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Thermophysical, crystalline and infrared studies of the 2- and 3-thiophenecarboxylic acids

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Abstract

A thermophysical study by differential scanning calorimetry (DSC) for the 2- and 3-isomers of thiophenecarboxylic acid, in the temperature intervals between $T = 268\,\mathrm{K}$ and their respective melting temperatures has been carried out, and enhancements in the heat capacity curves were observed. The supramolecular structure of both compounds was analysed by X-ray crystallography and IR spectroscopy to determine which structural modifications take place in the temperature range at which the heat absorption occurs. Changes in bands assigned mainly to δ(O–H) + ν(C–O), δ(C–H) + ν(C–S) and out of plane C–H vibrations point to structural modifications taking place in the temperature range at which the heat absorption occurs. All those groups are involved in the weak C–H···O or C–H···S contacts that form the crystal three-dimensional network and so it can be concluded that changes in these H-bond strength, are responsible for the small heat absorptions founded in the heat capacity curves.

Keywords: 2-Thiophenecarboxylic acid; 3-Thiophenecarboxylic acid; Heat capacities; Supramolecular structure; Phase transitions

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1. Introduction

The family of the five-membered heterocycles is of basic importance in chemistry [1] and among them the family of the thiophene derivatives. If benzenes are the paradigm of aromatic molecules [2], thiophenes are the simplest representatives of stable aromatic structures bearing sulphur. The sulphur atom in the five-membered ring acts as an electron donating heteroatom by contributing two electrons to the aromatic sextet, and thiophene is thus considered to be an electron-rich heterocycle. The chemistry of thiophene derivatives is consequently dominated by this effect. The large number of reports pertaining to the synthesis of thiophene and its derivatives indicates the continuing importance of these compounds in biology [3], chemistry [1], industry [4] and medicine [5].

In the context of a systematic study of the thermodynamic properties of thiophene derivatives we recently reported an experimental and theoretical thermochemical study [6] of the energetics of 2- and 3-thiophenecarboxylic acids and their relationship to benzoic acid. In this work we present a thermophysical study of the behaviour as a function of the temperature, by heat capacity measurements,

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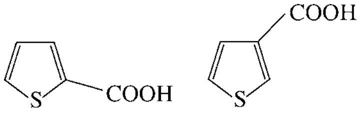


Fig. 1. 2- and 3-thiophenecarboxylic acids.

infrared spectroscopy as well as the analysis of their supramolecular structures (Fig. 1).

2. Experimental

2.1. Materials

2- and 3-thiophenecarboxylic acids (or α- and β-derivative, respectively) were commercially available from Lancaster, (mass fraction 0.99). 3-Thiophenecarboxylic acid was purified by crystallisation twice from ethanol–water mixture. The samples of the two acids were carefully dried under vacuum at 50 °C. Determination of purities, assessed by differential scanning calorimetry (DSC) by the fractional fusion technique [7] indicated that the mole fraction of impurities in the compounds were less than 0.001.

2.2. Calorimetry

A differential scanning calorimeter (Perkin-Elmer, Pyris 1) equipped with an intra-cooler unit was used. Its temperature and power scales were calibrated [8,9] at heating rates of 0.01 and 0.17 $\mathrm{K\,s^{-1}}$. The temperature scale was calibrated by measuring the melting temperature of the recommended high-purity reference materials: hexafluorobenzene, benzoic acid, tin, and indium [8,9]. The power scale was calibrated with high-purity indium (mass fraction: >0.99999) as reference material. Hexafluorobenzene, 99.9% purity, was supplied by Aldrich. Benzoic acid was NIST standard reference sample 39j. Indium and tin reference materials were supplied by Perkin-Elmer. Thermograms of samples hermetically sealed in volatile aluminium pans were recorded in a nitrogen atmosphere. For purity determinations and temperatures, enthalpies and entropies of fusion a heating rate of 0.01 $\mathrm{K\,s^{-1}}$ was used. For enthalpy transitions determinations a heating rate of 0.17 $\mathrm{K\,s^{-1}}$ was used. The estimated errors for temperature and enthalpy determinations were ±0.5 K and about 2%, respectively. All the pans were weighed before and after the experiments in order to confirm that no product leakage had occurred. The samples were weighed with a Mettler AT21 microbalance.

Heat capacities were determined following the experimental methodology described in [10]. Synthetic sapphire was used as an external standard for the heat capacity determinations and benzoic acid was used as reference material [9] for checking all the process. For heat capacity determinations, four to six samples weighing 10–25 mg were scanned for each compound in the temperature range from 268 K to its melting temperature using a heating rate of 0.17 $\mathrm{K\,s^{-1}}$. Each scan was divided into approximately 40 K intervals, overlapping each other to minimize base-line uncertainties. The temperature intervals where heat capacities were measured are: 268–308, 303–342, 338–379, 373–392 K for 2-thiophenecarboxylic acid and 268–307, 303–342, 338–389 K for 3-thiophenecarboxylic acid. The accuracy of the molar heat capacities was between 0.01 and 0.02 $C_{p,\mathrm{m}}$ and the standard deviations on the mean of the experimental results at $T = 298.15\,\mathrm{K}$ were ±0.002, ±0.013, $\mathrm{J\,g^{-1}\,K^{-1}}$ for the 2- and 3-isomers of thiophenecarboxylic acid, respectively.

2.3. Infrared spectroscopy

Infrared spectra were recorded on a Nicolet 750 Magna FTIR instrument. A SPECAC VTL-2 variable temperature cell was used to record the spectra at different temperatures. The samples were prepared as KBr pellets.

3. Results and discussion

3.1. Calorimetry

In Fig. 2, the DSC scans in heating, cooling and second heating obtained for the two compounds are shown.

The molar percent purities and the experimental values for the temperatures, enthalpies and entropies of the fusion transition with their standard deviations of experiments made with fresh samples are given in Table 1. The purity of the two compounds was high

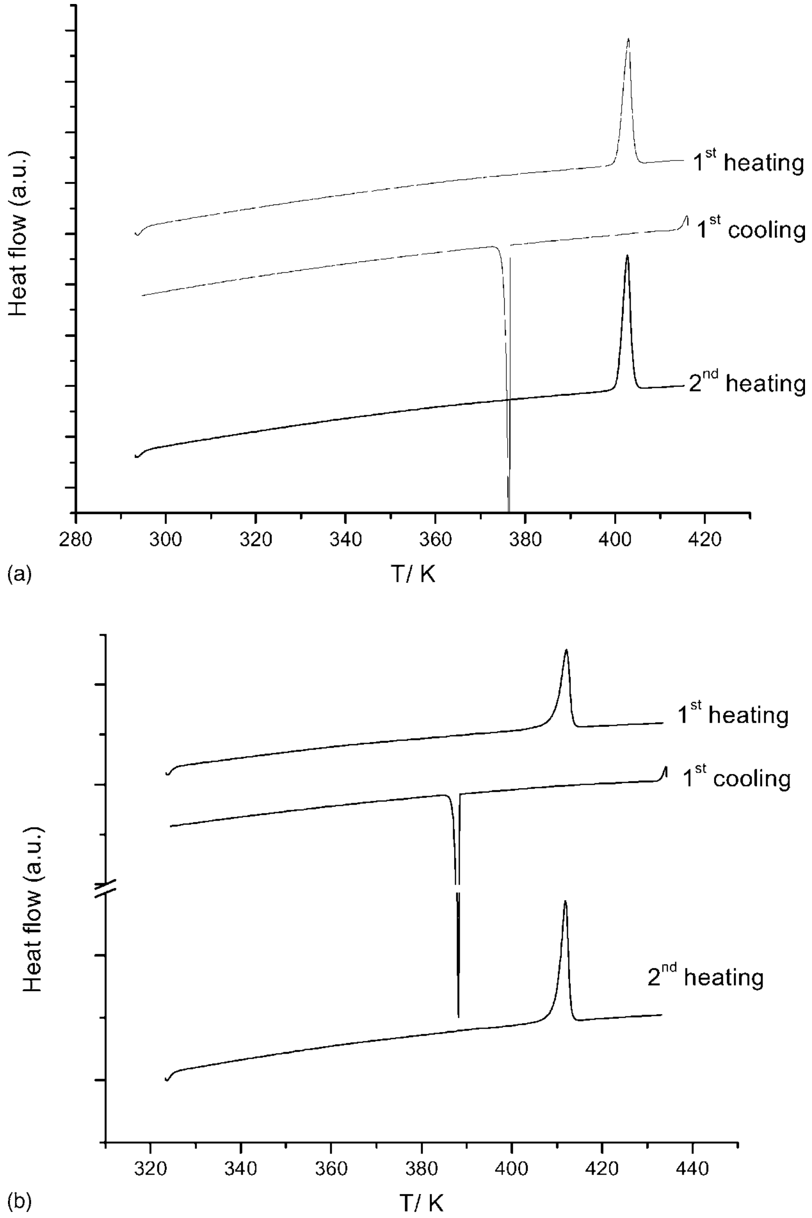


Fig. 2. Plot of the DSC scans obtained for of 2-thiophenecarboxylic acid (a); and 3-thiophenecarboxylic acid (b) in the temperature intervals between 268 K and after their melting temperatures.

enough to achieve reliable data for enthalpies of transitions and heat capacities.

The mean values obtained from heat capacity measurements for the two isomers of thiophenecarboxylic acid are given in Table 2 and the heat capacity curves obtained are shown in Fig. 3. The enhancements in the heat capacity curves of both compounds were reproducible and all experiments done with different samples showed the same behaviour. These enhancements in the heat capacities curves were also

Table 1
Results obtained from DSC measurements for the purity of the two isomers of thiophenecarboxylic acid: x denotes mole fraction, T_{fus} the temperature of fusion, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ the molar enthalpy of fusion, and $\Delta_{\mathrm{fus}}S_{\mathrm{m}}$ the molar entropy of fusion

m (mg)	x ($\times 10^2$)	T_{fus} (K)	$\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ (kJ mol^{-1})	$\Delta_{\mathrm{fus}}S_{\mathrm{m}}$ (J mol^{-1} K^{-1})
2-Thiophenecarboxylic acid				
1.106	99.928	400.6	21.6	53.8
1.171	99.928	400.9	21.9	54.6
1.624	99.944	400.8	20.7	51.7
1.214	99.934	400.9	20.1	50.1
1.316	99.937	401.0	21.0	52.3
Mean ± S.D.	99.934 ± 0.003	400.9 ± 0.1	21.0 ± 0.3	52.5 ± 0.8
3-Thiophenecarboxylic acid				
1.783	99.982	412.4	17.2	41.8
0.870	99.979	412.8	17.4	42.2
0.904	99.952	413.1	17.1	41.4
1.488	99.970	413.3	18.8	45.5
1.913	99.974	412.8	19.6	47.4
1.601	99.961	413.1	19.4	47.0
Mean ± S.D.	99.970 ± 0.005	412.9 ± 0.1	18.3 ± 0.5	44.2 ± 1.1

Table 2
Molar heat capacities of 2- and 3-thiophenecarboxylic acids

T (K)	C_p (J mol^{-1} K^{-1})	
	2-Thiophenecarboxylic acid	3-Thiophenecarboxylic acid
268.15	126.83	122.73
270.15	127.72	123.45
273.15	129.09	124.69
275.15	129.73	125.07
280.15	132.38	127.12
285.15	135.97	128.83
290.15	139.13	130.84
295.15	141.01	132.68
298.15	141.99	134.13
300.15	143.14	135.07
305.15	144.94	138.83
310.15	147.24	147.12
315.15	149.51	151.30
320.15	151.73	156.77
325.15	153.99	157.07
330.15	156.26	155.53
335.15	158.74	156.30
340.15	160.89	158.49
345.15	163.22	160.44
350.15	165.53	162.59
355.15	168.09	164.54
360.15	172.92	166.50
365.15	175.86	168.65
370.15	177.45	170.79
375.15	179.60	172.97
380.15	183.21	174.20
385.15	187.18	176.59
390.15	191.93	

obtained in experiments made after the fusion of the compounds, showing their reversibility.

The heat capacity curve of 2-thiophenecarboxylic acid shows two humps at 267–307 and 360–373 K. Their enthalpies and onset temperatures were determined from five DSC experiments using fresh samples. The entropies were calculated from the experimental results. For the hump observed at the lower temperature, $T = (279.7 \pm 0.3)$ K, $\Delta H = (0.077 \pm 0.002)$ kJ mol^{-1} and $\Delta S = (0.0879 \pm 0.0003)$ J K^{-1} mol^{-1} were determined. The temperature, enthalpy and entropy measured for the second hump are $T = (360.6 \pm 0.1)$ K, $\Delta H = (0.020 \pm 0.002)$ kJ mol^{-1}, and $\Delta S = (0.0266 \pm 0.0001)$ J K^{-1} mol^{-1}.

Heat capacity values obtained for 3-thiophenecarboxylic acid are lower than those obtained for the 2-thiophenecarboxylic acid. The heat capacity curve for this compound shows a hump between 308 and 334 K. The values obtained for their temperature (taken as onset), enthalpy and entropy were determined from four DSC experiments using fresh samples being $T = (310.4 \pm 0.4)$ K, $\Delta H = (0.079 \pm 0.004)$ kJ mol^{-1}, and $\Delta S = (0.6522 \pm 0.0004)$ J K^{-1} mol^{-1}.

In order to clarify the causes of these behaviours the supramolecular structure of both compounds was analysed by X-ray crystallography and IR spectroscopy to determine which structural modifications

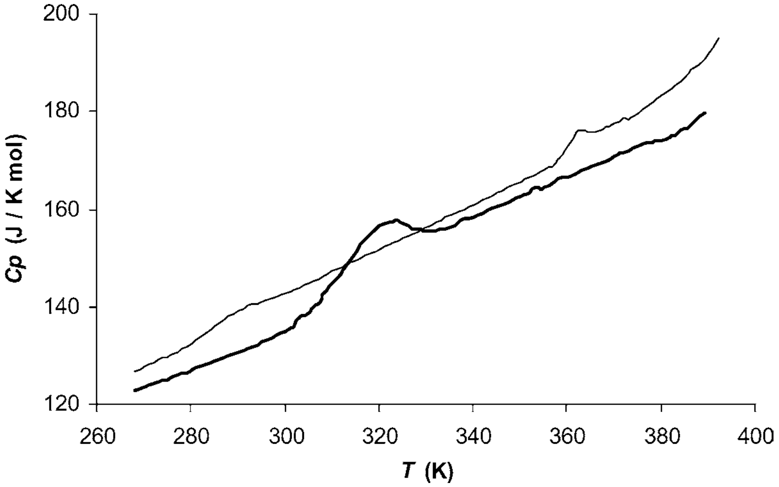


Fig. 3. Experimental heat capacities of 2-thiophenecarboxylic acid (thin line) and 3-thiophenecarboxylic acid (bold line).

take place in the temperature range at which the humps appears.

3.2. Preparation of isomers crystals: X-ray crystallography

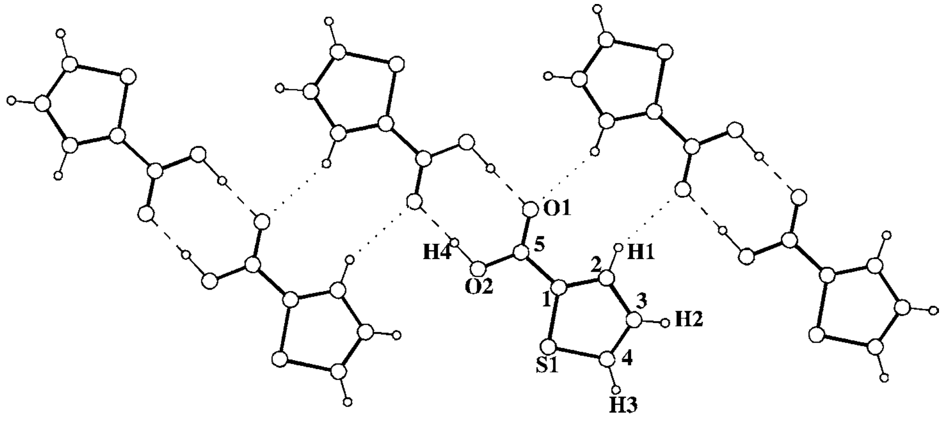
The crystal structure of both compounds has already been described [11] (CSD ref. codes: TPENAC [12], TPENAC01 [13], TPENAC02 [14] and THIPAC [15], respectively). The crystal structure of the 2-derivative [12–14] has been reported at room temperature and at 103 K whereas the 3-derivative [15] only at 103 K.

Several crystallisation attempts have been done in order to check the existence of polymorphism in the samples of both compounds used in this study. Recrystallisation of the 3-compound from water and a mixture of water and ethanol at different temperatures, resulted in two crystal habits: large needles (as reported in the previous papers [12,13,15]) and/or plates, depending on the amount of water used. The larger amount of water the greater the percentage of plates obtained. However, both types of crystals display the same cell dimensions and symmetry which were checked after recording, in our laboratory, the whole spectrum at room temperature and using both needle and plate samples.

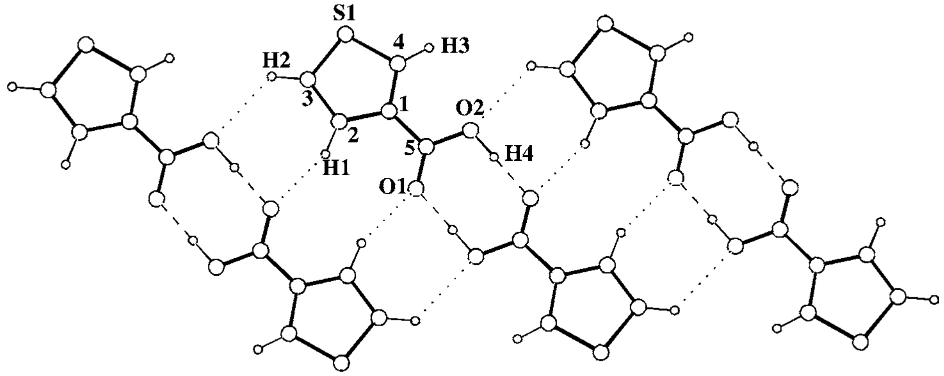
The refinement of the new data set, collected at room temperature for the 3-isomer (THIPAC), confirms that no phase transition takes place in the 103–293 K range of temperature. Therefore, intra and

Table 3
Intermolecular interactions (Å), (°)

	D–H	H···A	D···A	D–H···A
TPENAC (2-derivative)				
O2–H4···O1 ($-x$, $1-y$, $1-z$)	1.01 (9)	1.62 (8)	2.628 (2)	175 (8)
C2–H1···O1 ($-1-x$, $-y$, $1-z$)	0.92 (10)	2.50 (8)	3.339 (3)	152 (3)
C3–H2···O2 ($-1+x$, $-1+y$, z)	0.89 (2)	3.03 (6)	3.687 (3)	133 (7)
C4–H3···S1 ($-x$, $-1/2+y$, $1/2-z$)	0.91 (7)	3.12 (6)	3.823 (3)	136 (2)
THIPAC (3-derivative)				
O2–H4···O1 ($-x$, $1-y$, $-z$)	1.04	1.62	2.664 (8)	180
C2–H1···O1 ($1/2-x$, $3/2-y$, $-z$)	1.02	2.42	3.376 (8)	156
C3–H2···O2 ($1/2+x$, $1/2+y$, z)	1.03	2.65	3.340 (10)	125
C4–H3···S1 ($-x$, $-1/2+y$, $1/2-z$)	1.00	3.05	3.957 (8)	152



(a) **TPENAC02**



(b) **THIPAC**

Fig. 4. Part of the crystal structures (a) 2-thiophenecarboxylic and (b) 3-thiophenecarboxylic acids (CSD ref. codes: TPENAC02 and THIPAC) showing the same numbering system and the linkage of the dimers (dashed lines) through C–H···O contacts (dotted lines).

intermolecular parameters for the description of the structures have been computed [16] according to the atomic coordinates reported in [14] (TPENAC02) and [15] (THIPAC). For comparison purposes, the same numbering scheme (Table 3 and Fig. 4) has been used.

The crystal lattices of 2- and 3-thiophenecarboxylic acids do not incorporated water or solvent molecules.

At the time of the publications, at the beginning of the sixties, the notion of C–H···O hydrogen bonds was under investigation [17] and no molecular aggregation beyond dimer formation was discussed. However, the C–H···O interactions in Table 3 correspond to the shortest C–H···O distances mentioned in [12,15].

Inspection of the crystal packing of both molecules reveals the formation of centrosymmetric carboxylic hydrogen bonded dimer linked via pairs of C–H···O bonds creating hydrogen bond tapes (Fig. 4) that are then connected in a "herringbone" fashion by weak C–H···S contacts [17] to form a three-dimensional network (Fig. 5).

Although, these two structures have supramolecular features in common (Table 3), the donor–acceptor distance in the C–H···O contacts involving the hydroxyl O atom is greater in the 2-derivative (TPENAC) than in 3-derivative (THIPAC). This is probably due to the differences in the configuration of the five-membered ring (S atom position) and to the twist of the carboxylic

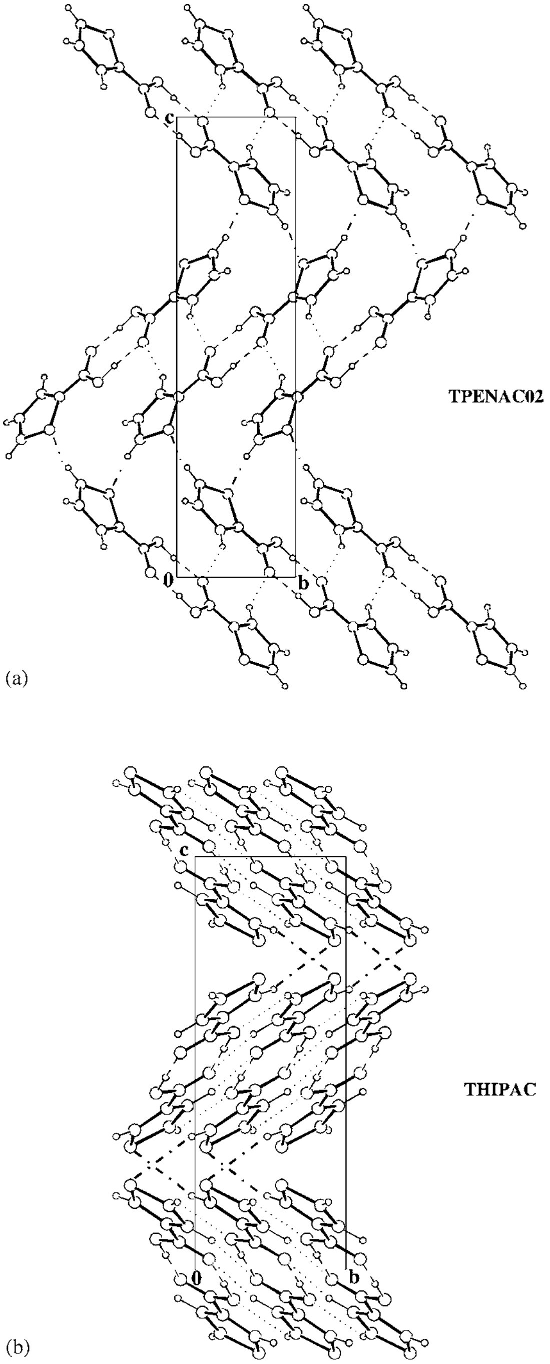


Fig. 5. (a) Crystal packing of the 2-derivative along **a**. (b) Crystal packing of the 3-derivative along **a** illustrating the packing of the tapes through C–H· · · S contacts (dotted–dashed lines).

groups (C2–C1–C5–O1 = −0.5 (3) and −3.4 Å (10°)) that produces a shift of the one dimer with respect to the other as shown in Fig. 6 where two pairs of dimers have been represented. The superposition has been done on the C5, C1 and C2 atoms of the molecule marked with a hash sign (#).

3.3. *Infrared spectroscopy*

Infrared spectroscopy has been widely used to study phase transitions, including solid to solid transitions [18,19] that can exist in a given sample. Frequencies, as well as bandwidths, change drastically within a narrow temperature range around that of the phase change. In addition infrared spectra are very sensitive to inter and intramolecular forces and in consequence, the study of the most temperature dependent vibrational bands give a great information about the modification of these forces acting in the crystal molecules.

IR spectra of 2- and 3-thiophenecarboxylic acids have been recorded at different temperatures from 273 to 415 K, in an attempt to clarify the processes related to the small heat absorptions observed in the heat capacity curves.

It must be stated that infrared spectra of these compounds are not well studied. To our knowledge there is only one experimental determination of the infrared spectra of 3-thiophenecarboxylic acid [20]. In the case of 2-thiophenecarboxylic acid there are three experimental studies [20–22] of its IR spectrum, but in one of them [21], the author did not show all the experimental frequencies, and only mentioned some of the bands. Recently an ab initio calculation of vibrational spectra of these compounds has been carried out by our group [6] but a complete and reliable assignment of bands to normal modes has not been achieved. Because of that, the analysis included in this section is based on temperature changes of key bands to which the assignment is rather clear.

The infrared spectra of both samples vary slightly with temperature and most of the changes in frequency and relative intensity are small and almost continuous confirming that the heat absorption observed does not correspond to a phase transition. Nevertheless the most significant modifications are observed in bands due mainly to OH and CH deformations mixed with CS and CO stretchings. A detailed plot of the frequency versus temperature of the δ(O–H) + ν(C–O)

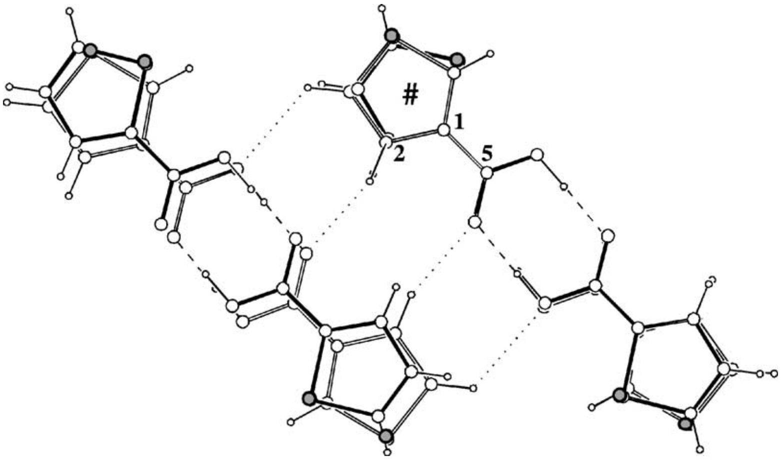


Fig. 6. Superposition of two pairs of dimers. For clarity purposes, hydrogen interactions have only been drawn in 3-derivative (THIPAC).

band for each compound, is displayed in Fig. 7. Frequency change of this bands is most abrupt in the temperature range at which the heat absorption occurs and this indicates structural modifications. All those groups are involved in the weak C–H· · · O or C–H· · · S contacts that form the crystal three-dimensional network and so it can be concluded that changes in these H-bond strength, are responsible for the heat absorptions shown in Fig. 3. All these bonds imply the C–H group and so the temperature behaviour of ν(C–H) stretching wavenumbers would also reflect the weakening of these H bonds. ν(CH) wavenumbers remain almost constant but slightly increase with temperature and reach their highest value in the liquid where C–H· · · O and C–H· · · S contacts seem to be broken. This frequency rise in the liquid also shows that in

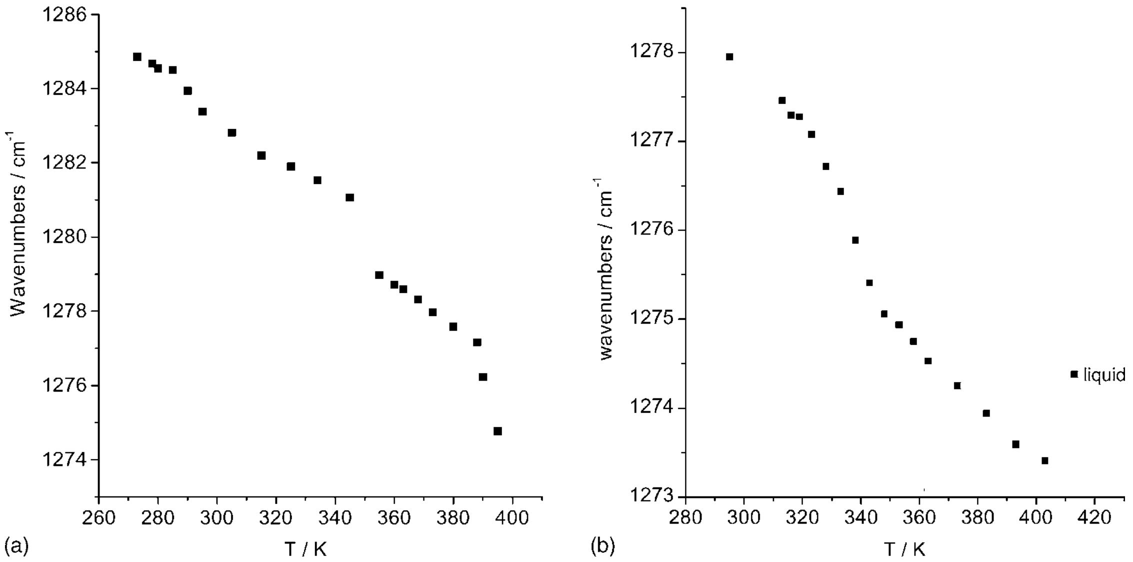


Fig. 7. Temperature dependence of [ν(C–O) + δ(O–H)] band wavenumbers of: (a) 2-thiophenecarboxylic acid; (b) 3-thiophenecarboxylic acid.

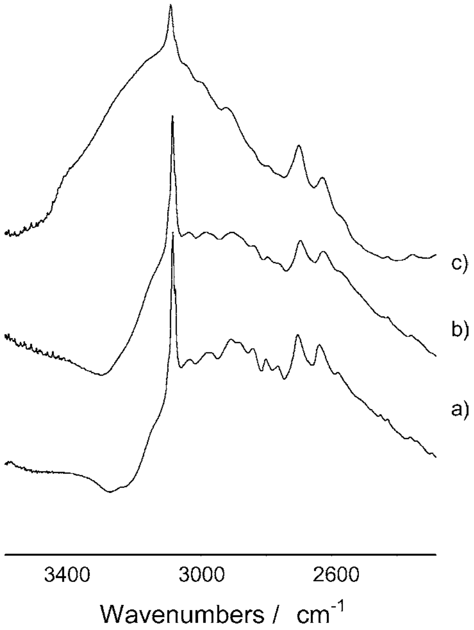


Fig. 8. ν(O–H) stretching region of 3-thiophenecarboxylic acid: (a) crystal, $T = 295$ K; (b) $T = 403$ K; (c) melt, $T = 413$ K.

these compounds the weak CH···O bonds yields to a red shift of the C–H stretching mode in the crystal phase as is the general behaviour [17].

The broad IR absorption characteristic of associated O–H···O bonds appears both in the crystal and also in the liquid although the blue frequency shift observed indicates that the O–H···O bond is weakened in the liquid. As no band corresponding to free ν(OH) groups is present in any case it must be concluded that the dimeric structure of these acids remains even in the liquid phase (see Fig. 8).

4. Conclusions

A thermophysical study of the behaviour as a function of the temperature was carried out for 2- and 3-thiophenecarboxylic acids.

Molar percent purities and the experimental values for the temperatures, enthalpies and entropies of the fusion transition with their standard deviations determined by DSC are $x = (99.934 \pm 0.003)\%$, $T = (400.9 \pm 0.1)$ K, $\Delta_{\rm fus}H = (21.0 \pm 0.3)$ kJ mol^{-1}, $\Delta_{\rm fus}S = (52.5 \pm 0.8)$ J mol^{-1} K^{-1}, respectively for the 2-thiophenecarboxylic acid and $x = (99.970 \pm 0.005)\%$, $T = (412.9 \pm 0.1)$ K, $\Delta_{\rm fus}H = (18.3 \pm 0.5)$ kJ mol^{-1}, $\Delta_{\rm fus}S = (44.2 \pm 1.1)$ J mol^{-1} K^{-1}, respectively, for the 3-thiophenecarboxylic acid.

Recrystallisation of the 3-thiophenecarboxylic acid from water and a mixture of water and ethanol at different temperatures, resulted in two crystal habits: large needles and/or plates, which relative abundance depend on the amount of water used. However, both types of crystals display the same cell dimensions and symmetry which were checked by X-ray crystallography.

Some enhancements in the lattice heat capacity curve prior to fusion were found in the DSC study. These thermal effects are small and one would not expect to see marked structural changes in the molecule. Supramolecular structure of both compounds has been analysed by IR spectroscopy to determine the causes of this humps. Changes in bands assigned mainly to δ(O–H) + ν(C–O), δ(C–H) + ν(C–S) and out of plane C–H vibrations point to structural modifications taking place in the temperature range at which the heat absorption occurs. All those groups are involved in the weak C–H···O or C–H···S contacts that form the crystal three-dimensional network and so it can be concluded that changes in these H-bond strength, might be responsible for the small heat absorptions founded in the heat capacity curves.

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