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# A calorimetric study of phase transitions for some cyclohexanediols[☆]

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**Abstract**

Phase transitions in solid *cis*-1,2-cyclohexanediol and *trans*-1,2-cyclohexanediol and *cis*/*trans*-1,4-cyclohexanediol have been studied by differential scanning calorimetry over the temperature range 241 to 383 K. Besides a low-temperature crystalline form, DSC curves show the existence of a solid rotator phase in *cis*-1,2-cyclohexanediol whilst for the others, only one solid phase is present. Enthalpies of sublimation and vaporization were determined by evaporation into a vacuum using an isothermal calorimeter.

*Keywords:* Cyclohexane diols; DSC; Enthalpy of sublimation; Enthalpy of vaporization; Isothermal calorimetry; Phase transitions

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## 1. Introduction

Enthalpies of sublimation and vaporization are very useful properties both for the indications they provide on the molecular structure of the phases involved and for calculation of other thermodynamic properties. For instance the usual procedure for determining enthalpies of solvation of solid or liquid non-electrolyte solutes is from the data of the enthalpy of sublimation or vaporization and from the enthalpy of solution, both of which are properties capable of experimental measurement. To refer the enthalpy data to a selected temperature value, accurate heat capacity data are needed.

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The aim of this paper is to present values for the enthalpies of sublimation and vaporization of some cyclohexanediols, data which are needed for the study of solution processes in progress in our laboratory.

Some organic compounds present more than one phase in the solid state. Once this possibility exists, a preliminary thermal study of the compounds must be undertaken in order to determine the limits for the temperature range of each phase. Thus before measuring the enthalpies of sublimation, DSC curves were recorded for the compounds involved in this study.

## 2. Experimental

*cis*-1,2-Cyclohexanediol and *trans*-1,2-cyclohexanediol purchased from Aldrich and *cis*/*trans*-1,4-cyclohexanediol from EGA-Chemie, labelled as 99% pure, were used without any further purification. No impurities were detected by IR spectroscopy and chromatography. Compounds were stored and handled in a dry nitrogen atmosphere.

Thermal studies were carried out with a Perkin-Elmer DSC 7 thermal analysis system over a temperature range from 240 K to the melting point of each compound. The scanning rate was 10 K $\text{min}^{-1}$. For cooling, circulating liquid nitrogen was used with the temperature controlled by a Perkin-Elmer CCA 7 accessory. After the first two cycles had been performed, constancy was obtained and then the DSC curves for heating and cooling runs were recorded. The samples (about 2 mg) were pressed in aluminium pans suitable for volatile substances. Temperature and enthalpy calibrations were performed with indium and zinc standards supplied by Perkin-Elmer for temperatures above 303 K and high grade cyclohexane and dichloroethane for subambient temperatures. Dry nitrogen was used as purge gas (20 $\text{cm}^3\ \text{min}^{-1}$), except in subambient experiments where helium was used. After calibration programmes had been performed seven runs for indium and cyclohexane were carried out. The uncertainties for onset temperatures and enthalpies were as follows: indium (0.18 K, 0.06 J $\text{g}^{-1}$), cyclohexane (0.38 K, 0.6 J $\text{g}^{-1}$). In this paper uncertainties always correspond to twice the standard deviation.

Vaporization and sublimation experiments were carried out with a Setaram C80 calorimeter to which a vacuum system consisting of a model 18 two-stage rotary pump and 500 CR turbomolecular pump from Edwards High Vacuum was coupled. Vacuum down to about $10^{-4}$ Pa was attained. Pressure readings were taken with an Edwards 1001 vacuum controller.

The effusion cell used for vaporization and sublimation was a stainless steel cylindrical tube 12 mm high and 8 mm internal diameter, closed with a threaded lid of the same material and sealed with a 1 mm thick Teflon disc pressed by the lid against the rim of the lower part of the cell. The lid has a central hole and a hole of 0.4 mm diameter was formed in the Teflon disc. The cell containing the sample was inserted at the bottom of a stainless steel cylindrical tube adapted to the size of the hole of the calorimeter block. In order to attain thermal equilibrium more easily, the external diameter of cell was just equal to that of the internal diameter of the tube. The connection to the vacuum line was made through a valve kept closed until thermal equilibrium was reached and then opened for carrying out the measurement. No weight loss of the sample was detected during the time required for thermal equilibration (about 2h).

The enthalpies of sublimation and vaporization were determined at 343 and 383 K, respectively. As *cis*-1,2-cyclohexanediol presents two solid phases, in order to have data for each of these, determinations were made at 343 and 366 K.

Naphthalene and water were used for enthalpy calibration sublimation and vaporization, respectively. The uncertainties for $\Delta_{\text{sub}}H$ of naphthalene and for $\Delta_{\text{vap}}H$ of water were 1.0 and 0.6 kJ mol$^{-1}$, respectively. From the values quoted for $\Delta_{\text{sub}}H$ of naphthalene [1] and $\Delta_{\text{vap}}H$ of water [2] the expected figures were obtained for $\Delta_{\text{sub}}H$ of adamantane [3] and $\Delta_{\text{vap}}H$ of toluene [3].

Under the experimental conditions used sublimation and vaporization were complete. Typical curves of sublimation and vaporization are shown in Figs. 1 and 2 respectively.

## 3. Results

The heating DSC curves of the three compounds studied are given in Fig. 3. The values obtained for the onset temperature and corresponding enthalpy for various phase transitions are presented in Table 1. Fig. 4 contains the cooling DSC curves obtained immediately after the heating run. Several cycles were carried out for each substance.

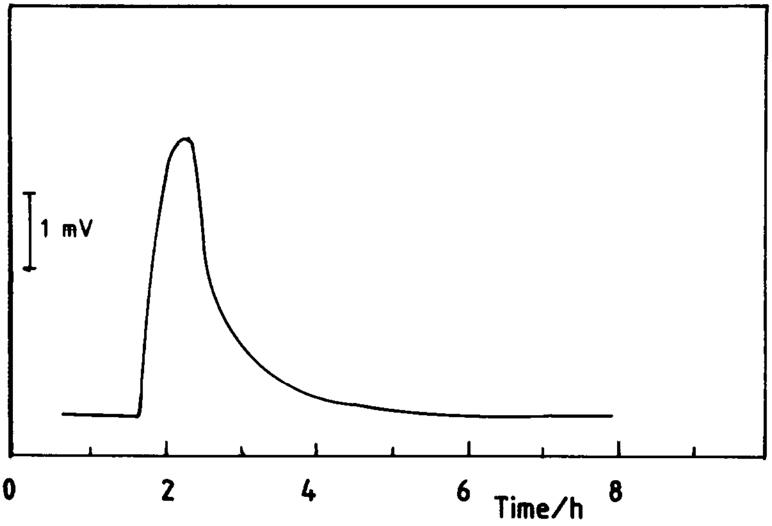

Fig. 1. A typical calorimetric sublimation curve of *trans*-1,2-cyclohexanediol. $T = 343$ K; $m = 0.0136$ g; 1J = 34.13 mV h; $\Delta_{\text{sub}}H = 85.6$ kJ mol$^{-1}$.

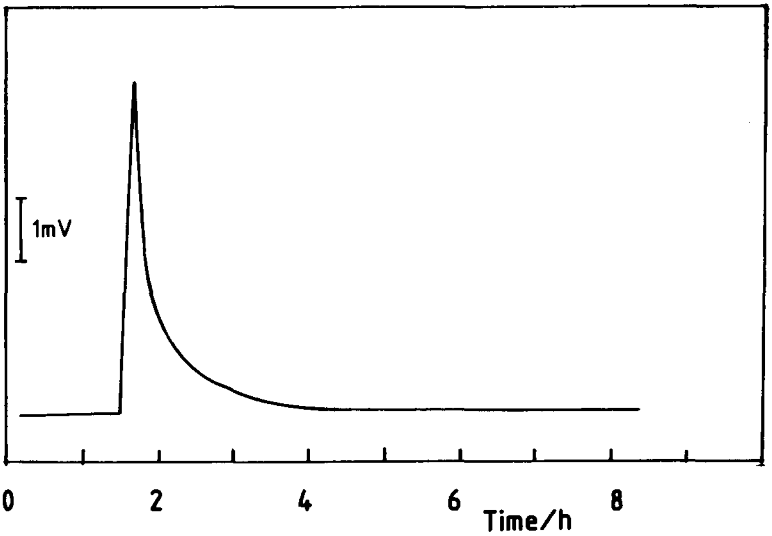

Fig. 2. A typical calorimetric vaporization curve of *trans*-1,2-cyclohexanediol. $T = 383$ K; $m = 0.0106$ g; 1J = 37.45 mV h; $\Delta_{vap}H = 67.7$ kJ mol$^{-1}$.

Table 2 shows the enthalpy of sublimation and vaporization values for the three compounds. The value obtained for the enthalpy of sublimation of the higher temperature *cis*-1,2-cyclohexanediol solid phase (crystal I) was $70 \pm 3$ kJ mol$^{-1}$. This result is not as precise as that given for the lower temperature phases owing to the small range of temperature over which the phase is stable.

## 4. Discussion

*trans*-1,2-Cyclohexanediol and *cis/trans*-1,4-cyclohexanediol do not show any solid–solid phase transitions before melting. The values calculated for entropy of fusion are 49.7 J K$^{-1}$ mol$^{-1}$ for the first and 46.4 J K$^{-1}$ mol$^{-1}$ for the second. These values are similar to those cited for the fusion of organic crystals [4–6].

A rather different pattern is exhibited by the *cis*-1,2-cyclohexanediol since it presents a first endothermic peak at 360.2 K with an entropy variation of 55.2 J K$^{-1}$ mol$^{-1}$, and a second one at 371.4 K with a change of entropy of 8.9 J K$^{-1}$ mol$^{-1}$. These correspond to solid–solid transition and fusion, respectively. By adopting the normal convention concerning the crystalline forms of a solid from higher to lower temperature, one says that the *cis*-1,2-isomer is stable as crystal I in the temperature range between 371.4 and 360.2 to which other crystalline forms are followed to a lower temperature.

It is worth noting that the value obtained for the entropy of the low-temperature crystal to crystal I transition is similar to those obtained for the fusion of the two other compounds and that a very small entropy variation accompanies the crystal I → liquid transformation. This means that crystal I has a structure similar to that of the liquid

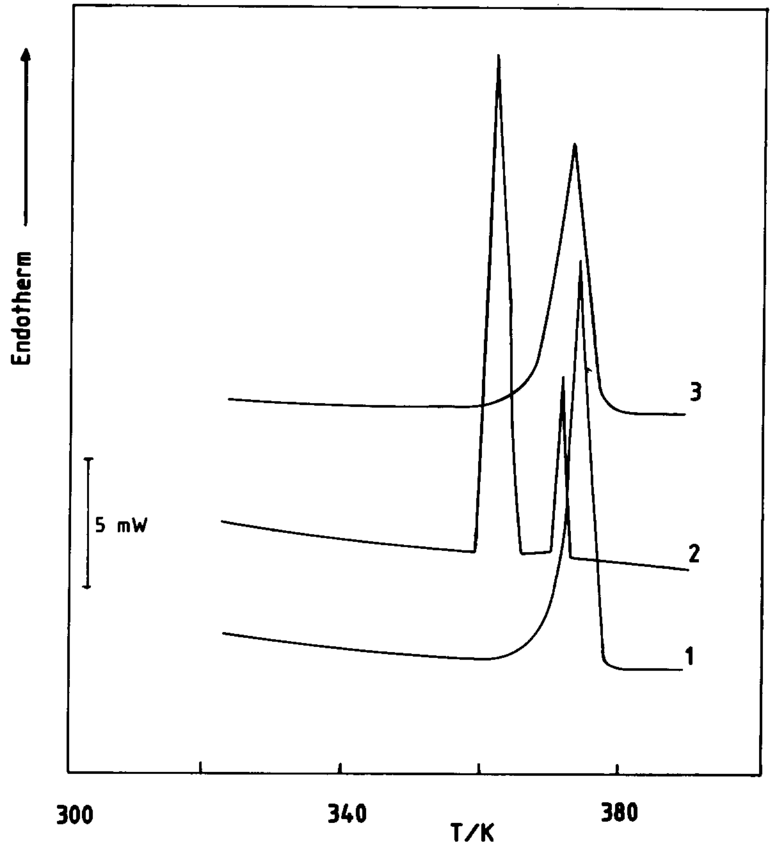

Fig. 3. DSC curves of cyclohexanediols. Heating runs. 1. *trans*-1,2-cyclohexanediol 2. *cis*-1,2-cyclohexanediol 3. *trans*/*cis*-1,4-cyclohexanediol.

phase. It has been proved by increasing the temperature that some solids give rise to a plastic crystal, also called rotator phase, before fusion takes place [7–9].

For polar molecules rotation is followed by an orientational disorder giving rise to an increase of entropy which comes close to that of the liquid state. In conclusion, crystal I of *cis*-1,2-cyclohexanediol is very likely a solid rotator phase. This type of structure has been identified with cyclic alcohols with five to eight carbon atoms in the ring [10–14].

The cooling DSC curve for *trans*-1,2-cyclohexanediol has the common form for organic crystals. A supercooling gap of about 30 K is observed before crystallization takes place. The 1,4 isomer behaves similarly but supercooling is about 40 K and the cooling curve shows a much broader peak.

Again *cis*-1,2-cyclohexanediol shows different behaviour. A first exothermic peak is observed at 367.4 K with an associated entropy variation of 9.0 J $mol^{-1}$ $K^{-1}$, a second at 343.3 K with a very small entropy and finally a large peak appearing somewhere

Table 1
Temperature and enthalpy of phase transitions for cyclohexanediols (heating run unless otherwise specified)

| Compound | $T_{trs}$/K | $\Delta_{trs}H$/(kJ mol$^{-1}$) | $\Delta_{trs}S$/(J K$^{-1}$ mol$^{-1}$) | $\Delta_{fus}H$/(kJ mol$^{-1}$) | $\Delta_{fus}S$/(J K$^{-1}$ mol$^{-1}$) |
|---|---|---|---|---|---|
| *trans*-1,2-Cyclohexanediol | 372.3 | – | – | 18.51 ± 0.03 | 49.7 ± 0.1 |
| *cis*-1,2-Cyclohexanediol | 343.3 [a] | 0.53 ± 0.10 | 1.5 ± 0.3 | – | – |
|  | 360.4 | 19.89 ± 0.22 | 55.2 ± 0.6 | – | – |
|  | 367.4 [a] | 3.05 ± 0.03 | 8.3 ± 0.1 | – | – |
|  | 371.6 | – | – | 3.32 ± 0.05 | 8.9 ± 0.1 |
| *cis*/*trans*-1,4-Cyclohexanediol | 368.7 | – | – | 17.1 ± 0.04 | 46.4 ± 0.1 |

[a] Cooling run.

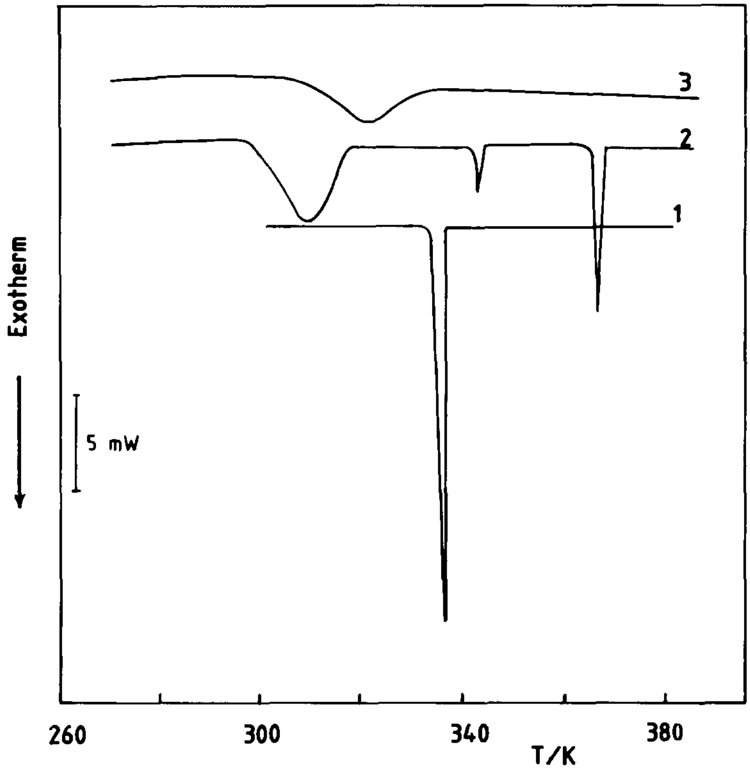

Fig. 4. DSC curves of cyclohexanediols. Cooling runs. 1. *trans*-1,2-cyclohexanediol 2. *cis*-1,2-cyclohexanediol 3. *trans*/*cis*-1,4-cyclohexanediol.

Table 2
Enthalpies of sublimation and vaporization for cyclohexanediols, measured at 343 and 383 K, respectively

| Compound | $\Delta_{sub}H$/(kJ mol$^{-1}$) | $\Delta_{vap}H$/(kJ mol$^{-1}$) |
|---|---|---|
| *trans*-1,2-Cyclohexanediol | 85.9 ± 1.4 | 68.1 ± 1.0 |
| *cis*-1,2-Cyclohexanediol[a] | 88.0 ± 1.9 | 68.2 ± 0.9 |
| *cis*/*trans*-1,4-Cyclohexanediol | 86.5 ± 1.9 | 69.2 ± 0.9 |

[a] Crystal I, $\Delta_{sub}H = (70 \pm 3)$ kJ mol$^{-1}$, measured at 366 K.

between 313 and 323. Svirbely and Goldhagen [15] identified by microscopy three phase transitions for *cis*-1,2-cyclohexanediol. The values of the temperature assigned to the transitions are not in agreement with those obtained in the present work.

The similarity of the values observed for the temperature and entropy for the higher temperature transition of *cis*-1,2-cyclohexanediol on both heating and cooling leads to the conclusion that it corresponds to the transformation of the liquid into crystal I. The transformation of crystal I into a lower temperature crystalline form takes place through the formation of an intermediate crystalline form (crystal II). Apparently this is a metastable form which gradually gives crystal III in the temperature range 313 to 323. Some more information from other techniques will be necessary to understand this behaviour completely.

From the cooling data it follows that supercooling is related to rotational freezing. In fact, supercooling for liquid–solid transformations is high whereas for liquid-to-solid rotator state transition very little supercooling is observed.

The differences in thermal behaviour lie naturally in differences between the molecular and crystal structure of the compounds. In *cis*-1,2-cyclohexanediol the OH groups are attached to the hexyl ring with one in an equatorial position and the other axial, whereas *trans*-1,2-cyclohexanediol is a diequatorial conformer [16, 17].

When the molecules are free, as for example in solution in an inert solvent, both compounds show intramolecular hydrogen bonds, which are stronger in the *cis* than in the *trans* form. No intramolecular bonding was observed for 1,4-cyclohexanediol isomer, as expected [17].

X-ray diffraction data show that the structure of 1,2-cyclohexanediols can be described as consisting of layers of dimers held together in a tridimensional hydrogen-bonding network [18, 19]. The difference between the two structures lies on the intermolecular bonding orientation, although we are unaware of any data on the structure of the 1,4-cyclohexanediol. On the basis of the values obtained for the enthalpies of sublimation in the solid state the three isomers have similar energies.

By increasing the temperature, as the molecular interactions get weaker a solid rotator state can be stabilized in the *cis*-1,2-cyclohexanediol owing to the intramolecular hydrogen bonds. Because in *trans*-1,2-cyclohexanediol these bonds are weak as compared to the *cis* isomer, and in 1,4-cyclohexanediol no intramolecular bonds are present, no solid rotator phase is allowed [17].

The values found for the enthalpies of sublimation corresponding to the low-temperature solid-to-gas phase transition are quite close for the three isomers. The same happens to the enthalpies of vaporization. The crystal I form of *cis*-1,2-cyclohexanediol has a lower value than crystal II, as expected.

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