 and 1.472 Å, and the bond lengths between oxygen and carbon are 1.221 and 1.219 Å for 2- and 3-acetylthiophene, respectively, in line with this effect. This behavior has been previously observed for the 2- and 3-thiophenecarboxylic acids ($C_{ring}{-}C(O)(OH)$: 1.458 and 1.464 Å for the 2- and 3-thiophenecarboxylic acids, respectively).

A population analysis using the natural bond orbital (NBO) analysis[39−41] 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

TABLE 9: Comparison of G2 and G3 Calculated Enthalpies of Formation, Using Atomization Reaction and Isodesmic Reactions (6−10) for 2- and 3-Acetylthiophenes with Experimental Values[a]

	G2						G3						
compound	atom	(6)	(7)	(8)	(9)	(10)	atom	(6)	(7)	(8)	(9)	(10)	exptl
2-acetylthiophene	−60.6	−62.9	−60.2	−57.9	−58.3	−61.5	−59.8	−62.9	−60.2	−60.0	−59.6	−61.8	−59.2 ± 2.1
3-acetylthiophene	−58.2	−60.5	−57.7	−55.4	−56.8	−59.0	−57.1	−60.2	−57.5	−57.3	−57.8	−59.1	−54.5 ± 1.8

[a] All values in kJ · mol^{-1}.

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 5.

Partial negative charges are located at the oxygen atom of the carbonyl group, at the C atoms of the thiophene ring, and at the C atom of methyl group, whereas partial positive charges are located at the sulfur atom of the ring and at the C atom of the CO group. The charge distribution does not appreciably change with the position of the $COCH_3$ group, 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 more than 78.5% of p character, whereas the hybridization of carbonyl oxygen atom is $sp^{1.3}$ (ca. 56% of p character). 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.[66] This behavior is observed in the compounds studied and was also observed in our previous studies on 2- and 3-thiophenecarboxylic acids,[11] and 2,5-thiophenedicarboxylic acid.[15]

3.3. Theoretical Determination of the Enthalpies of Formation. G2 and G3 calculated energies at 0 K, and enthalpies at 298 K, for the two compounds studied are given in Table 8.

The standard procedure in obtaining enthalpies of formation in Gaussian-n theories is through atomization reactions,[67,68] but there have been some suggestions[69−73] that there is an accumulation of errors in the application of this method to larger molecules. Glukhovtsev and Laiter[69] have shown that more accurate heats of formation can be derived by using isodesmic or homodesmotic reactions[74] rather than atomization energies. As Raghavachari et al.[75] 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“,[26] where all formal bonds between nonhydrogen atoms are separated into the simplest parent molecules containing these same kinds of linkages, to derive the theoretical enthalpies of formation.

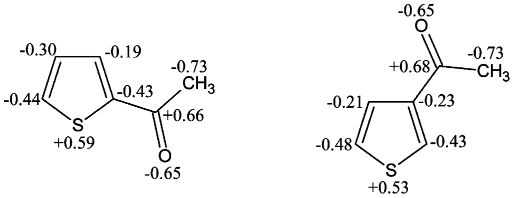


Figure 5. NBO atomic charges for 2- and 3-acetylthiophenes, calculated at the MP2(full)/6-31G(3df,2p) level.

In this work, we have calculated the enthalpies of formation of 2- and 3-acetylthiophenes, C_6H_6OS, using the atomization reactions and the bond separation isodesmic reaction 6:

$$C_6H_6OS\ (g) + 7\ CH_4\ (g) + H_2S\ (g) \rightarrow 3\ CH_3CH_3\ (g) + 2\ CH_2{=}CH_2\ (g) + 2\ CH_3SH\ (g) + 2\ H_2CO\ (g) \quad (6)$$

Other isodesmic reactions (7−10), using different compounds as references, have been used:

$$C_6H_6OS\ (g) + \text{benzene}\ (g) \rightarrow \text{thiophene}\ (g) + \text{acetophenone}\ (g) \quad (7)$$

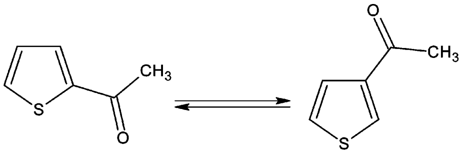
$$C_6H_6OS\ (g) + \text{water}\ (g) \rightarrow \text{thiophene}\ (g) + \text{acetic acid}\ (g) \quad (8)$$

$$C_6H_6OS\ (g) + \text{ethane}\ (g) \rightarrow \text{2- or 3-methylthiophene}\ (g) + \text{acetone}\ (g) \quad (9)$$

$$C_6H_6OS\ (g) + \text{methane}\ (g) \rightarrow \text{thiophene}\ (g) + \text{acetone}\ (g) \quad (10)$$

The G2 and G3 calculated enthalpies of formation are shown in Table 9.[76] The $\Delta_f H^o_m$ values obtained from atomization reactions at the G2 level have been modified by adding spin−orbit and bond additivity (BAC) corrections.[79] The method has been detailed in a previous study.[80]

As can be seen in this table, there is a very good agreement between theoretical and experimental values. Comparison of our experimental and theoretical results for the enthalpies of formation of the two isomers shows that 2-acetylthiophene is more stable than the 3-isomer, with an experimental enthalpy of isomerization $\Delta_r H$ of reaction 11 of 4.7 ± 2.8 kJ·mol^{-1}. Theoretical values of 2.4 and 2.7 kJ·mol^{-1} are calculated at the G2 and G3 level, respectively.



(11)

$\Delta\Delta_f H^o_m$ (g,298.15K) = 4.7 ± 2.8 kJ·mol^{-1}

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, as suggested by the natural bond orbital (NBO) analysis and the short distance calculated between these two atoms.

Our experimental results allow us to make a comparative analysis with anologous benzene derivatives. This can be done by an evaluation of the enthalpies of formation of the compounds shown in Figure 6. The enthalpy difference between benzene ($\Delta_f H^o_m$ (g): (82.6 ± 0.7)) and acetophenone ($\Delta_f H^o_m$ (g): (−86.7 ± 1.7) kJ·mol^{-1}) results in an enthalpy of −(169.3 ± 1.7) kJ·mol^{-1}. The enthalpy difference between 3-acetyl-

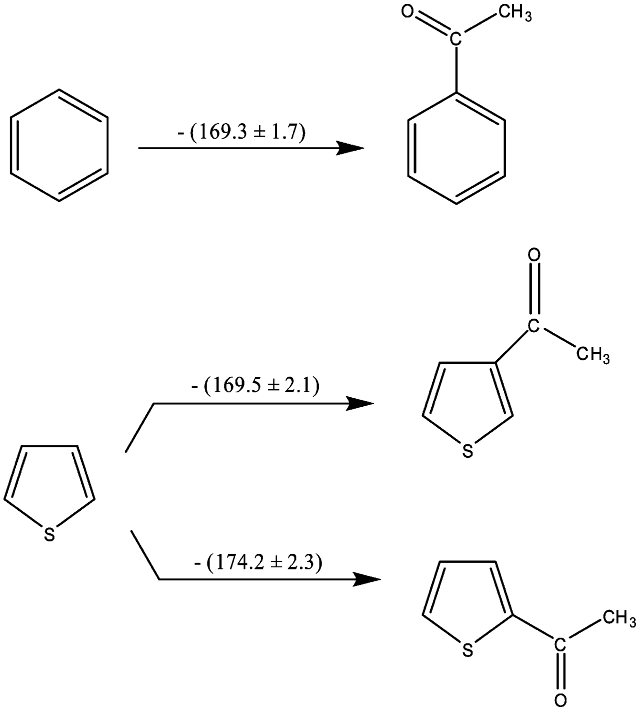


Figure 6. Comparative analysis with the anologous substituted benzene. $\Delta\Delta_f H°_m$ in kJ·mol^{-1} are shown in the arrows.

thiophene ($\Delta_f H^o_m$ (g): (-54.5 ± 1.8) kJ·mol^{-1}) and thiophene ($\Delta_f H^o_m$ (g): (114.9 ± 1.0) kJ·mol^{-1}) produces a similar effect, $-(169.5 \pm 2.1)$ kJ·mol^{-1}. If the same substitution is made at the 2-position, an effect of $-(174.2 \pm 2.3)$ kJ·mol^{-1} is produced. The difference found between the two thiophene isomers may be explained by the additional stabilizing effect produced by the favorable interaction between the carbonyl oxygen and the ring sulfur in 2-acetylthiophene.

4. Conclusions

The experimental enthalpies of formation of 2- and 3-acetylthiophene have been determined. Theoretical calculations of the enthalpies of formation at the G2 and G3 levels agree well with the experimental values. From experimental and theoretical results, 2-acetylthiophene is found to be more stable than the 3-isomer.

Molecular and electronic structures for the compounds studied have been obtained from theoretical calculations. The entire acetyl group appears to be attracted to the ring and to the sulfur atom in 2-acetylthiophene. The O−S distance is shorter than the sum of the Van der Waals radii. This interaction is not possible in the 3-isomer.

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Supporting Information Available: Summary of physical properties used for the correction of apparent mass to mass, conversion of the energy of the actual combustion bomb process to that of the isothermal process, and the correction to standard states; combustion results of the standard massic energies of combustion of 2- and 3- acetylthiophene, respectively; summary of the available literature values of the vaporization enthalpy standards for the correlation-gas chromatography calculations; retention times measured for 3-acetylthiophene and a series of standards. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) *Thiophene and Its Derivatives*; Gronowitz, S., Ed.; Wiley-Interscience: New York 1994, Part 5. (b) *Thiophenes and their Benzo Derivatives in Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Elsevier: Oxford, 1996; Vol. 2, Chapter 2.09−2.12. (c) Barbarella, G.; Melucci, M.; Sotgiu, G. *Adv. Mater.* **2005**, *17*, 1581−1593.

(2) Hosmane, R. S.; Liebman, J. F. *Tetrahedron Lett.* **1991**, *32*, 3949−3952.

(3) (a) Galpern, G. D. *Usp. Khim.* **1976**, *45*, 1395−1427. (b) Sharipov, A. Kh. *Chem. Technol. Fuels Oil* **2002**, *38*, 340−344.

(4) Kropp, K. G.; Fedorak, P. M. *Can. J. Microbiol.* **1998**, *44*, 605−622.

(5) (a) Angelici, R. J.; *Acc. Chem. Res.* **1988**, *21*, 387−394. (b) Bianchini, C.; Meli, A. *Acc. Chem. Res.* **1998**, *31*, 109−116. (c) Whitehurst, D. D.; Isoda, T.; Mochida, I. *Adv. Catal.* **1998**, *42*, 345−371.

(6) (a) Choong, I. C.; Lew, W.; Lee, D.; Pham, P.; Burdett, M. T.; Lam, J. W.; Wiesmann, C.; Luong, T. N.; Fahr, B.; DeLano, W. L.; McDowell, R. S.; Allen, D. A.; Erlanson, D.; Gordon, E. M.; O'Brien, T. *J. Med. Chem.* **2002**, *45*, 5005−5022; (b) Wu, C.; Decker, E. R.; Blok, N.; Bui, H.; You, T. J.; Wang, J.; Bourgoyne, A. R.; Knowles, V.; Berens, K. L.; Holland, G. W.; Brock, T. A.; Dixon, R. A. F. *J. Med. Chem.* **2004**, *47*, 1969−1986. (c) Sperry, J. B.; Wright, D. L. *Curr. Opin. Drug Discovery Dev.* **2005**, *8*, 723−740.

(7) Doré, K.; Dubus, S.; Ho, H. A.; Lévesque, I.; Brunette, M.; Corbeil, G.; Boissinot, M.; Boivin, G.; Bergeron, M. G.; Boudreau, D.; Leclerc, M. *J. Am. Chem. Soc.* **2004**, *126*, 4240−4244.

(8) (a) Cornil, J.; Beljonne, D.; Parente, V.; Lazzaroni, R.; Breads, J. L. *Handbook of Oligo- and Polythiophenes*; Wiley-VCH: Weinheim, Germany, 1999; pp 317−360. (b) Halik, M.; Klauk, H.; Zschieschang, U.; Schmid, G.; Ponomarenko, S.; Kirchmeyer, S.; Weber, W. *Adv. Mater.* **2003**, *15*, 917−922. (c) Rost, C.; Karg, S.; Riess, W.; Loi, M. A.; Murgia, M.; Kuccini, M. *Appl. Phys. Lett.* **2004**, *85*, 1613−1615. (d) Somanathan, N.; Radhakrishnan, S. *Int. J. Mod. Phys. B* **2005**, *19*, 4645−4676. (e) James, D. K.; Tour, J. M. *Top. Curr. Chem.* **2005**, *257*, 33−62. (f) Porzio, W.; Destri, S.; Pasini, M.; Bolognesi, A.; Angiulli, A.; Di Gianvincenzo, P.; Natali, D.; Sampietro, M.; Carione, M.; Fumagalli, L.; Ferrari, S.; Peron, E.; Perissinotti, F. *Mater. Sci. Eng., C* **2006**, *26*, 996−1001.

(9) (a) Roncalli, J. *Chem. Rev.* **1992**, *92*, 711−738. (b) Novak, P.; Müller, K.; Santhanam, K. S. V.; Haas, O. *Chem. Rev.* **1997**, *97*, 207−282. (c) *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; John Wiley: Chichester, U.K., 1997; Vols. 2 and 3. (d) Sirringhaus, H.; Tessler, N.; Friend, R. H.; *Science* **1998**, *280*, 1741−1744. (e) *Handbook of Oligo and Polythiophenes*; Fichou, D., Ed.; Wiley-VCH: Weinheim, Germany, 1999. (f) *Semiconducting Polymers*; Hadziioannou, G., van Hutten, P. F., Eds.; Wiley-VCH: Weinheim, Germany, 2000. (g) Perepichka, I. F.; Perepichka, D. F.; Meng, H.; Wudl, F.; Litvinenko, L. M. *Adv. Mater.* **2005**, *17*, 2281−2305. (h) Si, P.; Chi, Q.; Li, Z.; Ulstrup, J.; Moller, P. J.; Mortensen, J. *J. Am. Chem. Soc.* **2007**, *129*, 3888−3896.

(10) (a) Angelici, R. J. *Organometallics* **2001**, *20*, 1259−1275. (b) Sadimenko, A. P. *Adv. Heterocycl. Chem.* **2001**, *78*, 1−64. (c) Barbarella, G.; Melucci, M.; Sotgiu, G. *Adv. Mater.* **2005**, *17*, 1581−1593.

(11) Temprado, M.; Roux, M. V.; Jiménez, P.; Dávalos, J. Z.; Notario, R. *J. Phys. Chem. A* **2002**, *106*, 11173−11180.

(12) Roux, M. V.; Temprado, M.; Jiménez, P.; Dávalos, J. Z.; Foces-Foces, C.; García, M. V.; Redondo, M. I. *Thermochim. Acta* **2003**, *404*, 235−244.

(13) Roux, M. V.; Jiménez, P.; Notario, R.; Temprado, M.; Martín-Valcarcel, G.; Liebman, J. F. *ARKIVOC (Gainsville, FL, U.S.)* **2005**, *ix*, 364−374.

(14) Temprado, M.; Roux, M. V.; Jiménez, P.; Guzmán-Mejía, R.; Juaristi, E. *Thermochim. Acta* **2006**, *441*, 20−26.

(15) Roux, M. V.; Temprado, M.; Jiménez, P.; Notario, R.; Verevkin, S. P.; Liebman, J. F. *J. Phys. Chem. A* **2006**, *110*, 12477−12483.

(16) Roux, M. V.; Temprado, M.; Notario, R.; Chickos, J. S.; Santos, A. F. L. O. M.; Ribeiro da Silva, M. A. V. *J. Phys. Chem. A* **2007**, *111*, 5280−5286.

(17) (a) Marti, E. E. *Thermochim. Acta* **1973**, *5*, 173−218. (b) Palermo, E. F.; Chiu, J. *Thermochim. Acta* **1976**, *14*, 1−12.

(18) (a) Ribeiro da Silva, M. A.V.; Santos, L. M. N. B. F.; Schröder, B. *J. Chem Thermodyn.* **2006**, *38*, 1455−1460. (b) Ribeiro da Silva, M. A. V.; Santos, A. F. L. O. M. *J. Therm. Anal. Calorim.* **2007**, *88*, 7−17.

(19) Roux, M. V.; Dávalos, J. Z.; Jiménez, P.; Flores, H.; Saiz, J. L.; Abboud, J. L. M.; Juaristi, E. *J. Chem. Thermodyn.* **1999**, *31*, 635−646.

(20) Skinner, H. A.; Snelson, A. *Trans. Faraday Soc.* **1960**, *6*, 1776−1783.

(21) Coops, J.; Jessup, R. S.; van Nes, K. G. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York 1956; Vol. 1, Chapter 3.

(22) The NBS Tables of Chemical Thermodynamic Properties. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.

(23) Hu, A. T.; Sinke, G. C.; Månsson, M.; Ringnér, B. *J. Chem. Thermodyn.* **1972**, *4*, 283−299.

(24) Hubbard, W. N.; Scott, D. W.; Waddington, G. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Vol. 1, Chapter 5.

(25) Good, W. D.; Scott, D. W. In *Experimental Thermochemistry*; Skinner, H. A., Ed.; Interscience: New York, 1962; Vol. 2, Chapter 2.

(26) Wieser, M. E. *Pure Appl. Chem*. **2006**, *78*, 2051−2066.

(27) Adedeji, F. A.; Brown, D. L. S.; Connor, J. A.; Leung, M.; Paz-Andrade, M. I.; Skinner, H. A. *J. Organomet. Chem*. **1975**, *97*, 221−228.

(28) Santos, L. M. N. B. F.; Schröder, B.; Fernandes, O. O. P.; Ribeiro da Silva, M. A. V *Thermochim. Acta* **2004**, *415*, 15−20.

(29) Benson, S. W. *Thermochemical Kinetics. Methods for the Estimation of Thermochemical Data Rate Parameters*, 2nd ed.; Wiley: New York, 1976.

(30) Stull, D. R.; Westrum, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

(31) Sabbah, R.; Xu-wu, A.; Chickos, J. D.; Planas, Leitão, M. L.; Roux, M. V.; Torres, L. A. *Thermochim. Acta* **1999**, *331*, 93−204.

(32) (a) Knudsen, M.; *Ann. Phys*. **1909**, *28*, 75−130. (b) Colomina, M.; Jiménez, P.; Turrión, C. *J. Chem. Thermodyn.* **1982**, *14*, 779−784.

(33) Freeman, R. D.; Searcy, A. W. *J. Chem. Phys.* **1954**, *22*, 762−763.

(34) Chickos, J. S.; Hosseini, S.; Hesse, D. G. *Thermochim. Acta* **1995**, *249*, 41−62.

(35) Hehre, W. J.; Radom. L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(36) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(37) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221−7230.

(38) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764−7776.

(39) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066−4073.

(40) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926.

(41) Weinhold, F. Natural Bond Orbital (NBO) Analysis. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Ed.; Wiley: New York, 1998; Vol. 3, p 1792.

(42) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO*, version 3.1; Madison, WI 1988.

(43) Westrum, E. F., Jr. In *Combustion Calorimetry*; Sunner, S., Månsson, M., Eds.; Pergamon Press: Oxford, U.K., 1979; Chapter 7.

(44) Olofson, G. In *Combustion Calorimetry*; Sunner, S., Månsson, M., Eds.; Pergamon Press: Oxford, 1979; Chapter 6.

(45) The NBS Tables of Chemical Thermodynamic Properties, *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.

(46) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1989.

(47) Stull, D. R.; Westrum, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

(48) Chickos, J. S. *Thermochim. Acta* **1998**, *313*, 19−26.

(49) Chickos, J. S.; Hesse, D. G.; Liebman, J. F. *Struct. Chem.* **1993**, *4*, 261−269.

(50) Temprado, M.; Roux, M. V.; Umnahanant, P.; Zhao, H.; Chickos, J. S. *J. Phys. Chem B* **2005**, *109*, 12590−12595, and references cited.

(51) Chickos, J. S. In *Computational Thermochemistry, Prediction and Estimation of Molecular Thermodynamics*; Irikura, K. K., Frurip, D., J., Eds.; ACS Symposium Series 677; American Chemical Society: Washington, DC 1998; pp 76−85.

(52) Johnson, G. C. *J. Am. Chem. Soc.* **1947**, *69*, 150−152.

(53) Wang, X.; Deng, R.; Wu, J.; Chen, Z. *Acta Crystallogr., Sect. C: Cryst. Struct.* **1992**, *48*, 1295−1297.

(54) de Lima, G. M.; Neto, J. L.; Beraldo, H.; Siebald, H. G. L.; Duncalf, D. J. *J. Mol. Struct.* **2002**, *604*, 287−291.

(55) Gudasi, K. B.; Shenoy, R. V.; Vadavi, R. S.; Patil, S. A.; Nethaji, M. *J. Mol. Struct.* **2006**, *788*, 22−29.

(56) Cooney, J. M.; Gommans, L. M.; Nicholson, B. K. *J. Organomet. Chem.* **1988**, *349*, 197−207.

(57) Han, I.-S.; Kim, C. K.; Jung, H. J.; Lee, I. *Theor. Chim. Acta* **1996**, *93*, 199−210.

(58) Distefano, G.; de Palo, M.; Dal Colle, M.; Guerra, M. *J. Mol. Struct. (THEOCHEM)* **1998**, *455*, 131−140.

(59) Values for O and S atoms, 1.52 and 1.80 Å, respectively, taken from Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

(60) Jeon, K. O.; Yu, J. S.; Lee, C. K. *Heterocycles* **2003**, *60*, 2685−2705.

(61) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083−1096.

(62) Otsuji, Y.; Imoto, E. *Nippon Kagaku Zasshi* **1959**, *80*, 1199−1200.

(63) Sugimoto, Y.; Nishimura, S.; Imoto, E. *Bull. Univ. Osaka Prefect., Ser. A* **1959**, *8*, 71−81.

(64) Gronowitz, S. *Ark. Kemi* **1958**, *13*, 239−246.

(65) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502−16513.

(66) Carballeira, L.; Pérez-Juste, I. *J. Phys. Chem. A* **2000**, *104*, 9362−9369, and references therein.

(67) Notario, R.; Castaño, O.; Abboud, J.-L. M.; Gomperts, R.; Frutos, L. M.; Palmeiro, R. *J. Org. Chem.* **1999**, *64*, 9011−9014.

(68) Notario, R.; Castaño, O.; Gomperts, R.; Frutos, L. M.; Palmeiro, R. *J. Org. Chem.* **2000**, *65*, 4298−4302.

(69) Glukhovtsev, M. N.; Laiter, S. *Theor. Chim. Acta* **1995**, *92*, 327−332.

(70) Nicolaides, A.; Radom, L. *Mol. Phys.* **1996**, *88*, 759−766.

(71) Nicolaides, A.; Rauk, A.; Glukhovtsev, M. N.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 17460−17464.

(72) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063−1079.

(73) Raghavachari, K.; Stefanov, B. B.; Curtiss, L. A. *Mol. Phys.* **1997**, *91*, 555−560.

(74) Minkin, V. I. *Pure Appl. Chem.* **1999**, *71*, 1919−1981.

(75) Raghavachari, K.; Stefanov, B. B.; Curtiss, L. A. *J. Chem. Phys.* **1997**, *106*, 6764−6767.

(76) Experimental $\Delta_f H^\circ_m$ values for the reference compounds used in isodesmic reactions (6−10), methane, ethane, and ethylene, −74.6, −84.0, and 52.4 kJ·mol^{-1}, respectively, have been taken from Manion, J. A. *J. Phys. Chem. Ref. Data* **2002**, *31*, 123−172. $\Delta_f H^\circ_m$ values for methanethiol, formaldehyde, thiophene, benzene, acetophenone, acetic acid, acetone, 2-methylthiophene, and 3-methylthiophene, −22.9, −108.6, 115.0, 82.6, −86.7, −432.8, −217.1, 83.5, and 82.5 kJ·mol^{-1}, respectively, have been taken from ref 77. $\Delta_f H^\circ_m$ values for hydrogen sulfide and water, −20.5 kJ and −241.8 mol^{-1}, respectively, have been taken from ref 78.

(77) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; TRC Data Series; TRC: Texas, 1994; Vol. 1.

(78) *NIST-JANAF Thermochemical Tables*, 4th ed.; Chase, M. W., Jr. *J. Phys. Chem. Ref. Data* **1998**, *Monograph 9*, 1.

(79) Petersson, G. A.; Malick, D. K.; Wilson, W. G.; Ochterski, J. W.; Montgomery, J. A., Jr.; Frisch, M. J. *J. Chem. Phys.* **1998**, *109*, 10570−10579.

(80) Roux, M. V.; Jiménez, P.; Dávalos, J. Z.; Notario, R.; Juaristi, E. *J. Org. Chem.* **2001**, *66*, 5343−5351.