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2- and 3-furancarboxylic acids: a comparative study using calorimetry, IR spectroscopy and X-ray crystallography

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Abstract

A thermophysical study by DSC for the 2- and 3-isomers of furancarboxylic acid, in the temperature intervals between $T = 268\,\mathrm{K}$ and their respective melting temperatures has been carried out, and an enhancement in the heat capacity curve of the 3-isomer was observed. The IR spectroscopy did not show significant changes either in the frequency band or in the relative band intensity in the temperature range where the small heat absorption occurs. The X-ray analysis reveals that the main differences in their supramolecular structure consist of the assembly of the carboxylic dimers into sheets.

Keywords: 2-Furancarboxylic acid; 3-Furancarboxylic acid; Supramolecular structure; Heat capacity; Enthalpy of fusion; Entropy of fusion

1. Introduction

We are presently involved in a systematic study of the thermodynamic properties of five-membered aromatic heterocycles [1] bearing oxygen and sulfur. The simplest representatives of these stable aromatic structures are furans and thiophenes. Their structures can be assumed to be derived from benzene by the replacement of two annular CH groups by oxygen or sulfur, respectively. Furan and thiophene obey the $4n + 2\pi$ electron rule and they are considered to be aromatic compounds. In both families of compounds the heteroatom acts as an electron donating contributing with two electrons to the aromatic sextet and furan and thiophene are thus considered to be electron-rich heterocycles. The chemistry of these families of compounds is consequently dominated by this effect. The large number of reports pertaining to the synthesis of furan and thiophene and its derivatives indicates the continuing importance of these compounds in biology, chemistry, industry and medicine [1].

We recently reported an experimental and theoretical thermochemical study concerning the energetics of 2- and 3-thiophenecarboxylic [2] and furancarboxylic acids [3] and their relationship to benzoic acid together with a thermophysical and supramolecular study of 2- and 3-thiophenecarboxylic acids [4].

In the calorimetric study of 2- and 3-thiophenecarboxylic acids we observed some enhancements in the lattice heat capacity curves prior to fusion of these compounds. The analysis of their IR spectra allowed to correlate frequency changes in bands assigned to vibration groups involved in weak C–H···O or C–H···S contacts present in the crystal packing of these compounds.

These features prompted us to undertake the thermophysical study of the analogous furancarboxylic acids (Fig. 1) as a function of the temperature by heat capacity measurements and infrared spectroscopy in order to find out the influence of the heteroatom. The supramolecular structure has also been analysed by X-ray crystallography.

2. Experimental

2.1. Materials

2- and 3-furancarboxylic acids (or α and β derivatives, respectively) were commercially available from Lancaster

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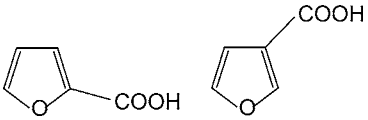

Fig. 1. 2- and 3-furancarboxylic acids.

(mass fraction 0.99). 2-Furancarboxylic acid was purified by crystallisation twice. The first from water and the second one from chloroform, and 3-furancarboxylic acid was purified by crystallisation twice from water. The samples of the two acids were carefully dried under vacuum at 50 °C. Determination of purities, assessed by DSC by the fractional fusion technique [5] 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 [6–8] at heating rates of 0.04 and 0.17 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 [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. All the pans were weighed before and after the experiments in order to confirm that no product had volatilised. The samples were weighed on a Mettler AT21 microbalance with a sensitivity of 1×10^{-6} g.

After calibration several runs with high-purity benzoic acid and indium as reference materials [9] were performed under the same conditions as the experimental determinations and the results are given in Table 1. The uncertainties of the experimental temperatures and enthalpies of fusion are expressed as the standard deviation of the mean of the experimental values obtained. The accuracy for the temperatures and enthalpies of fusion were calculated [10] by means of the expressions:

$$D(T_{\mathrm{fus}}) = 10^2 \left[\frac{T_{\mathrm{f}}(\mathrm{exp}) - T_{\mathrm{f}}(\mathrm{lit})}{T_{\mathrm{f}}(\mathrm{lit})} \right] \qquad (1)$$

and

$$D(\Delta_{\mathrm{fus}} H_{\mathrm{m}}) = 10^2 \left[\frac{\Delta_{\mathrm{fus}} H_{\mathrm{m}}(\mathrm{exp}) - \Delta_{\mathrm{fus}} H_{\mathrm{m}}(\mathrm{lit})}{\Delta_{\mathrm{fus}} H_{\mathrm{m}}(\mathrm{lit})} \right] \qquad (2)$$

as the percentage deviation of the experimental data with regard to the values given in the literature for both temperatures and enthalpies of fusion of benzoic acid and indium, respectively [9].

For determination of purity, melting temperature, and enthalpy of fusion, a heating rate of 0.04 K s^{-1} was used. For each compound, five to eight samples weighing 1–2 mg were recorded. A fresh sample was used for each run. Although the two furancarboxylic acids showed thermal stability in the fusion process, their temperatures and enthalpies of fusion were determined in the fusion peak of fresh samples.

Heat capacities were determined by the “scanning method” following the experimental methodology previously described [10–13] and using synthetic sapphire (α-aluminium oxide) as reference material [9–11]. For heat capacity determinations, four 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 K s^{-1}. In order to check the experimental method followed, heat capacity experiments with benzoic acid and synthetic sapphire as reference materials [9] in the temperature intervals T = 268–360, and T = 268–410 K, respectively were made. Table 2 gives the mean values for heat capacity determinations at the selected temperatures and their uncertainties expressed as the standard deviations of

Table 2
Heat capacities of α-aluminium oxide (synthetic sapphire) and benzoic acid

T (K)	$C_{p,\mathrm{m}}$ (J mol^{-1} K^{-1})		
	This work	Literature [9]	$D(C_{p,\mathrm{m}})$
α-Aluminium oxide			
289.15	78.7 ± 0.1	79.01	−0.4
300	79.2 ± 0.1	79.41	−0.3
350	88.5 ± 0.3	88.84	−0.4
400	95.4 ± 0.7	96.08	−0.7
Benzoic acid			
280	137.2 ± 0.6	138.44	−0.9
300	145.3 ± 0.7	147.64	−1.6
320	155.1 ± 0.7	156.87	−1.2
350	168.7 ± 0.8	170.70	−1.2

Table 1
Comparison between temperatures of fusion T_{fus} and enthalpies of fusion $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ obtained with our DSC apparatus for two reference materials and their selected values

Compound	Origin	N[b]	T_{fus} (K)			$\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ (kJ mol^{-1})		
			This work	Literature	$D(T_{\mathrm{fus}})$ (%)	This work	Literature	$D(\Delta_{\mathrm{fus}}H_{\mathrm{m}})$ (%)
Benzoic acid	NIST[a]	6	395.7 ± 0.1	395.50 ± 0.02 [9]	0.1	17.78 ± 0.13	18.063 ± 0.042 [9]	−1.6
Indium	Perkin-Elmer	8	430.5 ± 0.1	429.75 ± 0.04 [9]	0.2	3.24 ± 0.10	3.286 ± 0.013 [9]	−1.3

[a] National Institute of Standards and Technology.

[b] The number of DSC runs.

Table 3
Results obtained from DSC measurements for the purity of the two isomers of furancarboxylic 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	T_{fus} (K)	$\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ (kJ mol^{-1})	$\Delta_{\mathrm{fus}}S_{\mathrm{m}}$ (J mol^{-1} K^{-1})
2-Furancarboxylic acid				
2.387	0.9999	402.3	23.3	57.9
1.774	0.9999	403.0	22.1	54.8
1.673	0.9999	403.1	22.3	55.3
1.681	0.9998	402.0	23.4	58.2
0.970	0.9998	402.1	22.1	55.0
Mean ± standard deviation of the mean	0.9999 ± 0.0001	402.5 ± 0.2	22.6 ± 0.3	56.2 ± 0.7
3-Furancarboxylic acid				
1.102	0.9997	395.3	21.4	54.1
1.701	0.9997	395.2	21.6	54.7
1.219	0.9996	395.2	21.0	53.1
2.345	0.9996	394.1	21.3	54.0
1.706	0.9996	394.3	21.0	53.3
Mean ± standard deviation of the mean	0.9996 ± 0.0001	394.8 ± 0.3	21.3 ± 0.1	53.8 ± 0.3

the mean. A comparison of our results with those reported in the literature [9] is also given.

The quantity D($C_{p,\mathrm{m}}$) defined as

$$D(C_{p,\mathrm{m}}) = 10^2\left[\frac{C_{p,\mathrm{m}}(\mathrm{exp}) - C_{p,\mathrm{m}}(\mathrm{lit})}{C_{p,\mathrm{m}}(\mathrm{lit})}\right] \qquad (3)$$

Table 4
Molar heat capacities of 2- and 3-furancarboxylic acids

T (K)	$C_{p,\mathrm{m}}$ (J mol^{-1} K^{-1})	
	2-Furancarboxylic acid	3-Furancarboxylic acid
268.15	121.1	119.5
270.15	122.2	120.2
273.15	123.6	121.5
275.15	124.4	122.3
280.15	126.6	124.4
285.15	128.8	126.5
290.15	131.0	128.4
295.15	133.1	130.4
298.15	134.4	131.5
300.15	135.2	132.2
305.15	137.6	134.2
310.15	140.0	136.1
315.15	141.9	138.2
320.15	144.1	140.4
325.15	145.6	142.6
330.15	148.1	145.4
335.15	150.6	147.5
340.15	153.2	149.2
345.15	154.4	151.2
350.15	156.2	155.4
355.15	158.0	159.6
360.15	160.8	161.1
365.15	162.9	163.0
370.15	165.3	166.2
375.15	167.5	169.9
380.15	169.9	

$C_{p,\mathrm{m}}$(2-furancarboxylic acid, 268.15–381.15 K) $= -0.00005T^2 + 0.4616T + 1.4879$, $R^2 = 0.9995$; $C_{p,\mathrm{m}}$(3-furancarboxylic acid, 268.15–346.15 K) $= 0.0005T^2 + 0.1061T + 55.22$, $R^2 = 0.9992$.

gives the accuracy [10] of our measurements for the selected temperatures.

The temperature intervals where heat capacities were measured are: 268–306, 303–341, 323–352, 348–381 K for 2-furancarboxylic acid and 268–306, 303–342, 338–378, 373–379 K for 3-furancarboxylic acid. The standard deviations of the mean of the experimental results at $T = 298.15$ K were ±0.51 and ±0.40 J mol^{-1} K^{-1} for the 2- and 3-isomers of furancarboxylic acid, respectively.

2.3. Infrared spectroscopy

Infrared spectra of samples prepared as KBr pellets were recorded on a NICOLET 750 Magna FTIR spectrometer. A SPECAC VTL-2 variable temperature cell was used to obtain spectra at different temperatures in the range 300–410 K.

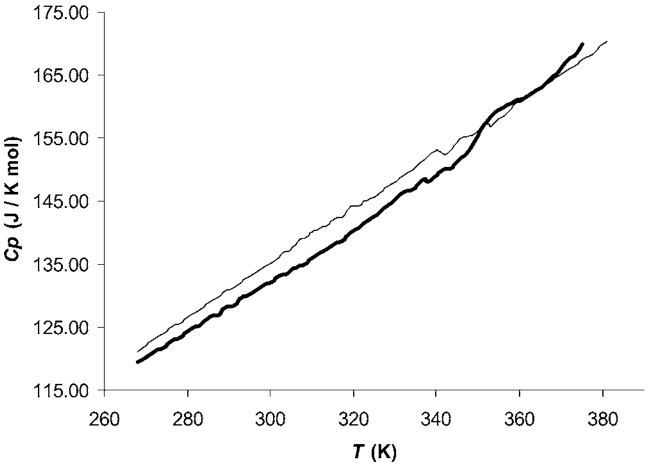

Fig. 2. Experimental heat capacities of 2-furancarboxylic (—) and 3-furancarboxylic acid (▬).

3. Results and discussion

3.1. Calorimetry

The mass, mole fraction and the experimental values of the temperatures, enthalpies and the calculated entropies of fusion from each experiment are given in Table 3. The mean values and standard deviation of the mean are included as the last entry for each compound studied. The purity of the two compounds was high enough to achieve reliable data for enthalpies of transitions and heat capacities.

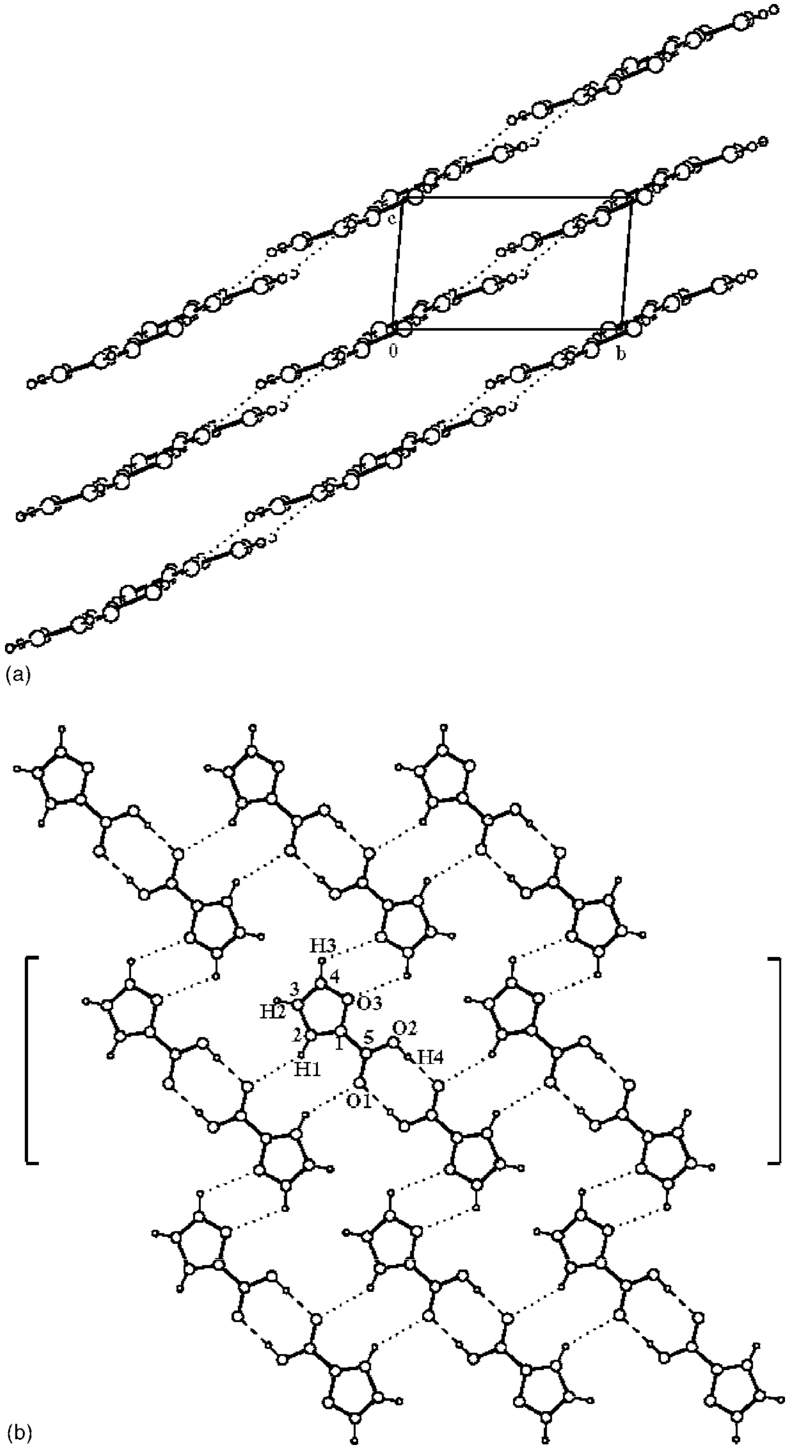

Fig. 3. (a) Crystal packing [24] of 2-furancarboxylic illustrating the layered structure; (b) part of one sheet showing the self-assembly of chains of dimers through C–H · · · O(furan) contacts. One of these chains is in brackets showing the numbering system used in this study. Dashed and dotted lines represent O–H · · · O and C–H · · · O hydrogen bonds.

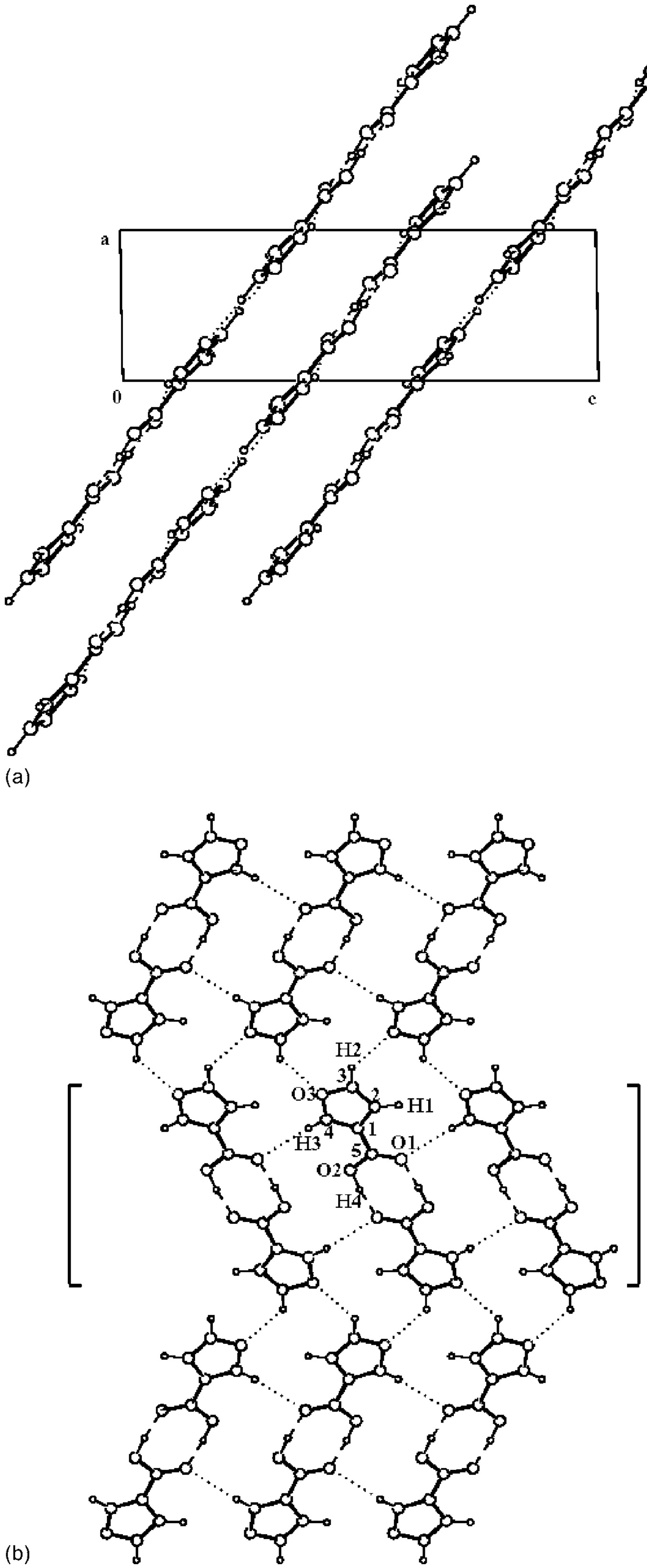

Fig. 4. (a) Crystal packing [24] of 3-furancarboxylic showing the stacking of the layers; (b) part of one sheet showing, in brackets, one chain with the numbering scheme used in this study. Dashed and dotted lines represent O–H · · · O and C–H · · · O contacts.

The mean values obtained from the heat capacity measurements and equations of $C_{p,\mathrm{m}}(T)$ for the two compounds studied are given in Table 4 and the experimental heat capacity curves obtained are shown in Fig. 2. An enhancement in the heat capacity curve of 3-furancarboxylic acid is observed at the temperature interval 346–366 K. This enhancement in the heat capacity curve was reproducible and all the experiments done with different samples showed the same behaviour. The temperature, enthalpy and entropy measured for this hump are: $T = 354.15\,\mathrm{K}$, $\Delta H = 0.021\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S = 0.059\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

It can be observed that heat capacities values obtained for 3-furancarboxylic acid before enhancement are lower than those obtained for the 2-furancarboxylic acid. The heat capacity values at $T = 298.15\,\mathrm{K}$ for the 2- and 3-furancarboxylic acids are 134.4 and $131.5\,\mathrm{J\,mol^{-1}\,K^{-1}}$, respectively.

3.2. X-ray crystallography

Although the X-ray crystal structure of the 2-furan [14–16] and 3-furan [17] carboxylic acids were already described (CSD [18] refcodes: FRANAC, FRANAC01, FRANAC02 and HIFKUC, respectively) they were included in this study in order to discuss its crystal packing with respect to the thiophenecarboxylic acid derivatives.

As in the thiophenecarboxylic acid derivatives [4,19–22], the secondary structure consists of centrosymmetric carboxylic hydrogen bonded dimers that are in turn connected by C–H · · · O(carboxylic) contacts [23] to form extended one-dimensional chains. Whereas in the thiophene family these chains were arranged in a "herringbone" fashion connected by weak C–H · · · S contacts, in the present compounds the chains, related by translation in the 2-furan and by two-fold screw axis in the 3-furan compounds, form layered structures by means of C–H · · · O(furan) contacts (Figs. 3a and 4a).

In both families, although each chain is formed by dimers related by unit cell translations (one of them in brackets in Figs. 3b and 4b) the main differences concern the number of C–H · · · O hydrogen bonds contacts between them. While in the 2-derivatives (Figs. 3b and 5a) the same pattern of hydrogen bonds are maintained in the 3-derivatives (Figs. 4b and 5b) the dimers are connected in a different way and only the O=C group is involved in C–H · · · O contacts (Table 5). This loss of hydrogen interactions is also reflected in the values of the packing coefficients (0.707 and 0.712 for the 2-, 3-furan versus 0.690 and 0.724 for the 2-, 3-thiophene derivatives). The smaller the number of contacts the lower the packing coefficient and therefore the smaller differences in the packing efficiency between the 2- and 3-furancarboxylic derivatives. Furthermore, it is worth noticing that in the 2-furan derivative, where the H-carboxylic atoms are disordered, the O–H · · · O bond shows a significantly shorter O · · · O distance.

3.3. Infrared spectroscopy

Infrared spectra of 3-furancarboxylic acid at different temperatures were recorded and analysed. Nevertheless no

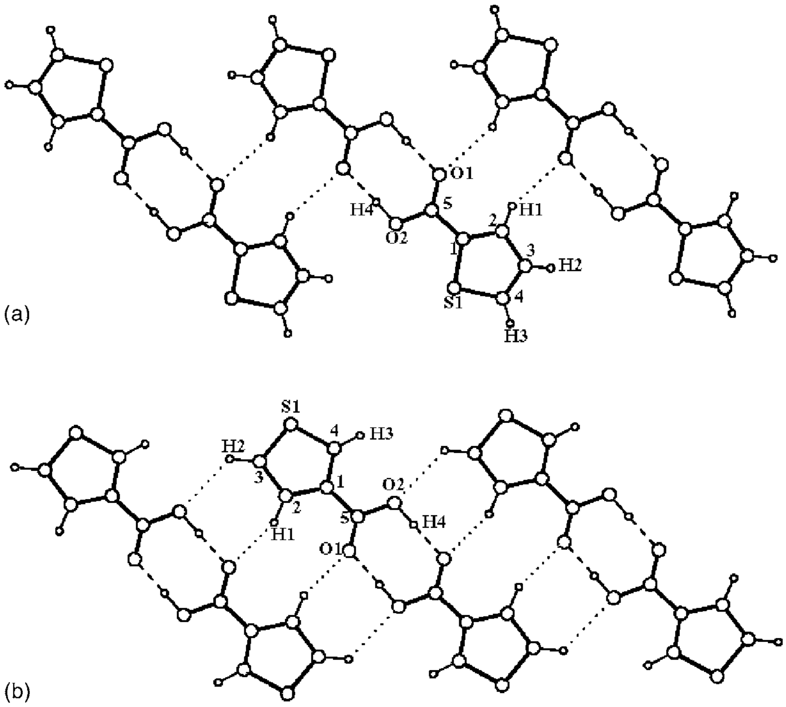

Fig. 5. One-dimensional chain [24] in the 2-thiophenecarboxylic acid (a) and in the 3-thiophenecarboxylic acid derivative (b) (CSD refcodes: TPENAC02 and THIPAC, respectively).

Table 5
Selected intermolecular parameters (Å) (angles, °)

	H···A	D···A	D–H···A
2-Furancarboxylic acid (FRANAC02)			
O2–H4···O1($1-x, -y, -z$)	1.78(4)	2.635(2)	179(3)
O1–H4′···O2($1-x, -y, -z$)	1.79(4)	2.635(2)	172(3)
C2–H1···O1($1-x, 1-y, 1-z$)	2.62(2)	3.411(1)	145(2)
C3–H2···O2($x, 1+y, z$)	3.17(2)	3.566(2)	107(1)
C4–H3···O3($-x, -y, -z$)	2.69(2)	3.203(2)	114(2)
3-Furancarboxylic acid (HIFKUC)			
O2–H4···O1($1-x, -y, 1-z$)	1.63(5)	2.653(4)	173(4)
C2–H1···O3($x, -1+y, z$)	2.79(3)	3.767(4)	164(2)
C3–H2···O3($-1-x, -1/2+y, 1/2-z$)	2.59(3)	3.410(4)	137(2)
C4–H3···O1($x, -1+y, z$)	2.49(4)	3.387(4)	164(3)

H4 and H4′ stand for the two positions of the carboxylic disordered H atom.

significant changes were observed either in frequency bands or in relative band intensities in the temperature range where the small heat absorption take place.

By comparison, infrared spectrum of 2-furancarboxylic acid was recorded at different temperatures. A similar behaviour to that described for 3-furancarboxylic acid was observed. As an anomalous enhancement is not evident in the heat capacity curve of 2-furancarboxylic acid it must be concluded that the small caloric absorption observed in the 3-furancarboxylic acid curve does not correspond to significant structural changes.

As expected important modification occur at the fusion temperatures of both compounds, but the broad absorption characteristic of associated O–H···O bonds remains, blue shifted, in the liquid and no band ascribable to free O–H stretching was observed indicating that dimers are present in this phase.

4. Conclusions

A thermophysical study of the behaviour as a function of the temperature was carried out for 2- and 3-furancarboxylic acids and a comparative analysis with analogous 2- and 3-thiophenecarboxylic acids was made.

A small enhancement in the lattice heat capacity curve prior to fusion of 3-furancarboxylic acid was found in the DSC study. The temperature, enthalpy and entropy measured for this hump are: $T = 354.15\,\mathrm{K}$, $\Delta H = 0.021\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S = 0.059\,\mathrm{J\,K^{-1}\,mol^{-1}}$. The same behaviour was found in 2- and 3-thiophenecarboxylic acids but with higher enthalpy values.

The crystal structure analysis reveals that the main differences between the furan and the thiophenecarboxylic derivatives are due to the different pattern of weak contacts joining the carboxylic dimers into chains and the way in which these chains are linked to build up the whole crystals. In the furan derivatives the differences in the crystal packing efficiency are smaller than in the thiophene derivatives.

In the study of their IR spectrum, no significant changes were observed either in frequency bands or in relative band intensities in the temperature range where the small heat absorption take place and it must be concluded that the small caloric absorption observed in the 3-furancarboxylic acid curve does not correspond to significant structural changes.

Acknowledgements

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