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THERMOCHEMICAL STUDY OF 2- AND 3-ALKYL SUBSTITUTED THIOPHENES
Energetic-structural correlations

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The standard (p^0=0.1 MPa) molar enthalpies of formation, in the condensed phase, of nine linear-alkyl substituted thiophenes, six in position 2- and three in position 3-, at T=298.15 K, were derived from the standard massic energies of combustion, in oxygen, to yield CO_2(g) and $H_2SO_4\cdot115H_2O$(aq), measured by rotating-bomb combustion calorimetry. The standard molar enthalpies of vaporization of these compounds were measured by high temperature Calvet Microcalorimetry, so their standard molar enthalpies of formation, in the gaseous phase, were derived.

The results are discussed in terms of structural contributions to the energetics of the alkyl-substituted thiophenes, and empirical correlations are suggested for the estimation of the standard molar enthalpies of formation, at T=298.15 K, for 2- and 3-alkyl-substituted thiophenes, both in the condensed and in the gaseous phases.

Keywords: *2-alkylthiophenes, 3-alkylthiophenes, Calvet microcalorimetry, combustion calorimetry, enthalpy of combustion, enthalpy of formation, enthalpy of vaporization, thiophene*

Introduction

Thiophene derivatives are of enormous practical importance because of their wide range of applications in many research and applied areas, such as medicine, pharmacy, biochemistry, environmental chemistry, electrical conductive polymers, industry, etc. More specifically the thiophene derivatives have shown insecticide activity [1], antibacterial activity [1–3], antiviral activity [1, 4, 5], antifungal activity [1, 6, 7], antioxidant activity [8, 9], antihelmitic activity [10], antiallergic activity [11] and antihypertensive activity [12]. They are also been used as novel anti-inflammatory and analgesic drugs [13–17] and due to their high biological activity they are being tried as potential anti-cancer agents [5, 18–24]. Apart the applications already cited, they have recently been used as good inhibitors of corrosion of metals in acidic media [25] and as building blocks for the oligo- and polythiophenes. The polythiophenes found a large variety of applications, such as in light emitting diodes (LED’s) [26–30], in field effect transistors (FET’s) [27–31], in rechargeable batteries and electrochromic devices [32, 33], in electrochemical sensors, modified electrodes, photovoltaic cells and nonlinear optical materials [32]. More recently, they are also being used in detection of cations, anions proteins and nucleic acids and so found applications in diagnostics, therapeutics and drug screening [29, 34]. More specifically, the poly-(3-alkylthiophenes) combine chemical stability, good melt and solution processability with the electronic and optical properties; they are also used as active materials in polymer-based LED’s and have useful physical properties such as electrical conductivity and electroluminescence [26, 32]. In particular, the poly-(3-methylthiophene) and the poly-(3-octylthiophene) are good electrochromic materials [33]. However, despite their importance, the knowledge of the energetic properties of these compounds is still scarce as only very few thermochemical studies are known.

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 work we present the results of the thermochemical research on sulfur heterocycles of the type alkyl-substituted thiophenes.

Experimental

Materials

Compounds and purity control

The alkyl substituted thiophenes namely, 2-ethylthiophene [CAS 872-55-9], 3-*n*-butylthiophene [CAS 34722-01-5], 3-*n*-hexylthiophene

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[CAS 1693-86-3] and 3-*n*-octylthiophene [CAS 65016-62-8], were obtained commercially from Sigma-Aldrich Chemical Co., whereas 2-*n*-propylthiophene [CAS 1551-27-5], 2-*n*-pentylthiophene [CAS 4861-58-9] and 2-*n*-octylthiophene [CAS 880-36-4] were purchased from Lancaster Synthesis Ltd., and 2-*n*-butylthiophene [CAS 1455-20-5] and 2-*n*-hexylthiophene [CAS 18794-77-9] were bought from Alfa Aesar. All the compounds are liquids at room temperature and have been purified by successive fractional distillations, under reduced pressure and stored under nitrogen atmosphere. The purity of the compounds was checked by GLC and C, H, S microanalyses.

Thianthrene, $C_{12}H_8S_2$, (Aldrich 99%), which used as a reference material for the rotating oxygen-bomb calorimetry, was purified by zone melting. Undecane ($C_{11}H_{24}$), 99+, was supplied by Aldrich Chemical Co.

Methods

Combustion calorimetry

The enthalpies of combustion were measured with the rotating-bomb calorimeter formerly used at the National Physical Laboratory, Teddington, UK [35, 36], with a tantalum-lined bomb of internal volume 0.329 dm^3 and a tantalum head. This apparatus, after having been installed in the University of Manchester, UK [37], has been transferred to Porto University, where some changes in the auxiliary equipment were made as previously described [38]. Water was added to the calorimeter from a weighted acrylic vessel, and for each experiment a correction to the energy equivalent was made for the deviation from 3965.0 g of the mass of water added. Calorimetric temperatures were measured to $1\cdot10^{-4}$ K with a quartz thermometer (Hewlett Packard HP 2804A) interfaced to a microcomputer programmed to compute the adiabatic temperature change. In the fore-period 125 readings are taken, whereas in the main period the number of readings is 100, followed by 125 readings in the after-period. For each experiment, the ignition temperature was chosen so that the final temperature would be close to T=298.15 K. The rotating mechanism allowed simultaneous axial and end-over-end rotation of the bomb. The rotation of the bomb was started when the temperature rise in the main period reached about 63% of its total value, and was continued throughout the rest of the experiment. Good *et al.* [39] have shown that by adopting this procedure, the frictional work due to the rotation of the bomb is automatically included in the temperature corrections for the work of water stirring and for the heat exchanged with the surrounding isothermal jacket. This one consists of a thermostatic water bath, in which the water circulating in the bath and inside the covering lid is maintained at ca. 301 K to 10^{-4} K using a temperature controller (Tronac PTC 41). Data acquisition and control of the calorimeter was performed using the program LABTERMO [40].

The energy equivalent of the calorimeter was determined from the combustion of benzoic acid (NBS Standard Reference Material 39i), having a massic energy of combustion under bomb conditions of $-(26434\pm3)$ J g^{-1}, as described previously [41]. Calibration experiments were carried out in oxygen, at the pressure of 3.04 MPa, with 1.00 cm^3 of water added to the bomb. The electrical energy for the ignition was determined from the change in potential across a capacitor when 40 V was discharged through a platinum ignition wire. For the cotton thread fuse (empirical formula $CH_{1.686}O_{0.843}$) the massic energy of combustion is assigned to $\Delta_c u^0 = -16250$ J g^{-1} [39], a value that was confirmed in our Laboratory. Corrections for nitric acid formation 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) [42]. From ten calibration experiments, the energy equivalent of the calorimeter, ε(calor)/(J K^{-1}) was found to be {20369.0±2.3 (0.011%)} for an average mass of water added to the calorimeter of 3965.0 g; the quoted uncertainty refers to the standard deviation of the mean.

The procedure described by Waddington *et al.* [43] for combustion calorimetry of organosulfur was followed. Samples of each compound, sealed into Melinex polyester bags, with 0.025 mm thickness, were ignited in oxygen at a pressure of 3.04 MPa with a volume of 15.00 cm^3 of desionized water added to the bomb. The energy of combustion of the Melinex used in each experiment, ΔU(melinex), was calculated using the value of the massic energy of combustion of Melinex as $\Delta_c u^0 = -(22902\pm5)$ J g^{-1}, measured by Skinner and Snelson [44] after making the correction for the mass fraction of water w=0.0032 [44]. The amount of nitric acid was determined by the Devarda's alloy method [45]. The densities of the title compounds were as follows: 2-ethylthiophene d=0.993 [46], 2-*n*-propylthiophene d=0.968 [47]; 2-*n*-butylthiophene d=0.97 [47]; 2-*n*-pentylthiophene d=0.944 [47]; 2-*n*-hexylthiophene d=0.935 [47]; 2-*n*-octylthiophene d=0.934 [47]; 3-*n*-butylthiophene d=0.957 [46]; 3-*n*-hexylthiophene d=0.937 [46]; 3-*n*-octylthiophene d=0.92 [46]. For each compound, $(\partial u/\partial p)_T$, at T=298.15 K, was assumed to be –0.2 J g^{-1} MPa^{-1}, a typical value for organic compounds [48]. Standard state corrections were calculated for the initial states by the procedures given by Hubbard *et al.* [49] and by Good and Scott [50].

Table 1 Typical combustion results at T=298.15 K (p^0=0.1 MPa), for the 2-alkylthiophenes

	2-Ethylthiophene	2-*n*-Propylthiophene	2-*n*-Butylthiophene	2-*n*-Pentylthiophene	2-*n*-Hexylthiophene	2-*n*-Octylthiophene
m(cpd)/g	0.46913	0.43611	0.54417	0.55977	0.45947	0.45959
m'(fuse)/g	0.00263	0.00248	0.00248	0.00312	0.00302	0.00370
m''(melinex)/g	0.04639	0.04276	0.03628	0.05231	0.04510	0.04507
T_i/K	297.2305	297.2639	297.0535	296.9804	297.1681	297.1483
T_f/K	298.1584	298.1521	298.1573	298.1524	298.1521	298.1551
ΔT_{ad}/K	0.89695	0.85767	1.07254	1.14083	0.95280	0.97565
ε_i/J K^{-1}	74.05	74.11	74.27	74.34	74.20	74.23
ε_f/J K^{-1}	73.34	73.45	73.86	74.05	73.81	73.93
ε(calor)/J K^{-1}	20370.67	20369.42	20372.35	20371.93	20376.53	20370.26
Δm(H_2O)/g	-0.4	-0.1	-0.8	-0.7	-1.8	-0.3
$-\Delta U$(IBP)^a/J	18336.83	17532.73	21928.74	23324.63	19484.39	19945.58
ΔU(fuse)/J	42.71	40.28	40.28	50.67	49.04	60.09
ΔU(melinex)/J	1062.51	979.35	830.86	1197.98	1032.81	1032.13
ΔU(HNO_3)/J	19.16	27.22	28.42	32.54	28.06	31.28
ΔU(ign)/J	1.08	1.09	1.09	1.09	1.08	1.09
ΔU_Σ/J	22.92	22.68	26.58	28.59	25.44	26.50
$-\Delta_c u^0$/J g^{-1}	36641.29	37750.11	38595.66	39328.38	39935.23	40896.41

m(cpd) is the mass of compound burnt in each experiment; m'(fuse) is the mass of the fuse (cotton) used in each experiment; m''(melinex) is the mass of melinex used in each experiment; T_i is the initial temperature rise; T_f is the final temperature rise; ΔT_{ad} is the corrected temperature rise; ε_i is the energy equivalent of the contents in the initial state; ε_f is the energy equivalent of the contents in the final state; ε(calor) energy equivalent of the calorimeter corrected for the deviation of mass of water added to the calorimeter; Δm(H_2O) is the deviation of mass of water added to the calorimeter from 3965.0 g; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; ΔU(fuse) is the massic energy of combustion of the fuse (cotton); ΔU(melinex) is the energy of combustion of the melinex; ΔU(HNO_3) is the energy correction for the nitric acid formation; ΔU(ign) is the electric energy for the ignition; ΔU_Σ is the standard state correction; $\Delta_c u^0$ is the standard massic energy of combustion. $^a\Delta U$(IBP) includes ΔU(ignition)

Table 2 Typical combustion results at T=298.15 K (p^0=0.1 MPa), for the 3-alkylthiophenes

	3-*n*-Butylthiophene	3-*n*-Hexylthiophene	3-*n*-Octylthiophene
m(cpd)/g	0.50466	0.47829	0.53400
m'(fuse)/g	0.00283	0.00285	0.00282
m''(melinex)/g	0.03657	0.03757	0.04456
T_i/K	297.1217	297.1458	297.0170
T_f/K	298.1511	298.1578	298.1691
ΔT_{ad}/K	1.00013	0.98206	1.12143
ε_i/J K^{-1}	74.24	74.15	74.34
ε_f/J K^{-1}	73.76	73.76	74.19
ε(calor)/J K^{-1}	20371.51	20374.02	20370.67
$\Delta m(H_2O)$/g	–0.6	–1.2	–0.4
$-\Delta U$(IBP)^a/J	20447.33	20080.26	22926.57
ΔU(fuse)/J	45.96	46.28	45.80
ΔU(melinex)/J	837.49	860.33	1020.47
$\Delta U(HNO_3)$/J	35.94	42.98	35.58
ΔU(ign)/J	1.09	1.08	1.09
ΔU_Σ/J	25.28	25.64	28.98
$-\Delta_c u^0$/J g^{-1}	38645.15	39944.45	40815.99

m(cpd) is the mass of compound burnt in each experiment; m'(fuse) is the mass of the fuse (cotton) used in each experiment; m''(melinex) is the mass of melinex used in each experiment; T_i is the initial temperature rise; T_f is the final temperature rise; ΔT_{ad} is the corrected temperature rise; ε_i is the energy equivalent of the contents in the initial state; ε_f is the energy equivalent of the contents in the final state; ε(calor) energy equivalent of the calorimeter corrected for the deviation of mass of water added to the calorimeter; $\Delta m(H_2O)$ is the deviation of mass of water added to the calorimeter from 3965.0 g; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; ΔU(fuse) is the massic energy of combustion of the fuse (cotton); ΔU(melinex) is the energy of combustion of the melinex; $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; ΔU(ign) is the electric energy for the ignition; ΔU_Σ is the standard state correction; $\Delta_c u^0$ is the standard massic energy of combustion. $^a\Delta U$(IBP) includes ΔU(ignition)

Thianthrene has been recommended as a test substance for bomb combustion calorimetry of organic sulfur compounds [51, 52] and so the accuracy of the calorimeter has been checked in our laboratory by measuring the energy of combustion of thianthrene in the pellet form, in oxygen at p=3.04 MPa, in the presence of 15.00 cm^3 of desionized water inside the bomb, yielding a massic energy of combustion, as the average of 10 experiments, $\Delta_c u^0$= –(33 468.3±2.4) J g^{-1}, in excellent agreement with the recommended value $\Delta_c u^0$= –(33 468±4) J·g^{-1} [53].

The water added to the calorimetric vase was weighed with a Mettler PC 8000 balance, sensitivity ±(1·10^{-1}) g, the necessary weighings for the combustion experiments were made in a Mettler Toledo 245 balance, sensitivity ±(1·10^{-5}) g,

The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission in 2005 [54].

Calvet Microcalorimetry

The standard molar enthalpies of vaporization have been measured using a Calvet High Temperature Microcalorimeter (Setaram, HT 1000D) using for the liquid compounds a similar technique [55] to the drop-method described for the sublimation of solids by Skinner *et al.* [56]. The detailed descriptions of the apparatus and of the experimental technique have been previously published [57].

Samples of about 5 mg of each compound, contained in thin glass capillary tubes and sealed at one end, were dropped from room temperature into the hot reaction vessel in the Calvet High Temperature Microcalorimeter (SETARAM HT 1000D), held at temperatures close to T=365 K and then removed from the hot zone by vacuum sublimation. The observed standard molar enthalpies of vaporization $\Delta^{g,T}_{1,298.15K}H_m$ have been corrected to T=298.15 K using $\Delta^{T}_{298.15K}H^0_m$(g) estimated by a group method based on the values of Stull *et al.* [58].

The calorimeter was calibrated *in situ*, making use of the reported standard molar enthalpy of vaporization at T=298.15 K, of undecane ($C_{11}H_{24}$), 99+, supplied by Aldrich Chemical Co., $\Delta^g_1 H^0_m$= (56.580±0.566) kJ mol^{-1} [53]. The calibration constants of the calorimeter were obtained as the average of six independent experiments, at T=365 K as: k=(0.9791±0.0009) for the vaporization of 2-ethylthiophene, and k=(1.0023±0.0035) for the vaporiza-

Table 3 Individual values of standard (p^0=0.1 MPa) massic energies of combustion, $\Delta_c u^0$, of the compounds, at T=298.15 K

2-Ethylthiophene	2-*n*-Propylthiophene	2-*n*-Butylthiophene	2-*n*-Pentylthiophene	2-*n*-Hexylthiophene	2-*n*-Octylthiophene	3-*n*-Butylthiophene	3-*n*-Hexylthiophene	3-*n*-Octylthiophene
				$-\Delta_c u^0$/J g^{-1}				
36652.68	37759.08	38595.66	39325.06	39931.57	40888.29	38641.54	39944.45	40812.10
36646.10	37744.72	38594.51	39326.39	39948.59	40890.28	38654.19	39934.33	40815.99
36648.30	37750.11	38606.12	39329.44	39933.64	40896.41	38645.15	39952.42	40812.58
36641.29	37740.25	38591.10	39332.17	39941.30	40902.54	38641.15	39934.33	40808.68
36637.90	37743.89	38602.84	39317.76	39935.23	40901.59	38642.66	39952.37	40818.69
36640.14	37751.57	38598.42	39328.38	39947.09	40887.98	38647.46	39948.99	40815.20
				[a]$-\langle\Delta_c u^0\rangle$/J g^{-1}				
36644.4±2.3	37748.3±2.8	38598.1±2.2	39326.5±2.0	39939.6±2.9	40894.5±2.7	38645.4±2.0	39944.5±3.4	40813.9±1.4

[a] Mean value and standard deviation of the mean

Table 4 Derived standard (p^0=0.1 MPa) molar values of 2- and 3-alkylthiophenes in the condensed phase, at T=298.15 K

Compound	$-\Delta_c U_m^0$(l)/kJ mol^{-1}	$-\Delta_c H_m^0$(l)/kJ mol^{-1}	$\Delta_f H_m^0$(l)/kJ mol^{-1}
2-Ethylthiophene (l)	4111.3±1.7	4120.1±1.7	13.6±1.9
2-*n*-Propylthiophene (l)	4764.7±2.0	4774.6±2.0	–11.1±2.2
2-*n*-Butylthiophene (l)	5413.4±2.2	5424.5±2.2	–40.5±2.4
2-*n*-Pentylthiophene (l)	6067.1±2.4	6079.5±2.4	–64.8±2.7
2-*n*-Hexylthiophene (l)	6721.9±2.8	6735.6±2.8	–88.1±3.1
2-*n*-Octylthiophene (l)	8029.9±3.3	8046.0±3.3	–136.4±3.7
3-*n*-Butylthiophene (l)	5420.0±2.2	5431.1±2.2	–33.9±2.4
3-*n*-Hexylthiophene (l)	6722.8±2.8	6736.4±2.8	–87.3±3.1
3-*n*-Octylthiophene (l)	8014.1±3.2	8030.2±3.2	–152.2±1.6

tion of all the other alkyl substituted thiophenes. The temperature was measured *in situ* using a small size Pt100 probe previously calibrated *vs.* a SPRT Tinsley (25 ohm; model 5187SA) probe. The dependency of the blank tube sign from the mass difference of the blank tubes in the reference and sample cell was taken into account [57]. The value of the enthalpy of vaporization at T=365 K was calculated from its value at T=298.15 K using literature values from Stull *et al.* [58]. The experimental procedure for the calibration experiments was the same as the one used for the experiments with the compounds.

Results and discussion

Tables 1 and 2 list typical combustion results respectively for each 2-alkylthiophene and 3-alkylthiophene in which $\Delta m(H_2O)$ is the deviation of the mass added to the calorimeter from 3965.0 g, the mass assigned to ε(calor), and ΔU_Σ is the correction to the standard state. The remaining quantities are as previously described [49].

The internal energy for the isothermal bomb process, ΔU(IBP), was calculated according to Eq. (1):

$$\Delta U(\mathrm{IBP}) = -\{\varepsilon(\mathrm{calor}) + c_p(\mathrm{H_2O,\,l})\Delta m(\mathrm{H_2O})\}\Delta T_{\mathrm{ad}} + (T_i - 298.15)\varepsilon_i + (298.15 - T_i - \Delta T_{\mathrm{ad}})\varepsilon_f + \Delta U(\mathrm{ign}) \quad (1)$$

where ΔT_{ad} is the calorimeter temperature change corrected for the heat exchange and the work of stirring.

For each compound, the products of combustion in the experiments consist of a gaseous phase and an aqueous mixture of sulfuric acid for which the thermodynamic properties are known. The values of $\Delta_c u^0$ refer to the reactions represented by Eq. (2)

$$\mathrm{C_aH_bO_cS_d(l)} + \left(a + \frac{b}{4} - \frac{c}{2} + \frac{3d}{2}\right)\mathrm{O_2(g)} + \left(116d - \frac{b}{2}\right)\mathrm{H_2O(l)} \rightarrow a\mathrm{CO_2(g)} + d(\mathrm{H_2SO_4}\cdot 115\mathrm{H_2O})(\mathrm{l}) \quad (2)$$

Table 3 lists, for each compound, the individual values of $\Delta_c u^0$ together with the mean and its standard deviation of the mean.

Table 4 lists the derived values of standard molar energies and enthalpies of reactions (2), respectively, $\Delta_c U_m^0$ and $\Delta_c H_m^0$, as well as the standard molar enthalpy of formation $\Delta_f H_m^0$, of the liquid compounds. In accordance with the normal thermochemical practice, the uncertainties assigned to the standard molar enthalpies of combustion and formation are twice the overall standard deviation of the mean and include the uncertainties in calibration and in the auxiliary quantities used. To derive $\Delta_f H_m^0$(l) from $\Delta_c H_m^0$(l), the standard molar enthalpies of formation of H_2O(l), CO_2(g) and H_2SO_4 in $115H_2O$(l), at T=298.15 K, respectively, –(285.830±0.042) kJ mol^{-1} [59], –(393.51±0.13) kJ mol^{-1} [59], and –(887.81±0.01) kJ mol^{-1} [42] were used.

Results of the microcalorimetric determinations of the enthalpy of vaporization of each compound are given in the Table 5. The observed enthalpies of vaporization, at experimental temperature T, $\Delta_{\mathrm{l,298.15K}}^{\mathrm{g,T}} H_m^0$, correspond to the mean values of 5 experiments with uncertainties given by their standard deviations, were corrected to T=298.15 K, by Eq. (3) using $\Delta_{\mathrm{298.15K}}^{\mathrm{T}} H_m^0$(g) estimated by a group scheme based on the values of Stull *el al.* [58].

$$\Delta_{\mathrm{l}}^{\mathrm{g}} H_m^0 (T = 298.15\ \mathrm{K}) = \Delta_{\mathrm{l,298.15K}}^{\mathrm{g,T}} H_m^0 - \Delta_{\mathrm{298.15K}}^{\mathrm{T}} H_m^0(\mathrm{g}) \quad (3)$$

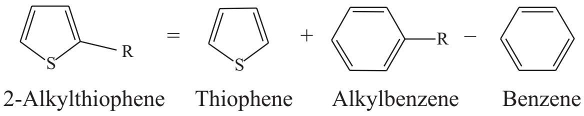
Table 5 Standard (p^0=0.1 MPa) molar enthalpies of vaporization, $\Delta_l^g H_m^0$, for the nine alkylthiophenes, at T=298.15 K, determined by Calvet microcalorimetry

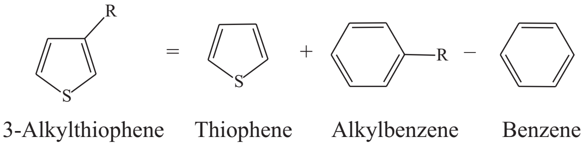
Compound	Number of experiments	T/K	$\Delta_l^{g,T} H_m^0$/ kJ mol^{-1}	$\Delta_{298.15K}^{T} H_m^0$(g)/ kJ mol^{-1}	$\Delta_l^g H_m^0$(298.15K)/ kJ mol^{-1}
2-Ethylthiophene (l)	5	364.9	49.8±0.3	10.14	39.7±0.9
2-*n*-Propylthiophene (l)	5	365.2	55.9±0.3	12.15	43.7±1.0
2-*n*-Butylthiophene (l)	5	365.1	62.6±0.1	14.04	48.5±1.1
2-*n*-Pentylthiophene (l)	5	365.2	68.0±0.3	15.99	52.0±1.2
2-*n*-Hexylthiophene (l)	5	365.2	74.3±0.3	17.88	56.4±1.3
2-*n*-Octylthiophene (l)	5	365.1	87.1±0.1	21.68	65.4±1.4
3-*n*-Butylthiophene (l)	5	365.1	63.3±0.2	14.04	49.3±1.1
3-*n*-Hexylthiophene (l)	5	365.1	76.3±0.3	17.86	58.5±1.3
3-*n*-Octylthiophene (l)	5	365.2	89.4±0.1	21.73	67.6±1.5

Table 6 Standard (p^0=0.1 MPa) molar enthalpies of formation, in both condensed and gaseous phase, and standard molar enthalpies of vaporization, at T=298.15 K

Compound	$\Delta_f H_m^0$(l)/kJ mol^{-1}	$\Delta_l^g H_m^0$(298.15K)/kJ mol^{-1}	$\Delta_f H_m^0$(g)/kJ mol^{-1}
2-Ethylthiophene (l)	13.6±1.9	39.7±0.9	53.3±2.1
2-*n*-Propylthiophene (l)	–11.1±2.2	43.7±1.0	32.6±2.4
2-*n*-Butylthiophene (l)	–40.5±2.4	48.5±1.1	8.0±2.6
2-*n*-Pentylthiophene (l)	–64.8±2.7	52.0±1.2	–12.8±3.0
2-*n*-Hexylthiophene (l)	–88.1±3.1	56.4±1.3	–31.7±3.4
2-*n*-Octylthiophene (l)	–136.4±3.7	65.4±1.4	–71.0±4.0
3-*n*-Butylthiophene (l)	–33.9±2.4	49.3±1.1	15.4±2.6
3-*n*-Hexylthiophene (l)	–87.3±3.1	58.5±1.3	–28.8±3.4
3-*n*-Octylthiophene (l)	–152.2±1.6	67.6±1.5	–84.6±2.2

The schemes applied for those corrections are:





The uncertainties associated to the standard enthalpies of vaporization, T=298.15 K, are twice the standard deviation of the mean and include the uncertainty associated with the calibration procedure.

The derived standard molar enthalpies of formation in the liquid and in the gaseous phases, at T=298.15 K, are also summarized in Table 6.

Table 7 reports literature [60] values of the standard (p^0=0.1 MPa) molar enthalpies of formation, in the gaseous phase, $\Delta_f H_m^0$(g), *vs.* the number, n_{CH_2}, of methylene groups in the molecules of *n*-alkanes and *n*-alkylbenzenes. The plot of these enthalpies of formation *vs.* the number of methylene groups in the molecules, gives two excellent straight lines, as shown in Fig. 1, with the Eq. (4) for the *n*-alkanes and Eq. (5) for the *n*-alkylbenzenes:

$$\Delta_f H_m^0\,(g)\;/\;kJ\;mol^{-1} = -20.618 n_{CH_2} - 84.363 \quad (R^2 = 0.9999) \tag{4}$$

$$\Delta_f H_m^0\,(g)\;/\;kJ\;mol^{-1} = -21.020 n_{CH_2} - 50.660 \quad (R^2 = 1.0000) \tag{5}$$

These equations show the well known fact that the energetic increment for the entrance of a methylene group in the linear chain of the alkanes and alkane-substituted compounds is approximately 21 kJ mol^{-1}. If the same kind of plots is done for 2-alkyl-substituted thiophenes and for 3-alkyl-substituted thiophenes, excellent straight lines are also obtained, as shown in Figs 2 and 3, respectively, yielding the Eqs (6) and (7), respectively, for 2-alkyl-substituted thiophenes and 3-alkyl-substituted thiophenes:

$$\Delta_f H_m^0\,(g)\;/\;kJ\;mol^{-1} = -20.768 n_{CH_2} + 72.614 \quad (R^2 = 0.9982) \tag{6}$$

$$\Delta_f H_m^0(\mathrm{g}) / \mathrm{kJ\ mol^{-1}} = -25.000 n_{\mathrm{CH_2}} + 92.333 \quad (R^2 = 0.9955) \tag{7}$$

again showing an identical enthalpic increment and good linear correlations with coefficients of regression closed to the unit. 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 $\Delta_f H_m^0(\mathrm{g})$ for the compounds for which the respective experimental determination was not performed. Table 8 shows the estimated enthalpies of formation calculated from Eqs (6) and (7), 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 (6) and (7) for the estimation of the standard molar enthalpies of formation, in the gaseous phase, of

Table 7 Literature [60] values of the standard (p^0=0.1 MPa) molar enthalpies of formation, in the gaseous phase, $\Delta_f H_m^0$(g), *vs.* the number, $n_{\mathrm{CH_2}}$, of methylene groups in the molecules of *n*-alkanes and *n*-alkylbenzenes

Compound	Molecular formula	$n_{\mathrm{CH_2}}$	$\Delta_f H_m^0$(g)/kJ mol^{-1}
		n-Alkanes	
Ethane	CH_3CH_3	0	–83.8±0.3
Propane	$CH_3CH_2CH_3$	1	–104.7±0.5
n-Butane	$CH_3(CH_2)_2CH_3$	2	–125.7±0.6
n-Pentane	$CH_3(CH_2)_3CH_3$	3	–146.9±0.8
n-Hexane	$CH_3(CH_2)_4CH_3$	4	–166.9±0.8
n-Heptane	$CH_3(CH_2)_5CH_3$	5	–187.6±1.3
n-Octane	$CH_3(CH_2)_6CH_3$	6	–208.5±1.3
n-Nonane	$CH_3(CH_2)_7CH_3$	7	–228.2±0.6
n-Decane	$CH_3(CH_2)_8CH_3$	8	–249.5±1.3
n-Undecane	$CH_3(CH_2)_9CH_3$	9	–270.8±2.5
n-Dodecane	$CH_3(CH_2)_{10}CH_3$	10	–289.4±2.1
		n-Alkylbenzenes	
Methylbenzene	$C_6H_5–CH_3$	0	50.5±0.5
Ethylbenzene	$C_6H_5–CH_2CH_3$	1	30.0±1.0
n-Propylbenzene	$C_6H_5–(CH_2)_2CH_3$	2	7.9±0.7
n-Butylbenzene	$C_6H_5–(CH_2)_3CH_3$	3	–11.8±1.2
n-Decylbenzene	$C_6H_5–(CH_2)_9CH_3$	9	–138.6±2.3

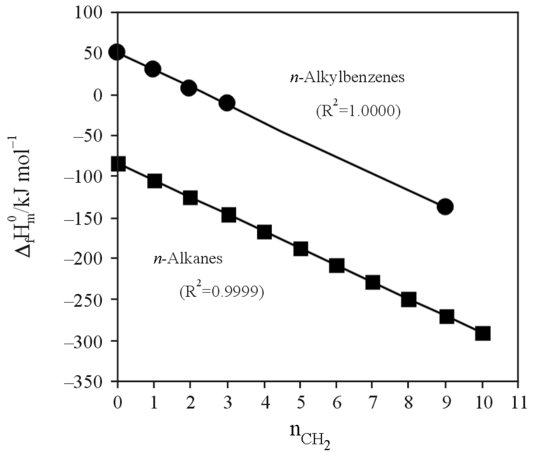


Fig. 1 Plot of the standard molar enthalpies of formation in the gaseous state, $\Delta_f H_m^0$, with the number of methylene groups of the alkyl chain ($n_{\mathrm{CH_2}}$), ■ – in *n*-alkanes and ● – in *n*-alkylbenzenes

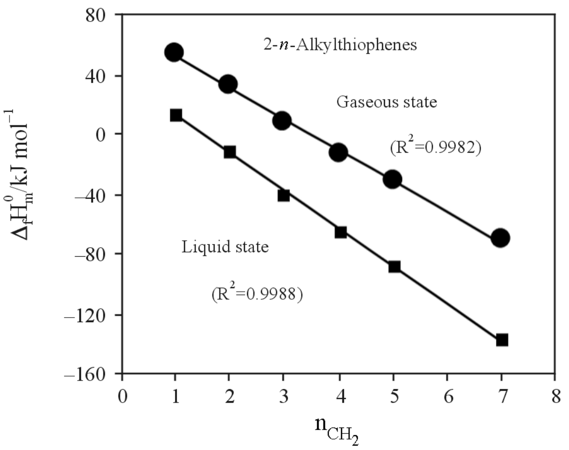


Fig. 2 Plot of the standard molar enthalpies of formation of 2-*n*-alkylthiophenes ● – in the gaseous and ■ – in the liquid states, with the number of methylene groups of the alkyl chain ($n_{\mathrm{CH_2}}$)

2-alkyl-substituted thiophenes and 3-alkyl-substituted thiophenes.

It is worthwhile to notice that the same kind of correlations can be established for the standard molar enthalpies of formation of the liquid 2-alkythiophenes and 3-alkylthiophenes, as can be seen from the straight lines of these correlations, depicted in Figs 2 and 3, respectively. These correlations follow the Eqs (8) and (9), respectively for 2-alkythiophenes and 3-alkylthiophenes:

$$\Delta_f H_m^0\,(\mathrm{l})\,/\,\mathrm{kJ\ mol^{-1}} = -25.051\mathrm{n}_{\mathrm{CH_2}} + 37.300 \quad (R^2 = 0.9988) \tag{8}$$

$$\Delta_f H_m^0\,(\mathrm{l})\,/\,\mathrm{kJ\ mol^{-1}} = -29.575 n_{\mathrm{CH_2}} + 59.742 \quad (R^2 = 0.9969) \tag{9}$$

These straight lines, implying the constancy of the energetic increment of the methylene group in the alkyl chains of the compounds in the condensed phase are surprising, but are an indication that the enthalpies of vaporization of these compounds must also follow a linear correlation with the number of methylene groups of the alkyl chains, a fact that is clearly shown by the corresponding plots shown in Fig. 4, for the enthalpies of vaporization of 2-alkythiophenes and

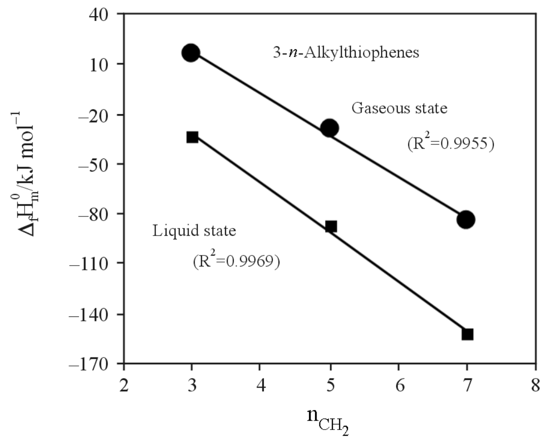


Fig. 3 Plot of the standard molar enthalpies of formation of 3-*n*-alkylthiophenes ● – in the gaseous and ■ – in the liquid states, with the number of methylene groups of the alkyl chain ($\mathrm{n_{CH_2}}$)

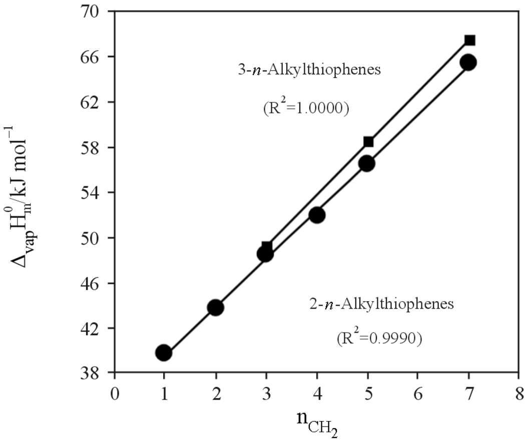


Fig. 4 Plot of the standard molar enthalpies of vaporization ($\Delta_{vap}H_m^0$) of ● – 2-*n*-alkylthiophenes and ■ – 3-*n*-alkylthiophenes, with the number of methylene groups of the alkyl chain ($\mathrm{n_{CH_2}}$)

Table 8 Experimental and estimated values of the standard (p^0=0.1 MPa) molar enthalpies of formation of 2-alkyl-substituted thiophenes and 3-alkyl-substituted thiophenes

Alkylthiophene	$n_{\mathrm{CH_2}}$	$\Delta_f H_m^0$(g)/kJ mol^{-1}		δ=Exp–Est/ kJ mol^{-1}
		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

3-alkylthiophenes, to which correspond the Eqs (10) and (11), respectively:

$$\Delta_{1}^{g}H_{m}^{0}\ /\ \text{kJ mol}^{-1} = -4.264\text{n}_{\text{CH}_2} + 35.314 \quad (R^2 = 0.9990) \tag{10}$$

$$\Delta_{1}^{g}H_{m}^{0}\ /\ \text{kJ mol}^{-1} = -4.575\text{n}_{\text{CH}_2} + 35.592 \quad (R^2 = 1.000) \tag{11}$$

Conclusions

As conclusions, the present study shows that it was possible to establish linear correlations of the standard molar enthalpies of formation, both in the gaseous and in the liquid phases, with the number of methylene groups in the alkyl chains of the 2-alkylthiophenes and 3-alkylthiophenes as well as a linear correlations between the enthalpies of vaporization and the number of methylene groups in the alkyl chains of the 2-alkylthiophenes and 3-alkylthiophenes. It was also shown that these correlations yield reliable estimated values for those properties, for the compounds of the same families, for which experimental values are not available. The similarity of the values derived as enthalpic increments in the gaseous states for *n*-alkanes, *n*-alkylbenzenes, 2-alkylthiophenes and 3-alkylthiophenes, respectively –20.6, –21.0, –20.8 and –25.0 kJ mol^{-1} show that the methylene molecular increments do not introduce different specific enthalpic effects in saturated hydrocarbons, alkyl substituted aromatic hydrocarbons and alkyl substituted sulfur heterocycles.

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