Journal of Thermal Analysis and Calorimetry, Vol. 95 (2009) 2, 333–344

ENERGETICS OF SOME SULPHUR HETEROCYCLES
Thiophene derivatives

M. A. V. Ribeiro da Silva[*] *and Ana Filipa L. O. M. Santos*

Centro de Investigação em Química, Department of Chemistry, Faculty of Science, University of Porto, Rua do Campo Alegre 687 4169-007 Porto, Portugal

The present work is part of a broader research program on the energetics of formation of heterocycles, aiming the study of the enthalpic effects of the introduction of different substituents into heterocycles. In this work we present the results of the thermochemical research on sulphur heterocycles of the type substituted thiophenes with different kind of substituents, mainly alkyl, ester, acetyl, carboxamide, acetamide, carbonitrile and carboxaldehyde.

The standard ($p°$=0.1 MPa) molar enthalpies of formation, in the condensed phase, at T=298.15 K, of a large number of substituted thiophenes, were derived from their standard massic energies of combustion, measured by rotating-bomb combustion calorimetry, while the standard molar enthalpies of vaporization or sublimation of those compounds were obtained either by high temperature Calvet Microcalorimetry, or by the temperature dependence of their vapour pressures determined by the Knudsen effusion technique. The standard molar enthalpies of formation, of the studied sulphur heterocycles in the gaseous phase, were then derived. The results are interpreted in terms of structural contributions to the energetics of the substituted thiophenes, the internal consistency of the results is discussed and, whenever appropriate and possible, empirical correlations are suggested for the estimation of standard molar enthalpies of formation, at T=298.15 K, of substituted thiophenes. A Table of enthalpic increments for different group substituents in positions 2 or 3 of the thiophene ring has been established.

Keywords: *acetylthiophenes, alkylthiophenes, thiopheneacetic acid methyl esters, thiopheneacetonitriles, thiophenecarbonitriles, thiophenecarboxaldehydes, thiophenecarboxamides*

Introduction

Thiophene based compounds have been a constant matter of investigation due to their wide range of applications. They are the precursors of many drugs with high therapeutical potential, being used in the treatment of cancer [1–3], osteoporosis [4], hypertension [5], Alzheimer’s disease [6], human immunodeficiency virus (HIV-1) [7–9], and others. Biotin, [10–12] a tetrahydrothiophene, is the most important naturally occurring thiophene derivative; it is a water–soluble vitamin, acting as a coenzyme in carboxylation and decarboxylation, *in vivo*, and is involved in the synthesis of long-chain fatty acids [13]. More specifically the thiophene derivatives have shown insecticide activity [14], antibacterial activity [14–16], antiviral activity [14, 17, 18], antifungal activity [14, 19, 20], antioxidant activity [21, 22], anthelmintic activity [23], antiallergic activity [24]. Moreover, these organic sulphur heterocycles comprise a significant portion of the organosulphur compounds in petroleum, coal and other fossil fuels [25], being obtainable as by-products of petroleum distillation [26]; they are removed from these byproducts through a chemical process called hydrodesulphurization, over heterogeneous catalysts [27, 28]. Apart the applications already cited, they have recently been used as good inhibitors of corrosion of metals in acidic media [29] and as building blocks for the oligo- and polythiophenes. Polymerization of thiophene and its derivatives yields the polythiophenes, an important representative class of conducting conjugated polymers, which found application in the area of new materials because of their chemical, thermal and electrical stabilities, as well as easiness of preparation. They are used in light emitting diodes (LED’s) [30], field-effect transistors (FET’s) [31], thin-film transistors (TFT’s) [32], sensors [33], batteries [34], in the detection of biological [35] and genetic material [36]. However, despite their wide importance, the knowledge of the energetic properties of these compounds is still scarce.

The present work is not only a contribution to improve this situation, but also part of a broader research program on the energetics of formation of heterocycles, being carried out on our Research Group, which aims the study of the enthalpic effects of the introduction of different substituents into heterocycles. In this paper we present a review of the literature results for these sulphur heterocycles and discuss the relations between their energetics and structure.

---

[*] Author for correspondence: risilva@fc.up.pt

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

All the compounds whose results are presented in this paper were commercially obtained and further purified by distillation (in the case of liquids) or by sublimation under reduced pressure in the case of the solids. The purity of each compound was accessed by gas-liquid chromatography prior to the experimental measurements.

Table 1 registers the literature values [37–44] of the standard (p°=0.1 MPa) molar enthalpies of formation, at T=298.15 K, in the condensed state, derived from rotation-bomb combustion calorimetry [37, 45–50], the values of the standard molar enthalpies of vaporization for the liquid compounds, measured by High Temperature Calvet Microcalorimetry [51–53] and, in the case of solid compounds, the enthalpies of sublimation derived from the temperature dependence of the vapour pressure measured by the Knudsen effusion method [54–57].

For some of the compounds whose standard molar enthalpies of formation were experimentally determined, computational thermochemistry calculations have also been performed. Standard *ab initio* molecular orbital calculations [58] were performed with the Gaussian 03 series of programs [59]. The energy of the compounds studied was calculated using Gaussian n-theories at the G2 [60] and G3 [61] levels. We have also reoptimized the geometries at the MP2(full)/6-31G(3d,2f) level to obtain more reliable molecular structures for the compounds studied.

Table 1 Standard (p°=0. 1 MPa) molar enthalpies of formation, in both condensed and gaseous phase, and standard molar enthalpies of phase transition, at T=298. 15 K

Compound	$\Delta_f H^0_m$(cr,l)/ kJ mol^{-1}	$\Delta^g_{cr,l} H^0_m$ (T=298.15 K)/ kJ mol^{-1}	$\Delta_f H^0_m$(g)/ kJ mol^{-1}	Ref.
2-Ethylthiophene (l)	13.6±1.9	39.7±0.9	53.3±2.1	[37]
2-*n*-Propylthiophene (l)	–11.1±2.2	43.7±1.0	32.6±2.4	[37]
2-*n*-Butylthiophene (l)	–40.5±2.4	48.5±1.1	8.0±2.6	[37]
2-*n*-Pentylthiophene (l)	–64.8±2.7	52.0±1.2	–12.8±3.0	[37]
2-*n*-Hexylthiophene (l)	–88.1±3.1	56.4±1.3	–31.7±3.4	[37]
2-*n*-Octylthiophene (l)	–136.4±3.7	65.4±1.4	–71.0±4.0	[37]
3-*n*-Butylthiophene (l)	–33.9±2.4	49.3±1.1	15.4±2.6	[37]
3-*n*-Hexylthiophene (l)	–87.3±3.1	58.5±1.3	–28.8±3.4	[37]
3-*n*-Octylthiophene (l)	–152.2±1.6	67.6±1.5	–84.6±2.2	[37]
2,5-Dimethylthiophene (l)	10.4±1.7	40.2±0.9	50.6±1.9	[38]
2-Thiopheneacetic acid methyl ester (l)	–330.4±2.4	61.9±1.4	–268.5±2.8	[39]
3-Thiopheneacetic acid methyl ester (l)	–328.5±2.0	60.9±1.3	–267.6±2.4	[39]
2-Acetylthiophene (l)	–118.0±1.7	58.8±1.2	–59.2±2.1	[40]
3-Acetylthiophene (cr)	–129.1±1.4	76.4±1.1	–54.5±1.8	[40]
2-Acetyl-3-methylthiophene (l)	–148.0±2.0	57.1±2.4	–90.9±3.1	[41]
2-Acetyl-4-methylthiophene (l)	–155.4±2.1	63.0±2.6	–92.4±3.3	[41]
2-Acetyl-5-methylthiophene (l)	–158.0±2.1	62.0±2.6	–96.0±3.3	[41]
3-Acetyl-2,5-dimethylthiophene (l)	–184.5±2.4	61.3±1.3	–123.2±2.7	[38]
2-Thiophenecarboxaldehyde (l)	–62.0±1.5	54.9±1.1	–7.1±1.9	[42]
3-Thiophenecarboxaldehyde (l)	–60.0±1.5	52.6±1.2	–7.4±1.9	[42]
3-Methyl-2-thiophenecarboxaldehyde (l)	–98.3±1.7	57.7±1.3	–40.6±2.1	[42]
5-Methyl-2-thiophenecarboxaldehyde (l)	–93.5±1.7	56.2±1.2	–37.3±2.1	[42]
5-Ethyl-2-thiophenecarboxaldehyde (l)	–132.3±2.0	62.2±1.3	–70.1±2.4	[42]
2-Thiophenecarboxamide (cr)	–171.1±1.2	107.1±0.4	–64.0±1.3	[43]
2-Thiopheneacetamide (cr)	–197.2±1.8	109.2±0.5	–88.0±1.9	[43]
2-Thiophenecarbonitrile (l)	198.5±1.6	49.5±1.1	248.0±1.9	[44]
3-Thiophenecarbonitrile (l)	197.0±1.4	51.6±1.9	248.6±2.4	[44]
3-Methyl-2-thiophenecarbonitrile (l)	157.6±1.7	54.4±1.2	212.0±2.1	[44]
2-Thiopheneacetonitrile (l)	167.6±1.8	60.5±1.3	228.1±2.2	[44]
3-Thiopheneacetonitrile (l)	166.7±1.8	61.1±1.3	227.8±2.2	[44]

Results and discussion

n-Alkyl-substituted thiophenes

The plot of the enthalpies of formation in the gaseous phase, against the number of methylene groups, n_{CH_2}, in the alkyl chain, gives for 2-alkyl-substituted thiophenes and for 3-alkyl-substituted thiophenes, two excellent straight lines, as shown in Fig. 1, yielding the Eqs (1) and (2), respectively, for 2-alkyl-substituted thiophenes and 3-alkyl-substituted thiophenes, with coefficients of regression closed to the unit:

$$\Delta_f H^0_m(\text{g})/\text{kJ mol}^{-1} = -20.786 n_{CH_2} + 72.614 \quad (R^2 = 0.9982) \qquad (1)$$

$$\Delta_f H^0_m(\text{g})/\text{kJ mol}^{-1} = -25.000 n_{CH_2} + 92.333 \quad (R^2 = 0.9955) \qquad (2)$$

These equations confirm that the enthalpic increment for the entrance of a methylene group in the linear alkyl chain of *n*-alkyl-substituted thiophenes is also approximately 21 kJ mol^{-1}, as the literature data [62] yields for *n*-alkanes (Eq. (3)) and for the *n*-alkylbenzenes (Eq. (4)).

$$\Delta_f H^0_m(\text{g})/\text{kJ mol}^{-1} = -20.618 n_{CH_2} - 84.363 \quad (R^2 = 0.9999) \qquad (3)$$

$$\Delta_f H^0_m(\text{g})/\text{kJ mol}^{-1} = -21.020 n_{CH_2} + 50.660 \quad (R^2 = 1.0000) \qquad (4)$$

whose plots are also depicted in Fig. 1.

These relationships between the standard molar enthalpies of formation in the gaseous phase and the number of methylene groups in the structure of the alkyl-substituted thiophenes enables the estimation of $\Delta_f H^0_m$ (g) for other alkyl-substituted thiophenes for which the respective experimental determination was not performed. Table 2 shows the estimated enthalpies of formation calculated from Eqs (1) and (2) together with the deviations, δ, of these estimated values to the experimental ones. As it can be seen, these deviations are small, being of the same order of magnitude of the uncertainties associated to the experimental values, which gives confidence to the use of Eqs (1) and (2) for the estimation of the standard molar enthalpies of formation, in the gaseous phase, of 2-alkyl-substituted thiophenes and 3-alkyl-substituted thiophenes.

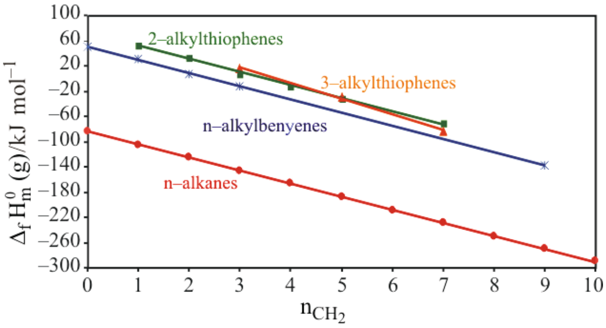


Fig. 1 Plots of the gaseous standard molar enthalpies of formation, at T=298.15 K, *vs*. the number of methylene groups in the alkyl chain

2,5-Dimethylthiophene

Using the literature values of the standard molar enthalpies of formation, in the gaseous state, for thiophene

Table 2 Experimental and estimated values of the standard (p°=0. 1 MPa) molar enthalpies of formation of 2-*n*-alkyl-substituted thiophenes and 3-*n*-alkyl-substituted thiophenes, at T=298. 15 K

Alkylthiophene	n_{CH_2}	$\Delta_f H^0_m$(g)/kJ mol^{-1}		δ = Exp–Est
		Experimental	Estimated	
2-Ethylthiophene	1	53.3 ± 2.1	51.8	1.5
2-*n*-Propylthiophene	2	32.6 ± 2.4	31.1	1.5
2-*n*-Butylthiophene	3	8.0 ± 2.6	10.3	– 2.3
2-*n*-Pentylthiophene	4	– 12.8 ± 3.0	–10.5	– 2.3
2-*n*-Hexylthiophene	5	–31.7 ± 3.4	– 31.3	– 0.4
2-*n*-Heptylthiophene	6	–	– 52.1	–
2-*n*-Octylthiophene	7	– 71.0 ± 4.0	– 72.8	1.8
3-Ethylthiophene	1	–	67.3	–
3-*n*-Propylthiophene	2	–	42.3	–
3-*n*-Butylthiophene	3	15.4 ±2.6	17.3	–1.9
3-*n*-Pentylthiophene	4	–	– 7.7	–
3-*n*-Hexylthiophene	5	–28.8 ± 3.4	– 32.7	3.9
3-*n*-Heptylthiophene	6	–	– 57.7	–
3-*n*-Octylthiophene	7	– 84.6 ± 2.2	– 82.7	– 1.9

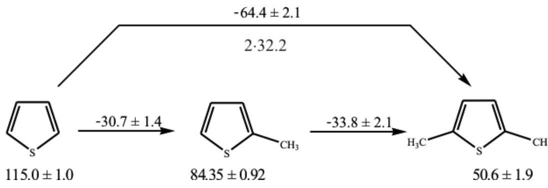


Fig. 2 Enthalpic increments for the formation of 2,5-dimethylthiophene from thiophene or 2-methylthiophene

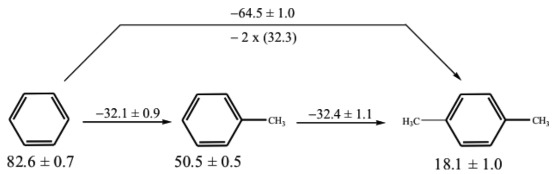


Fig. 3 Enthalpic increments for the formation of *p*-xylene from benzene or toluene

115.0±1.0 kJ mol^{-1} [63] and 2-methylthiophene 84.35±0.92 kJ mol^{-1} [64], the enthalpic increment of the substitution of an H atom by a –CH_3 group in the 2– position of the thiophene ring is –30.7±1.4 kJ mol^{-1}. Using the value of the standard molar enthalpy of formation, in the gaseous phase, of 2,5-dimethylthiophene, reported in Table 1, one calculates the enthalpic increment relative to the entrance of a second –CH_3 group in the 5– position of the thiophene ring to yield the 2,5-dimethylthiophene, as –33.8±2.1 kJ mol^{-1}, as shown in the scheme of Fig. 2, where all the values are in kJ mol^{-1}.

Within the associated uncertainties, we can conclude that there is no significant energetic effect caused by the introduction of a second methyl group in 2-methylthiophene to yield 2,5-dimethylthiophene, neither when an H atom, in the 2– position of the thiophene ring is substituted by a methyl group to give the 2-methylthiophene.

Our experimental results allow us to make a comparative analysis with the analogous substituted benzenes. From the literature values of the standard molar enthalpies of formation, in the gaseous state, of benzene 82.6±0.7 kJ mol^{-1} [62], toluene 50.5±0.5 kJ mol^{-1} [62] and *p*-xylene 18.1±1.0 kJ mol^{-1} [62], we obtain the values given in the scheme of Fig. 3.

Within the experimental uncertainties associated, the resulting enthalpic increments of the addition of a –CH_3 group in the 2– position and of a second –CH_3 group in the 5– position of the thiophene ring are equal to the respective additions to the benzene ring, that is, the energetic effects obtained from the conversion of benzene→toluene→*p*-xylene are similar to the same effects of the conversion of thiophene→2-methylthiophene→2,5-dimethylthiophene. We can conclude that the energetic effects involved in the stabilization due to the substitution of two H atoms by two –CH_3 groups in the 2 and 5 positions of thiophene and in the 1,–4– positions of benzene are equal, –64.4±2.1 kJ mol^{-1} and –64.5±1.0 kJ mol^{-1}, respectively, showing that these substitutions do not induce different specific enthalpic effects.

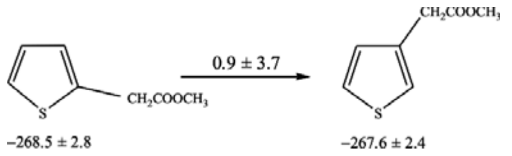


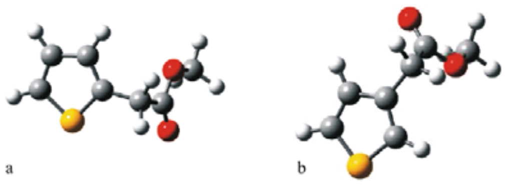
Fig. 4 Thermoneutral isomerization

2- and 3-thiopheneacetic acid methyl esters

From the experimental available values of the standard molar enthalpies of formation, in the gaseous phase, of the 2- and 3-thiopheneacetic acid methyl esters, it is seen that, within the associated uncertainties, the isomerization is thermoneutral as shown in Fig. 4.

Theoretical calculations

Figure 5 shows the calculated molecular structures optimized for both isomers of thiopheneacetic acid methyl esters.



2-Thiopheneacetic acid methyl ester   2-Thiopheneacetic acid methyl ester

Fig. 5 Calculated molecular structures, optimized at the MP2(full)/6-31G(3df,2p) level

The standard procedure to obtain enthalpies of formation in Gaussian *n*-theories is through atomization reactions, but there have been some suggestions [65] that there is an accumulation of errors in the application of this method to larger molecules. It has been shown [66] that more accurate enthalpies of formation can be derived using isodesmic or homodesmotic reactions rather than atomization energies. However, one deficiency of the isodesmic reaction approach is that many different isodesmic reactions can be set up for the same molecule yielding different results. So, it has been proposed [67] to use a standard set of isodesmic reactions, 'the bond separation reactions' [58] where all formal bonds between non-hydrogen atoms are separated into the simplest parent molecules containing these same kind of linkages, to derive the theoretical enthalpies of formation. For the two thiopheneacetic acid methyl esters, $C_7H_8O_2S$, the bond separation isodesmic reaction is:

Table 3 Comparison of G3 calculated enthalpies of formation, using atomization and isodesmic reactions for 2- and 3-thiopheneacetic acid methyl esters, with the experimental values. All values are in kJ mol^{-1}

	Experimental value	G3			
		Atomization reaction	Reaction 5	Reaction 6	Mean value
2-Thiopheneacetic acid methyl ester	–268.5±2.8	–262.8	–266.2	–261.6	–263.5
3-Thiopheneacetic acid methyl ester	–267.6±2.4	–266.1	–269.4	–265.8	–267.1

$$C_7H_8O_2S+8CH_4+H_2S+H_2O\rightarrow$$
$$\rightarrow 3C_2H_6+2C_2H_4+2CH_3SH+2CH_3OH+H_2CO \quad (5)$$

We also obtained the enthalpies of formation of both isomers using another isodesmic reaction with methyl thiophenes as references:

$$C_7H_8O_2S+CH_4\rightarrow$$
$$\rightarrow \text{2- or 3-methylthiophene}+CH_3CO_2CH_3 \quad (6)$$

The calculated values of the enthalpies of formation of 2- and 3-thiopheneacetic acids methyl esters at G3 level of theory, using atomization, bond separation isodesmic reaction (Eq. (5)) and isodesmic reaction (Eq. (6)) are registered in Table 3, showing a good agreement between the theoretical and experimental values. The G3 calculated isomerization enthalpy is –3.6 kJ mol^{-1} in a reasonable agreement with the experimental difference 0.9±3.7 kJ mol^{-1}.

The 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 that observed for carboxyl groups.

Acetylthiophene derivatives

From the literature data, the standard molar enthalpies of formation, in the gaseous state, of furan and of acetylfuran, respectively –34.8±0.7 kJ mol^{-1} [62] and –207.4±1.3 [68] kJ mol^{-1}, one calculates that the enthalpic increment for the entrance of a $-COCH_3$ group into the furan ring is –172.6±1.5 kJ mol^{-1}. From the literature value of the standard molar enthalpy of formation, in the gaseous phase, of pyridine, $\Delta_f H_m^0(C_5H_5N, g)$=140.4±0.7 kJ mol^{-1} [62], and of acethylpyridine, $\Delta_f H_m^0(C_5H_4NCOCH_3, g)$= –41.3±2.9 kJ mol^{-1} [69], the calculated enthalpic increment for the entrance of a $-COCH_3$ group into the pyridine ring is –181.7±3.0 kJ mol^{-1}, whereas the enthalpic increment for the entrance of such group in the benzene ring, is calculated as –169.3±1.7 kJ mol^{-1} from the enthalpies of formation of benzene and of acetophenone, respectively, 82.6±0.7 kJ mol^{-1} [62], and –86.7±0.7 kJ mol^{-1} [62], as it is resumed in Fig. 6.

This scheme shows that the entrance of the $-COCH_3$ group in the position 2– of thiophene and in the position 2– of the furan rings gives the same stabilization effect, within the associated uncertainties. In the benzene the stabilization increment is slightly lower since there is no stabilizing resonance through the ring between the oxygen atom of the acetyl group and the heteroatom, which happens in the cases of thiophene, furan and pyridine. The interaction is more effective in the pyridine ring, since the entrance of the $-COCH_3$ group produces a bigger stabilization than in the other cases.

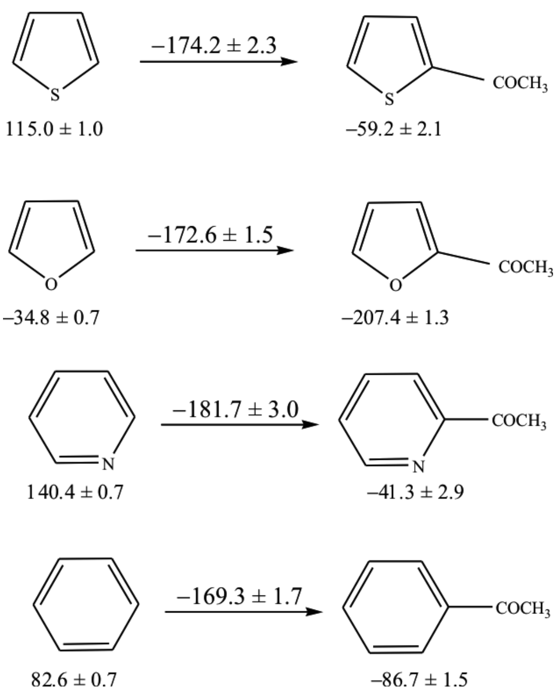


Fig. 6 Enthalpic increments for the formation of 2-acetylthiophene, 2-acetylfuran, 2-acetylpyridine and acetophenone

The experimental values of the standard molar enthalpies of formation in the gaseous state, of the 2– and 3-acetylthiophenes, show that 2-acetylthiophene is more stable than the 3-acetylthiophene, as can be seen in Fig. 7. This is due to the stabilizing effect of the resonance interaction between the oxygen of the acetyl group and the sulphur atom through the cycle. Figures 6 and 7 also show that the entrance of the acetyl group in the benzene ring and in the position 3– of the thiophene

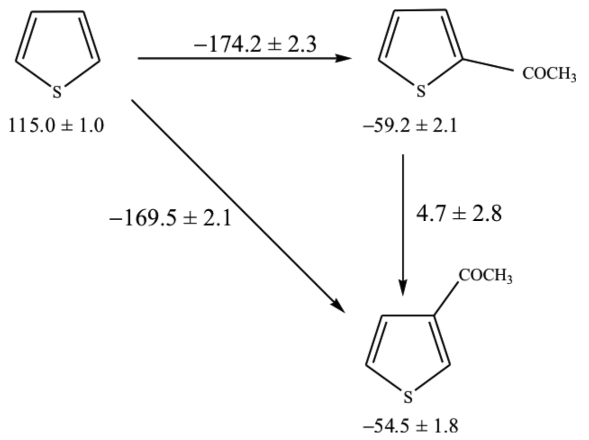


Fig. 7 Enthalpic increments for the introduction of an acetyl group on the positions 2- or 3- of the thiophene ring and for the isomerization 2-acetylthiophene→3-acetylthiophene

ring have the same stabilizing effect, since the respective enthalpic increments are equal, which shows that the interaction between the $-COCH_3$ group and the sulphur heteroatom does not happen in the 3-acetylthiophene. The isomerization enthalpy 2-acetylthiophene→3-acetylthiophene is 4.7±2.8 kJ mol^{-1}, being the difference between the two isomers due to that additional stabilizing effect.

Theoretical calculations

Figure 8 shows the calculated molecular structures optimized for both isomers of acetylthiophene.

The values of the standard molar enthalpies of formation of 2– and 3-acetylthiophenes were calculated at the G2 and G3 levels of theory, using atomization, bond separation isodesmic reaction (Eq. (7)) and isodesmic reaction (Eq. (8)), being the values registered in Table 4.

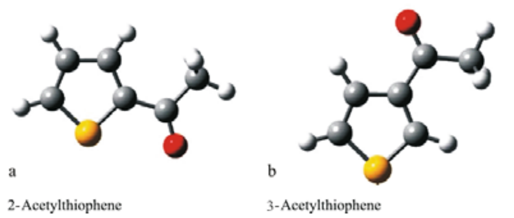

a 2-Acetylthiophene b 3-Acetylthiophene

Fig. 8 Calculated molecular structures, optimized at the MP2(full)/6-31G(3df,2p) level

$$C_6H_6OS+7CH_4+H_2S\rightarrow \rightarrow 3C_2H_6+2C_2H_4+2CH_3SH+2H_2CO \qquad (7)$$

$$C_6H_6OS+\text{benzene}\rightarrow\text{thiophene}+\text{acetophenone} \qquad (8)$$

The table shows that the experimental values of the enthalpies of formation are in a reasonable agreement with the ones calculated by computational thermochemistry. Both the experimental and the theoretical values show that 2-acetylthiophene is the most stable isotope.

The scheme of Fig. 9 shows the enthalpic increments for the entrance of a methyl group in the positions *ortho*, *meta* and *para* of 2-acetylthiophene, as well as the different enthalpies of isomerization.

Within the associated uncertainties, the 3-methyl-2-acetylthiophene and the 4-methyl-2-acetylthiophene are enthalpically similar, with an isomerization enthalpy of –1.5±4.5 kJ mol^{-1}; the same is the case of 4-methyl-2-acetylthiophene and the 5-methyl-2-acetylthiophene with an isomerization enthalpy of –3.6±4.7 kJ mol^{-1}. Considering the structures represented above, one would expect 4-methyl-2-acetylthiophene as the most stable isomer because, in this case, the substituent groups are furthest apart, leading to less steric interactions. However, 5-methyl-2-acetylthiophene is the most stable isomer and 3-methyl-2-acetylthiophene is the least stable one, due to the steric effect caused by the proximity between methyl and acetyl groups.

From the literature data, the standard molar enthalpies of formation, in the gaseous state, of 2-methylthiophene 84.35±0.92 kJ mol^{-1} [64],

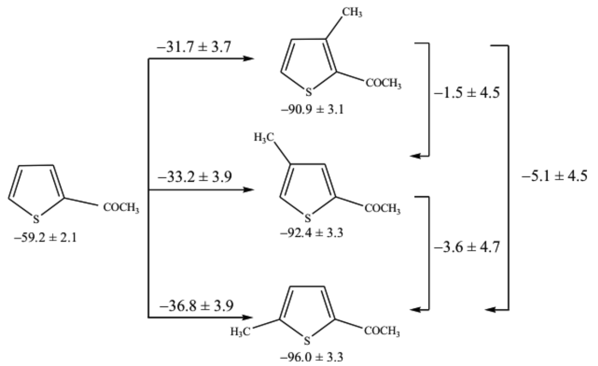


Fig. 9 Enthalpic increments of the introduction of a methyl group in 2-acetylthiophene

Table 4 Comparison of G2 and G3 calculated enthalpies of formation, using atomization and isodesmic reactions for 2- and 3-acetylthiophenes, with experimental values. All values are in kJ mol^{-1}

	Experim. value	G2			G3		
		Atom. reaction	Reaction 7	Reaction 8	Atom. reaction	Reaction 7	Reaction 8
2-Acetylthiophene	–59.2±2.1	–60.6	–62.9	–62.9	–59.8	–62.9	–60.2
3-Acetylthiophene	–54.5±1.8	–58.2	–60.5	–60.5	–57.1	–60.2	–57.5

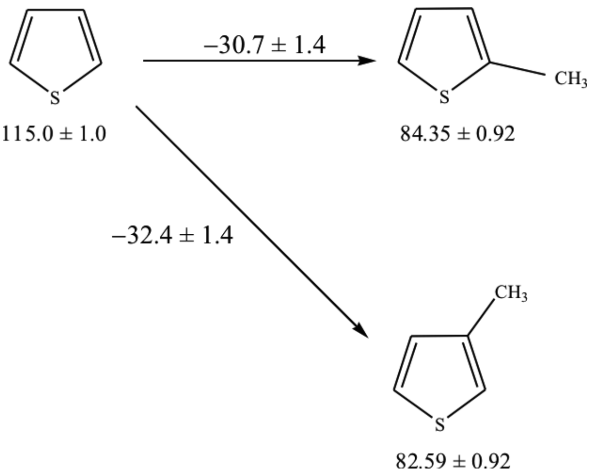


Fig. 10 Enthalpic increments of the introduction of a methyl group in the thiophene ring

3-methylthiophene 82.59±0.92 kJ mol^{-1} [70], together with the same thermodynamic parameter of thiophene, 115.0±1.0 kJ mol^{-1} [63], allows us to calculate the enthalpic increments for the entrance of a –CH$_3$ group in the positions 2- or 3– of the thiophene ring as –30.7±1.4 kJ mol^{-1} and –32.4±1.4 kJ mol^{-1}, respectively, as shown in Fig. 10.

The resulting enthalpic increments of the addition of a methyl group in the 3- and 4- positions of 2-acetylthiophene molecule are in accordance with the same entrance in the 3– position of the thiophene ring to yield the 3-methylthiophene. In the case of 5-methyl-2-acetylthiophene, the addition of the methyl group has a greater stabilizing effect than the same entrance in the 2- position of the thiophene ring.

Thiophenecarboxaldehyde derivatives

From the values of the standard molar enthalpies of formation, in the gaseous phase, of thiophene, $\Delta_f H_m^0$(C$_4$H$_4$S, g)=115.0±1.0 kJ mol^{-1} [64], and of the 2– and 3– thiophenecarboxaldehyde, the enthalpic increments calculated for the introduction of a –CHO group in the positions 2– and 3– of the thiophene ring are, respectively, –122.1±2.1 kJ mol^{-1} and –122.4±2.1 kJ mol^{-1}, as shown in the scheme of Fig. 11. The stabilization enthalpic increment of the substitution of a hydrogen atom in the 2- or 3- position of the thiophene ring by a –CHO group is exactly the same, showing that the molecular increment in either structural position does not induce different enthalpic effects. Since the two isomers have the same enthalpic stability, the isomerization enthalpy, –0.3±2.7 kJ mol^{-1}, is close to zero.

The same kind of analysis can be made for the analogues substituted benzene and furan, as it is shown in the schemes of Fig. 12, through the values

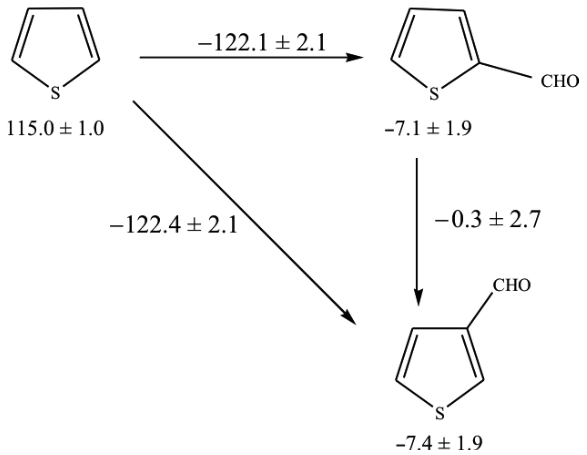


Fig. 11 Enthalpic increment of the isomerization 2→3 of thiophenecarboxaldehyde

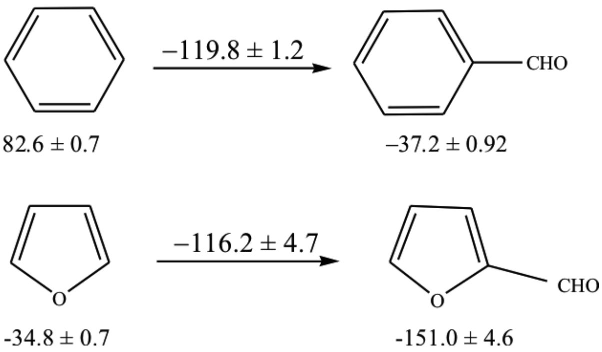


Fig. 12 Enthalpic increment of the entrance of a –CHO group in the benzene and in the furan rings

of the standard molar enthalpies of formation, in the gaseous state, of benzene 82.6±0.7 kJ mol^{-1} [62], benzaldehyde –37.2±0.92 kJ mol^{-1} [62], furan –34.8±0.7 kJ mol^{-1} [62] and 2-furancarboxaldehyde –151.0±4.6 kJ mol^{-1} [62]). The addition of a carboxaldehyde group to the benzene and to the furan rings yields enthalpic increments of –119.8±1.2 kJ mol^{-1} and –116.2±4.7 kJ mol^{-1}, respectively, being in both cases similar, within the associated uncertainties, to the enthalpic increment calculated above for the entrance of a –CHO group in the 2– or 3– position of the thiophene ring.

The enthalpic increments of the introduction of one methyl group in the 3– and 5– positions of the 2-thiophenecarboxaldehyde, as well as the entrance of an ethyl substituent on the 5– position of the same molecule are shown in the scheme of Fig. 13, and were determined through the values of the standard molar enthalpies of formation, in the gaseous state, registered in Table 1.

From the literature values of the standard molar enthalpies of formation, in the gaseous state, of 2-methylthiophene 84.35±0.92 kJ mol^{-1} [64], 3-methylthiophene 82.59±0.92 kJ mol^{-1} [70], and

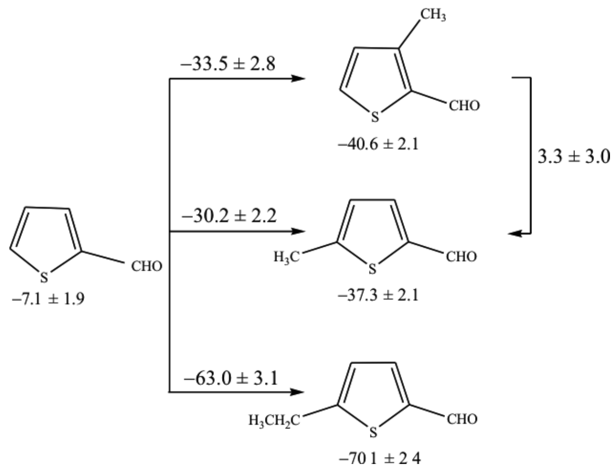


Fig. 13 Enthalpic increments of the entrance of a –CH_3 group in 3– or 5– positions and the a –CH_2CH_3 group 5– position of the 2-thiophenecarboxaldehyde

2-ethylthiophene together with the $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{0}$ (C_4H_4S, g), we calculate the enthalpic increments for the entrance of a –CH_3 group in the positions 2– or 3– of the thiophene ring as, respectively, –30.7±1.4 kJ mol^{-1} and –32.4±1.4 kJ mol^{-1}, and the increment for the addition of an ethyl group to the 2-position of the same ring, as –61.7±2.3 kJ mol^{-1}. Comparing these resulting increments of the entrance of a methyl group in position 3– or 5– of 2-thiophenecarboxaldehyde with the respective entrance of this group in position 3– or 2– of the thiophene ring, it is noticed that they are equal within the associated experimental uncertainties, so it is concluded that the introduction of a –CH_3 group in the thiophene ring or in the 2-thiophenecarboxaldehyde involves similar energetic effects. It can also be seen, in the scheme of Fig. 13, that the isomerization enthalpy corresponding to the 3→5 positions is small, having the two isomers a similar enthalpic stability. In the same way, it can be also noticed that, within the associated uncertainties, there is no enthalpic difference produced by the entrance of an ethyl group in the 5– position of 2-thiophenecarboxaldehyde and in the 2– position of the thiophene ring, being the stabilization effect similar in both compounds.

Thiophenecarbonitrile and acetonitrile derivatives

From the literature data, the standard molar enthalpies of formation, in the gaseous state of benzene and of benzenonitrile are, respectively 82.6±0.7 kJ mol^{-1} [62] and 215.7±2.1 kJ mol^{-1} [71], from which one calculates that the enthalpic increment for the entrance of a –CN group into the benzene ring is 133.1±2.2 kJ mol^{-1}. From the literature value of the standard molar enthalpy of formation, in the gaseous phase, of thiophene, $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{0}$ (C_4H_4S, g)=115.0±1.0 kJ mol^{-1} [63], and the values reported in Table 1, the enthalpic increments calculated for the introduction of a –CN group in the positions 2– and 3– of the thiophene ring are, respectively, 133.0±2.1 kJ mol^{-1} and 133.6±2.6 kJ mol^{-1}, so they are equal within the uncertainties associated, as shown in Fig. 14. The values of these enthalpic increments are also equal, within the associated uncertainties, to the enthalpic increment calculated above, for the entrance of a –CN group into the benzene ring, showing that these substitutions in either ring do not induce different specific enthalpic effects.

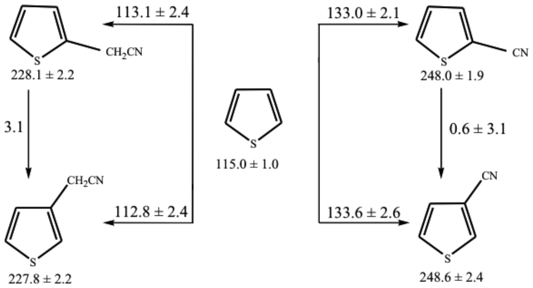


Fig. 14 Enthalpic increments of the introduction of a –CN group or a –CH_2CN group in the positions 2- and 3- of the thiophene ring

In the same way, as it is shown in Fig. 14, the values of the standard molar enthalpies of formation, in the gaseous state, registered in Table 1, together with the literature value of $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{0}$ (C_4H_4S, g), shows that the enthalpic increments for the entrance of a –CH_2CN group in positions 2– or 3– of the thiophene ring, yields enthalpic increments which are equal within the uncertainties associated with them.

The enthalpic increments associated to the transformation thiophenecarbonitrile→thiopheneacetonitrile are registered in Fig. 15 and show that, within the uncertainties associated, they are equal, whenever we consider the 2– or 3– substituted thiophenes.

It is worth to notice that the transformations of thiophenecarbonitriles into thiopheneacetonitriles are the result of the introduction of a methylene group

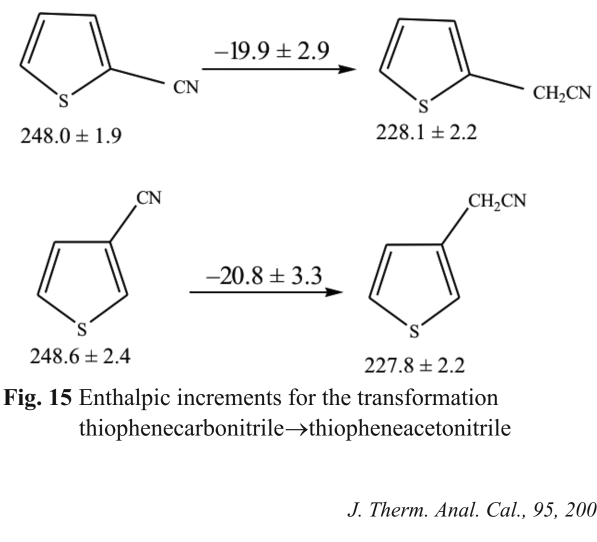


Fig. 15 Enthalpic increments for the transformation thiophenecarbonitrile→thiopheneacetonitrile

into the substituent group of the thiophene yielding, as shown above in this paper, an enthalpic increment that within the associated uncertainties, is in agreement with the values of the enthalpic increments of the addition of a methylene group in the *n*-alkanes, calculated as –20.62 kJ mol^{-1} [62], and with the methylene increments found for the alkane chains of alkyl thiophenes: –20.8 kJ mol^{-1} for 2-alkylthiophenes and of –25.0 kJ mol^{-1} for 3-alkylthiophenes.

From the literature value of the standard molar enthalpy of formation, in the gaseous phase, of 3-methylthiophene, $\Delta_f H^0_m$(3-methylthiophene, g)= 82.59±0.92 kJ mol^{-1} [70], and the enthalpic increment of the entrance of the –CN group in the positions 2– of the thiophene ring, 133.0±2.1 kJ mol^{-1}, as shown in Fig. 14, one estimates the standard molar enthalpy of formation of gaseous 3-methyl-2-thiophenecarbonitrile, as 215.6±2.7 kJ mol^{-1}, as shown in Fig. 16, in very good agreement with the experimental value of 212.0±2.1 kJ mol^{-1} as registered in Table 1.

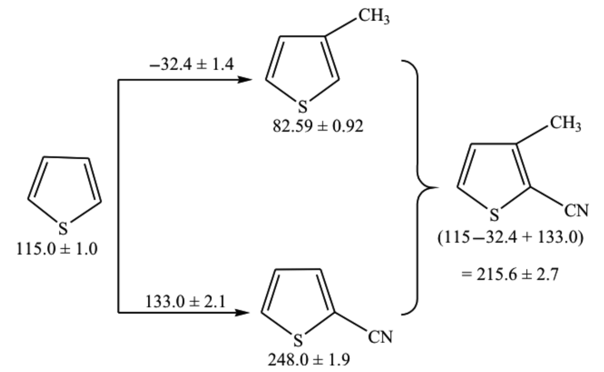


Fig. 16 Estimation of the standard molar enthalpy of formation of 3-methyl-2-thiophenecarbonitrile, using enthalpic increments

Thiophenecarboxamide and acetamide

The enthalpic increment for the entrance of a –CONH$_2$ group into the position 2– of the thiophene ring is –179.0±1.6 kJ mol^{-1}, as seen in Fig. 17, calculated from the literature value of the standard molar enthalpy of formation, in the gaseous phase, of thiophene, $\Delta_f H^0_m$(C_4H_4S, g)=115.0±1.0 kJ mol^{-1} [63], and the value of the standard molar enthalpy of formation, in the gaseous phase, of 2-thiophenecarboxamide, reported in Table 1. The same kind of analysis can be made for the analogue substituted benzene, as it is shown in Fig. 18, through the literature values the standard molar enthalpies of formation, in the gaseous state, of benzene and of benzenecarboxamide that are, respectively, 82.6±0.7 kJ mol^{-1} [62] and –100.9±1.2 kJ mol^{-1} [62]. The addition of a carboxamide group to the benzene ring yields an enthalpic increment of –183.5±1.4 kJ mol^{-1}, which is similar, within the associated uncertainties, to the enthalpic increment calculated above, for the entrance of a –CONH$_2$ group into the thiophene ring. In both cases, the entrance of the carboxamide group has a stabilizing effect in the ring, because it allows an electronic delocalization between the oxygen double bond and the ring.

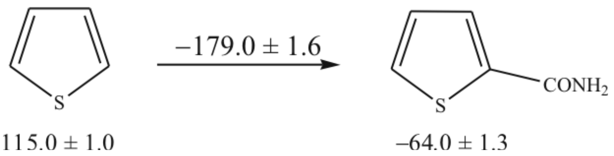


Fig. 17 Enthalpic increment of the introduction of a –CONH$_2$ group in the position 2- of the thiophene ring

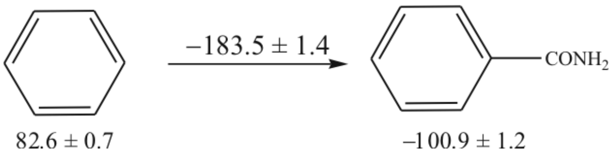


Fig. 18 Enthalpic increment of the introduction of a –CONH$_2$ group in the benzene ring

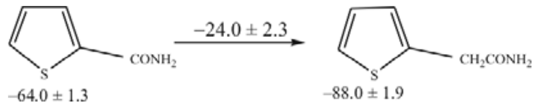


Fig. 19 Enthalpic increments for the transformation 2-thiophenecarboxamide→2-thiopheneacetamide

The enthalpic increment of the introduction of a methylene group into the –CONH$_2$ substituent of thiophene, to yield the corresponding acetamide derivative, is –24.0±2.3 kJ mol^{-1}, as noticed in Fig. 19, which was obtained through the values of the

Table 5 Enthalpic increments in the thiophene ring, at *T*=298. 15 K

Substituent group	Δ/kJ mol^{-1}	
	2–position	3–position
–CH_3	–30.7±1.4	–32.4±1.4
–CH_2CH_3	–61.7±2.3	–
–*n*-$(CH_2)_2CH_3$	–82.4±2.6	–
–*n*-$(CH_2)_3CH_3$	–107±2.8	–99.6±2.8
–*n*-$(CH_2)_4CH_3$	–127.8±3.2	–
–*n*-$(CH_2)_5CH_3$	–146.7±3.5	–143.8±3.5
–*n*-$(CH_2)_7CH_3$	–186.0±4.1	–199.6±2.4
–CH_2COOCH_3	–383.5±3.0	–382.6±2.6
–$COCH_3$	–174.2±2.3	–169.5±2.1
–CHO	–122.1±2.1	–122.4±2.1
–$CONH_2$	–179.0±2.6	–
–CH_2CONH_2	–203.0±2.1	–
–CN	133.0±2.1	133.6±2.6
–CH_2CN	113.1±2.4	112.8±2.4

Table 6 Test of applicability: Estimative of enthalpies of formation, in the gaseous state

Compound	$\Delta_f H^0_m$(g)/kJ mol^{-1}			δ=Exp–Est/ kJ mol^{-1}
	Experimental	Estimated	Scheme of estimation	
2,5-Dimethylthiophene	50.6±1.9	53.6±2.2	tf+2·(2-CH_3)	–3.0±2.9
2-Acetyl-3-methylthiophene	–90.9±3.1	-91.6±2.9	tf+(2-$COCH_3$)+(3-CH_3)	0.7±4.2
2-Acetyl-4-methylthiophene	–92.4±3.3	-91.6±2.9	tf+(2-$COCH_3$)+(3-CH_3)	–0.8±4.4
2-Acetyl-5-methylthiophene	–96.0±3.3	-89.9±2.9	tf+(2-$COCH_3$)+(2-CH_3)	–6.1±4.4
3-Acetyl-2,5-dimethylthiophene	–123.2±2.7	-115.9±3.1	tf+(3-$COCH_3$)+2′ (2-CH_3)	–7.3±4.1
3-Methyl-2-thiophenecarboxaldehyde	–40.6±2.1	-39.5±2.7	tf+(3-CH_3)+(2-CHO)	–1.1±3.4
5-Methyl-2-thiophenecarboxaldehyde	–37.3±2.1	-37.8±2.7	tf+(2-CH_3)+(2-CHO)	0.5±3.4
5-Ethyl-2-thiophenecarboxaldehyde	–70.1±2.4	-68.8±3.3	tf+(2-CH_2CH_3)+(2-CHO)	–1.3±4.1
3-Methyl-2-thiophenecarbonitrile	–212.0±2.1	-215.6±2.7	tf+(3-CH_3)+(2-CN)	3.6±3.4

standard molar enthalpies of formation, in the gaseous state, registered in Table 1. This value is in agreement, within the associated experimental uncertainties, with the enthalpic increment of the successive addition of a methylene group in the *n*-alkanes, –20.62 kJ mol^{-1}, in the linear alkyl chains of 2-*n*-alkylthiophenes, –20.8 kJ mol^{-1}, and in 2-thiophenecarbonitrile derivatives, –19.9±2.9 kJ mol^{-1}, as shown above in this paper.

From the above discussion, we can conclude that the introduction of a carboxamide group in the position 2– of thiophene and in benzene do not produce different specific enthalpic effects. The transformation of 2-thiophenecarboxamide in 2-thiopheneacetamide involves the same monotonous enthalpic increment for the addition of a methylene group, already seen in other compounds and other thiophene derivatives.

Conclusions

The conclusions of the above discussion suggests that, with the experimental data already known for the standard molar enthalpies of formation, in the gaseous state, at T=298.15 K, for substituted thiophenes, it would be possible to establish reliable empirical correlations for the estimation of the standard molar enthalpies of formation of other substituted thiophene type of compounds.

So, a table of enthalpic increments for different group substituents in positions 2– or 3– of the thiophene ring can be established by calculating the differences between the already experimentally known standard molar enthalpies of formation of the substituted thiophenes and the same parameter for thiophene itself. The result of this procedure is given in Table 5.

In order to test the validity of applying this approach for the estimation of the standard molar enthalpies of formation of other substituted thiophene compounds, we applied the increments of this table to the estimation of the standard molar enthalpies of formation of other poly-substituted thiophenes for which experimental values are already available. The results of this test are presented in Table 6, in which it is shown that the difference between the experimental and estimated value, δ=Exp–Est, are in most of the cases smaller than the experimental uncertainties ascribed to the experimental available values.

In conclusion, the results presented in this paper show internal consistency, giving confidence for estimating the standard molar enthalpies of formation of other substituted thiophenes.

Acknowledgements

Thanks are due to Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal and to FEDER for financial support to Centro de Investigação em Química, University of Porto. A.F.L.O.M.S. thanks FCT and the European Social Fund (ESF) under the Community Support Framework (CSF) for the award of a Post-doc fellowship (SFRH/BPD/41601/2007).

References

1 W. N. Neira, M. I. Rivera, G. Kohlhagen, M. L. Hursey, P. Pourquier, E. A. Sausville and Y. Pommier, Mol. Pharmacol., 56 (1999) 478.

2 R. Villar, I. Encio, M. Migliaccio, M. J. Gil and V. Martinez-Merino, Bioorg. Med. Chem., 12 (2004) 963.

3 M. B. Sahasrabudhe, M. K. Nerurkar, M. V. Nerurkar, B. D. Tilak and M. D. Bhavsar, Br. J. Cancer, 14 (1960) 547.

4 A. V. Kalinin, M. A. Reed, B. H. Norman and V. Snieckus, J. Org. Chem., 68 (2003) 5992.

5 R. K Russell, J. B. Press, R. A. Rampulla, J. J. McNally, R. Falotico, J. A. Keiser, D. A. Bright and A. Tobia, J. Med. Chem., 31 (1988) 1786.

6 W. C. McCormick and I. B. Abrass, Lancet 352 Supl. IV (1998) 6.

7 C. E. Stephens, T. M. Felder, J. W. Sowell, G. Andrei, J. Balzarini, R. Snoeck and E. De Clercq, Bioorg. Med. Chem., 9 (2001) 1123.

8 J. B. Hudson, R. J. Marles, C. S. Breau, L. Harris and J. T. Arnason, Photochem. Photobiol., 60 (1994) 591.

9 G. Guillet, J. Harmatha, T. G. Waddell, B. J. R. Philogène and J. T. Arnason, Photochem. Photobiol., 71 (2000) 111.

10 http://ec. europa. eu/food/fs/sc/scf/out106_en. pdf published online by the Scientific Committee for Food (05/07/2004).

11 http://en. wikipedia. org/wiki/Biotin (15/03/2007).

12 http://pt. wikipedia. org/wiki/Biotina (15/03/2007).

13 R. M. Acheson, An Introduction to the Chemistry of Heterocyclic Compounds, 2nd Ed., Wiley International Edition, U.S.A (1967).

14 F. C. Meotti, D. O. Silva, A. R. S. Santos, G. Zeni, J. B. T. Rocha and C. W. Nogueira, Environm. Toxicol. Pharmacol., 37 (2003) 37.

15 I. C. F. R. Ferreira, R. C. Calhelha, L. M. Estevinho and M. J. R. P. Queiroz, Bioorgan. Med. Chem. Lett., 14 (2004) 5831.

16 S. Tehranchian, T. Akbarzadeh, M. R. Fazeli, H. Jamalifr and A. Shafiee, Bioorgan. Med. Chem. Lett., 15 (2005) 1023.

17 R. L. Jarvest, I. L. Pinto, S. M. Ashman, C. E. Dabrowski, A. V. Fernandez, L. J. Jennings, P. Lavery and D. G. Tew, Bioorgan. Med. Chem. Lett., 9 (1999) 443.

18 C. E. Stephens, T. M. Felder, J. W. Sowell Sr., G. Andrei, J. Balzarini, R. Snoeck and E De Clercq, Bioorgan. Med. Chem., 9 (2001).

19 D. Mares, B. Tosi, F. Poli, E. Andreotti and C. Romagnoli, Microbiol. Res., 159 (2004) 295.

20 C. K. Ryu, S. K. Lee, J. Y. Han, O. J. Jung, J. Y. Lee and S. H. Jeong, Bioorgan. Med. Chem. Lett., 15 (2005).

21 J. Malmström, M. Jonsson, I. A. Cotgreave, L. Hammarström, M. Sjödin and L. Engmann, J. Am. Chem. Soc., 123 (2001) 3434.

22 I. C. F. R. Ferreira, M. J. R. P. Queiroz, M. Vilas-Boas, L. M. Estevinho, A. Begouin and G. Kirsch, Bioorgan. Med. Chem. Lett., 16 (2006) 1384.

23 I. C. González, L. N. Davis and C. K. Smith, Bioorgan. Med. Chem. Lett., 14 (2004) 4037.

24 D. L. Temple, J. P. Yevich, R. R. Covington, C. A. Hanning, R. J. Seidehamel, H. K. Mackey and M. J. Bartek, J. Med. Chem., 22 (1979) 505.

25 C. J. Thompson, H. J. Coleman, L. Mikkelsen, D. Yee, C. C. Ward and H. T. Rall, Anal. Chem., 28 (1956) 1384.

26 G. D. Galpern, Usp. Khim., 45 (1976) 1395.

27 R. J. Angelici, Acc. Chem. Res., 21 (1988) 387.

28 C. Bianchini and A. Meli, Acc. Chem. Res., 31 (1998) 109.

29 M. Benabdellah, A. Aouniti, A. Dafali, B. Hammouti, M. Benkaddour, A. Yahyi and A. Ettouhami, Appl. Surf. Sci., 252 (2006).

30 R. D. McCullough, Adv. Mater., 10 (1998) 93.

31 F. Garnier, G. Horowitz, X. Peng and D. Fichou, Adv. Mater., 2 (1990) 592.

32 C. D. Dimitrakopoulos and P. R. L. Malenfant, Adv. Mater., 14 (2002) 99.

33 M. Giannetto, V. Mastria, G. Mori, A. Arduini and A. Secchi, Sensor. Actuat. B – Chem., 115 (2006) 62.

34 G. Tourillon, Handbook of Conducting Polymers, T. A. Skotheim, Ed. ; Marcel Dekker: New York (1986) 293.

35 M. B.-Abérem, H.-Anh Ho and M. Leclerc, Tetrahedron, 60 (2004) 11169.

36 K. Doré, S. Dubus, H. -A. Ho, I. Lévesque, M. Brunette, G. Corbeil, M. Boissinot, G. Boivin, M. G. Bergeron, D. Boudreau and M. Leclerc, J. Am. Chem. Soc., 126 (2004) 4240.

37 M. A. V Ribeiro da Silva and A. F. L. O. M. Santos, J. Therm. Anal. Cal., 88 (2007) 7.

38 M. A. V. Ribeiro da Silva and A. F. L. O. M. Santos, J. Chem. Thermodyn., 40 (2008) 1217.

39 M. V. Roux, M. Temprado, R. Notário, J. S. Chickos, A. F. L. O. M. Santos and M. A. V. Ribeiro da Silva, J. Phys. Chem. A, 111 (2007) 5280.

40 M. V. Roux, M. Temprado, P. Jiménez, R. Notário, J. S. Chickos, A. F. L. O. M. Santos and M. A. V. Ribeiro da Silva, J. Phys. Chem., A 111 (2007) 11084.

41 M. A. V. Ribeiro da Silva and A. F. L. O. M. Santos, J. Chem. Thermodyn., 40 (2008) 1309.

42 M. A. V. Ribeiro da Silva and A. F. L. O. M. Santos, J. Chem. Thermodyn., 40 (2008) 917.

43 M. A. V. Ribeiro da Silva and A. F. L. O. M. Santos, J. Chem. Thermodyn., 40 (2008) 166.

44 M. A. V. Ribeiro da Silva and A. F. L. O. M. Santos, J. Chem. Thermodyn., 40 (2008) 225.

45 J. Coops, R. S. Jessup and K. G. van Nes, in: F. D. Rossini (Ed.), Experimental Thermochemistry, vol. 1, Interscience: New York, 1956 (Chapter 3).

46 J. D. Cox, H. A. Gundry and A. J. Head, Trans. Faraday Soc., 60 (1964) 653.

47 H. A. Gundry and A. J. Head, J. Chem. Thermodyn., 10 (1978) 195.

48 M. D. M. C. Ribeiro da Silva, P. Souza and G. Pilcher, J. Chem. Thermodyn., 21 (1989) 173.

49 M. A. V. Ribeiro da Silva, M. L. C. C. H. Ferrão and A. J. M. Lopes, J. Chem. Thermodyn., 25 (1993) 229.

50 M. A. V. Ribeiro da Silva, J. M. Gonçalves and G. Pilcher, J. Chem. Thermodyn., 29 (1997) 253.

51 F. A. Adedeji, D. L. S. Brown, J. A. Connor, M. Leung, M. I. Paz-Andrade and H. A. Skinner, J. Organomet. Chem., 97 (1975) 221.

52 M. A. V. Ribeiro da Silva, M. A. R. Matos and L. M. P. F. Amaral, J. Chem. Thermodyn., 27 (1995) 565.

53 L. M. N. B. F. Santos, B. Schröder, O. O. P. Fernandes and M. A. V. Ribeiro da Silva, Thermochim. Acta, 415 (2004) 15.

54 M. A. V Ribeiro da Silva and M. J. S. Monte, Thermochim. Acta, 171 (1990) 169.

55 M. A. V Ribeiro da Silva, M. L. C. C. H. Ferrão, M. J. S. Monte, J. M. Gonçalves and F. Jiye, J. Chem. Thermodyn., 31 (1999) 1067.

56 M. J. S. Monte, A. R. R. P. Almeida and M. A. V. Ribeiro da Silva, J. Chem. Thermodyn., 36 (2004) 385.

57 M. A. V. Ribeiro da Silva, M. J. S. Monte and L. M. N. B. F. Santos, J. Chem. Thermodyn., 38 (2006) 778.

58 W. J. Hehre, L. Radom, P. V. R. Schleyer and J. A. Pople, Ab Initio Molecular Orbital Theory, Wiley, New York 1986.

59 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson,

H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian03, Revision C. 02, Gaussian Inc., Pittsburgh, PA (2004).

60 L. A. Curtiss, K. Raghavachari, G. W. Trucks and J. A. Pople, J. Chem. Phys., 94 (1991) 7221.

61 L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov and J. A. Pople, J. Chem. Phys., 109 (1998) 7764.

62 J. B. Pedley, Thermochemical Data and Structures of Organic Compounds, Vol. 1, TRC Data Series: College Station, TX (1994).

63 W. N. Hubbard, D. W. Scott, F. R. Frow and G. Waddington, J. Am. Chem. Soc., 77 (1955) 5855.

64 R. E. Pennington, H. L. Finke, W. N. Hubbard, J. F. Messerly, F. R. Frow, I. A. Hossenlopp and G. Waddington, J. Am. Chem. Soc., 78 (1956) 2055.

65 L. A. Curtiss, K. Raghavachari, P. C. Redfern and J. A. Pople, J. Chem. Phys., 106 (1997) 163.

66 M. N. Glukhovtsev and S. Laiter, Theor. Chim. Acta, 92 (1995) 327.

67 K. Raghavachari, B. B. Stefanov and L. A. Curtiss, J. Chem. Phys., 106 (1997) 6764.

68 M. A. V. Ribeiro da Silva and L. M. P. F. Amaral, J. Chem. Thermodyn. Doi: 10. 1016/j. jct. 2008. 08. 004

69 V. L. S. Freitas, L. I. P. Oliveira and M. D. M. C. Ribeiro da Silva, J. Chem. Thermodyn., 39 (2007) 39.

70 J. D. Cox, G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, London (1970).

71 F. W. Evans and H. A. Skinner, Trans. Faraday Soc., 55 (1959) 255.

DOI: 10.1007/s10973-008-9583-0