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Heat capacities and enthalpies of transitions of three nitrobenzonitriles

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Abstract

Thermophysical study of the behaviour, as a function of temperature, of the 2-, 3- and 4-isomers of nitrobenzonitriles was carried out by differential scanning calorimetry, in the temperature intervals between 268 K and its respective melting points. The temperatures, enthalpies and entropies of the fusion processes were measured. Several phase transitions were observed for the 2- and 4-isomers and their temperatures, enthalpies and entropies are given.

Heat capacities of the 2-, 3- and 4-isomers of nitrobenzonitriles were measured by differential scanning calorimetry between 268 K and their melting temperature and the results obtained were correlated as a function of temperature.

Keywords: 2-Nitrobenzonitrile; 3-Nitrobenzonitrile; 4-Nitrobenzonitrile; Phase transition; Heat capacity; Differential scanning calorimeter; Enthalpy of fusion

1. Introduction

In the last few years, we have been involved in a systematic study of the thermochemical and thermophysical properties of benzene derivatives [1–3]. The aim of these studies being the quantitative assessment of structural effects in these compounds. In a previous paper [3], we have seen that the relative stabilities of the isomeric dinitrobenzenes and dimethylphthalates remain very confused, so, in order to provide an answer, we decided to begin the study of the isomeric mixed nitrobenzonitrile samples.

The thermochemical study involves the experimental determination, for the three isomers, of their enthalpies of combustion and vapour pressures in a temperature interval, to calculate the enthalpies of sublimation and formation in condensed and gas states. Enthalpies of sublimation are performed at temperatures other than the reference temperature, $T = 298.15$ K. Corrections to standard state at 298.15 K, require information on the heat capacities of the condensed and gas phases, and the knowledge of the behaviour of the compounds, as a function of the temperature, in the interval separating the experimental and reference temperatures.

In this work, we report the thermophysical study and behaviour as a function of the temperature, by DSC, of the three isomers of nitrobenzonitrile (Fig. 1).

The study was made in the temperature interval between 268 K and its respective melting temperatures, and the complete morphology of the heat capacity curve for each compound was determined.

Several solid–solid phase transitions, in addition to the fusion one, were found for the 2- and 4-isomers

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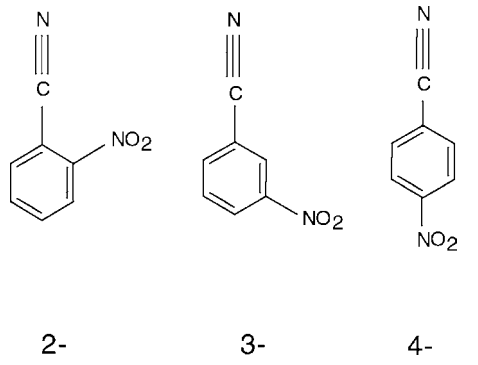

Fig. 1. The 2-, 3- and 4-isomers of nitrobenzonitriles.

and their temperatures, enthalpies and entropies were determined.

No values for any of these magnitudes were found in the literature for comparison with our results.

2. Experimental procedure

The three compounds, were supplied by Aldrich, purity >99% for 2-nitrobenzonitrile, >98% for 3-nitrobenzonitrile and >97% for 4-nitrobenzonitrile. Samples were crystallized three times from ethanol. Purities of the three compounds were assessed using DSC by the fractional fusion technique [4] having <0.001 mole fraction impurities.

A differential scanning calorimeter (Perkin-Elmer Pyris 1) equipped with an intra-cooler unit was used. Its temperature and power scales were calibrated [5,6] at heating rates 0.04, 0.08 and 0.17 K seg^{-1}.

Its temperature scale was calibrated measuring the melting temperature of the recommended high-purity reference materials: benzoic acid, tin and indium [6]. The power scale was calibrated with high-purity indium (mass fraction: >0.99999) as reference material. 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 over the entire temperature range in a nitrogen atmosphere at scanning rates of 0.04, 0.08 and 0.17 K seg^{-1}. For purity determinations and temperatures, enthalpies and entropies of fusion a heating rate of 0.04 K seg^{-1} was used.

For enthalpy transition determinations, four samples weighing 3–5 mg were generally recorded at 0.17 K seg^{-1}. At this heating rate we obtained more defined peaks in the transitions with less transitions enthalpy. The values given are the mean values of the results. The estimated errors were ±0.5 K and about 2% for temperature and enthalpy determinations, respectively. All the pans were weighed 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 [2]. Synthetic sapphire was used as external standard for the heat capacity determinations and benzoic acid was used as reference material [6] 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 260 to its melting temperature using a heating rate of 0.17 K seg^{-1}. Each scan was divided into approximately 30 K runs, overlapping each other to minimize base-line uncertainties. The temperature intervals where heat capacities were measured are: 268–307, 300–345 and 335–378 K for 2- and 3-nitrobenzonitrile and 268–307, 300–345, 335–378 and 370–412 K for 4-nitrobenzonitrile. 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 were ±0.005, ±0.003, ±0.003 J g^{-1} K^{-1} for the 2-, 3- and 4-isomers of nitrobenzonitrile, respectively.

3. Experimental results

In Figs. 1 and 2, the DSC scans obtained for the specified compounds, in heating, using a rate of 0.17 K seg^{-1} are shown. From these results we can see particular aspects of their behaviour.

DSC scan for 2-nitrobenzonitrile shows a transition peak, at $T = 338.1$ K, before its melting process at $T = 382.7$ K. The DSC scan obtained for 3-nitrobenzonitrile shows a well-defined curve for the compound with no phase transitions in the temperature interval between 268 K and its melting temperature, $T = 389.7$ K.

For the 4-nitrobenzonitrile, the DSC scan shows two broad and not well-defined peaks between 335 and

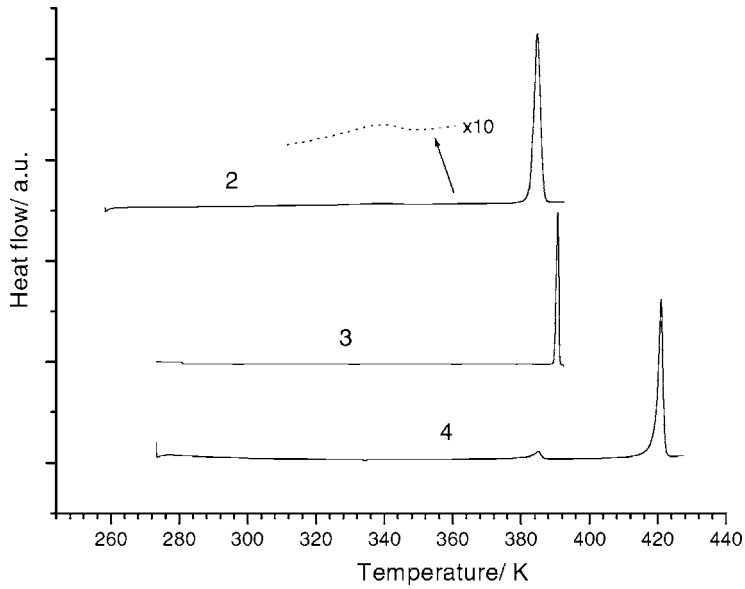

Fig. 2. Plot of the DSC scans obtained for 2-, 3- and 4-nitrobenzonitriles in the temperature intervals between 268 K and after their melting temperatures.

378 K followed by a well-defined one at $T = 386.0$ K and its melting peak at $T = 420.6$ K. A more detailed analysis of the behaviour of this compound in the temperature interval between 335 and 378 K can be seen in Fig. 3 and the two different peaks corresponding at phase transitions IV–III and III–II can be observed. In this temperature interval, four experiments were made and the same behaviour was always observed.

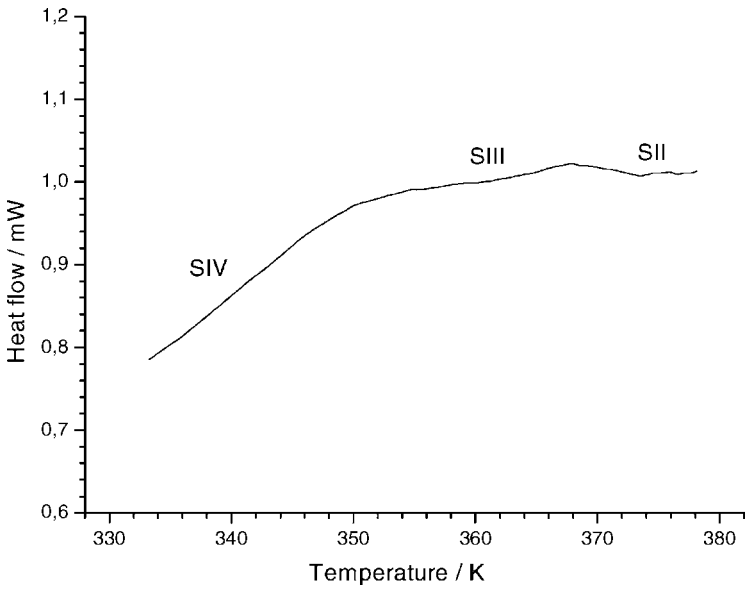

Fig. 3. Expanded plot of the behaviour of 4-nitrobenzonitrile.

Table 1
Purity and thermal functions of the phase transitions of nitrobenzonitriles

Isomer	Purity	Transition	T (K)	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
2	99.96	II–I	338.1 ± 0.7	1.57 ± 0.10	4.66 ± 0.30
		I–IL	382.7 ± 0.1	15.72 ± 0.02	41.08 ± 0.06
3	99.87	I–IL	389.7 ± 0.1	20.49 ± 0.27	52.57 ± 0.69
4	99.92	IV–III	349.0 ± 0.1	0.45 ± 0.02	1.30 ± 0.05
		III–II	366.7 ± 0.1	0.04 ± 0.01	0.10 ± 0.02
		II–I	386.0 ± 0.1	1.01 ± 0.03	2.62 ± 0.08
		I–IL	420.6 ± 0.2	17.73 ± 0.06	42.15 ± 0.14

The different phases found for the three compounds were named following the usual rules and they are represented in the following schemes:

2-nitrobenzonitrile :

$$\text{phase II (II)} \underset{T=338.1\,\text{K}}{\rightarrow} \text{phase I (I)} \underset{T=382.7\,\text{K}}{\rightarrow} \text{isotropic liquid (IL)}$$

3-nitrobenzonitrile :

$$\text{phase I (I)} \underset{T=389.7\,\text{K}}{\rightarrow} \text{isotropic liquid (IL)}$$

4-nitrobenzonitrile :

$$\text{phase IV (IV)} \underset{T=349.0\,\text{K}}{\rightarrow} \text{phase III (III)} \underset{T=366.7\,\text{K}}{\rightarrow} \text{phase II (II)} \underset{T=386.0\,\text{K}}{\rightarrow} \text{phase I (I)} \underset{T=420.6\,\text{K}}{\rightarrow} \text{isotropic liquid (IL)}$$

Table 1 gives the molar percent purities and the experimental values for the temperatures, enthalpies and entropies of the transitions found. The results given are the mean values and standard deviations of four experiments made with fresh samples. The purity of the three nitrobenzonitriles was high enough to achieve reliable data for enthalpies of transitions and heat capacities.

The values obtained from heat capacity measurements for the three isomers of nitrobenzonitrile are given in Table 2 and the heat capacities curves obtained are given in Fig. 4. For 3-nitrobenzonitrile, heat capacity values from temperature $T = 350.2$ K correspond to a premelting process.

The experimental values of the heat capacities have been fitted to polynomial equations by the

Table 2
Experimental molar heat capacities of 2-, 3- and 4-nitrobenzonitriles

T (K)	$C_{p,\text{m}}$ (J K^{-1} mol^{-1})		
	2-Isomer	3-Isomer	4-Isomer
268	155.4	152.0	155.0
270	156.2	152.3	155.9
275	158.4	155.0	158.5
280	161.0	157.5	160.7
285	163.5	159.6	163.1
290	165.8	162.0	165.5
295	168.2	164.0	168.0
298.15	169.8	165.6	168.5
300	170.8	166.5	170.5
305	–	168.2	172.7
310	–	170.4	174.5
315	–	172.2	176.9
320	–	174.6	179.7
325	–	177.2	183.2
330	–	179.0	186.8
335	–	181.9	–
340	–	184.2	–
345	–	187.9	–
350	–	191.4	–
355	205.5	196.2	–
360	207.8	202.9	237.6
365	210.7	213.3	–
370	214.5	226.0	260.9
375	223.6	238.1	276.1
380	–	–	308.6
385	–	–	–
390	–	–	–
395	–	–	230.7
400	–	–	230.2
405	–	–	231.8
410	–	–	233.8
415	–	–	–

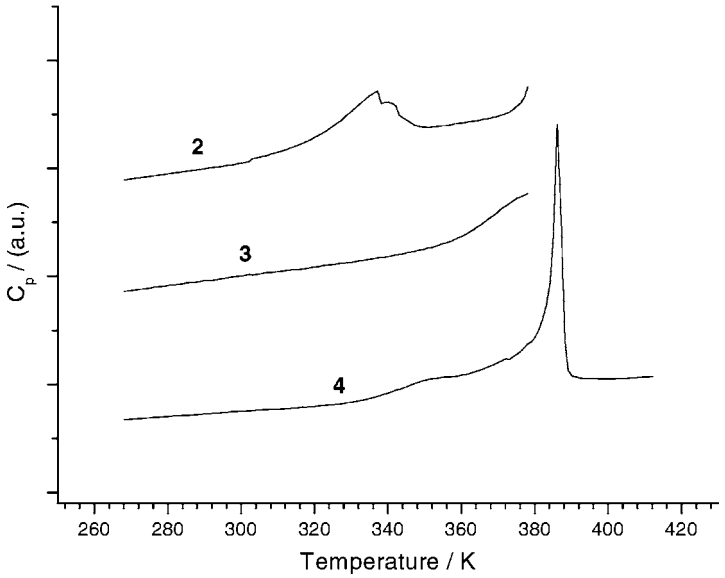

Fig. 4. Experimental heat capacities of the 2-, 3- and 4-nitrobenzonitriles.

least-squares method. For the solid phase II of 2-nitrobenzonitrile, corresponding to the temperature interval between 268.2 and 300.2 K, the experimental heat capacities are represented by the curve

$$C_{p,\mathrm{m}} = 131.2 - 0.2613T + 0.0013T^2$$

For the solid phase of 3-nitrobenzonitrile between 268.2 and 345.2 K

$$C_{p,\mathrm{m}} = 125.2 - 0.1696T + 0.001T^2$$

For 4-nitrobenzonitrile, the calculated polynomial equation for the solid phase IV, corresponding to the temperature interval 268.2–330.2 K

$$C_{p,\mathrm{m}} = 57.1 + 0.2729T + 0.0003T^2$$

By comparison of the values obtained for the heat capacities of 2-, 3- and 4-nitrobenzonitriles, at a temperature of 298.15 K, can be observed that the difference between the values obtained between the 2- and 4-isomers is $1.3\,\mathrm{J\,K^{-1}\,mol^{-1}}$. For comparison between 2- and 3-nitrobenzonitriles this difference increases to $4.2\,\mathrm{J\,K^{-1}\,mol^{-1}}$ being at $T = 298.15\,\mathrm{K}$, $C_{p,\mathrm{m}}(2\text{-}) > C_{p,\mathrm{m}}(4\text{-}) > C_{p,\mathrm{m}}(3\text{-})$.

Acknowledgements

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