

THERMODYNAMIC PROPERTIES OF MOLECULAR ORGANIC CRYSTALS CONTAINING NITROGEN, OXYGEN AND SULFUR. III. MOLAR HEAT CAPACITIES MEASURED BY DIFFERENTIAL SCANNING CALORIMETRY

H.G.M. DE WIT, J.C.A. OFFRINGA, C.G. DE KRUIF and J.C. VAN MILTENBURG

Laboratory of General Chemistry, State University of Utrecht, De Uithof, 3584 CH Utrecht (The Netherlands)

(Received 29 November 1982)

ABSTRACT

In this paper we report on the heat capacities of 18 organic compounds, which form molecular crystals, in the temperature interval 300–450 K. The measurements are performed using DSC technique.

INTRODUCTION

This paper is the last in a series of three, concerning the thermodynamic properties of organic crystals. During the last decade it has been shown that the method of atom–atom potentials pioneered by Kitaigorodsky [1] and Williams [2] is a valuable method in obtaining thermodynamic and other (i.e. vibrational) information from the structure of molecular crystals. In our laboratory one of the main objectives is the improvement of this method. This is mainly done by performing calculations of the lattice energy of organic crystals which contain hydrogen bonds. Besides structural information, accurate knowledge of thermodynamic properties is required to meet this goal.

The lattice energy as calculated from the structural data is directly related to the enthalpy of sublimation, an accessible experimental quantity [3]. As already mentioned in part I of this series, where we have reported on the enthalpy of sublimation of 28 compounds, it is necessary to correlate the experimental data of the structure with the thermodynamic data. This is done to ensure that the atom–atom potential parameters are derived from a consistent set of data. In practice this means that the enthalpy of sublimation should be corrected for the contribution of the difference in specific heat between the solid and the vapor phase over a temperature range, which is determined by the temperature of the crystal structure determination and

the temperature at which the enthalpy of sublimation is determined for a compound.

A second reason for the measurement of the specific heat is to establish whether or not a transition has taken place in the temperature interval defined above. If this check is not performed it may happen that the measured enthalpy of sublimation belongs to a crystalline modification other than that of the structure determination. If this is the case, the potential parameters would not be based on the correct correlation. Depending on the position of the temperature interval on the absolute temperature scale, we had to make use of two different methods of obtaining the desired information, notably adiabatic and differential scanning calorimetry. In this paper we will report the specific heat data from those compounds that have their temperature intervals between 300 and 450 K. Results on the remaining compounds are reported in part II of this series [4]. In order to be sure that both sets of calorimetric data were consistent, we included two compounds, maleic anhydride and imidazole, from the adiabatic series in this work.

EXPERIMENTAL

Samples

All compounds used were obtained commercially. They were purified by vacuum sublimation as described in part I of this series [3]. The crystal structures of the samples were checked before and after the measurements by means of X-ray powder diffraction analyses. The same samples as used for the determination of the enthalpy of sublimation, were used, and for maleic anhydride and imidazole the samples from the adiabatic experiments.

Apparatus

A Perkin-Elmer DSC 2 calorimeter was used for the specific heat measurements as a function of temperature. In order to be able to use a sampling method, following a suggestion by Mraw and Naas [5], the DSC 2 was

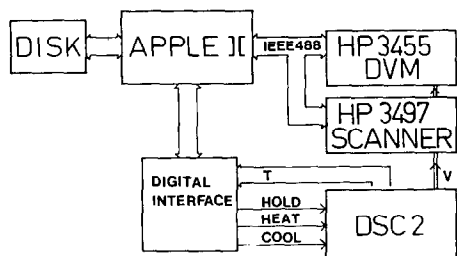


Fig. 1. Schematic diagram of the apparatus.

connected with an Apple II microcomputer via a digital interface. The equipment used is depicted schematically in Fig. 1. The analog signal of the DSC 2 was sampled by the Apple II microcomputer using an HP 3455 A digital voltmeter (via an HP3497 A scanner). All the command and data lines were optically coupled in order to prevent ground loops.

Procedure

To measure the heat capacity of the compound under consideration two successive runs were made: the first with two empty sample containers, and the second with the same containers, one empty and one filled with approximately 15 mg of compound. As the baseline (isothermal) of the DSC changed between these two runs a sampling method had to be used to meet this difficulty. The sampling method implies that before and after a measuring cycle, over a certain temperature interval, the baseline is measured and subtracted from the measured heat capacity values. A typical measuring cycle is shown in Fig. 2, and consists of:

- (1) a stabilization period S , at the end of which the initial value of the isothermal baseline is measured and denoted as M' ;
- (2) to avoid transient effects at the start of the temperature increment period, the values measured over a temperature interval E are neglected;
- (3) after this interval the measuring signal is sampled over a temperature interval M , the highest possible speed, and averaged over 1 K intervals;
- (4) after halting the temperature increase a second stabilization period is entered, at the end of which the final value of the isothermal baseline is measured. Next these two baseline values are linearly interpolated at 1 K intervals, as indicated by the dashed lines in Fig. 2, and subtracted from the averaged analog signal.

In the second run the data from the first run are subtracted point by point from the data from the second one, thus correcting for the heat capacity of the sample container itself. All measurements were made using a heating rate of $5^{\circ}\text{C min}^{-1}$. This led to the optimal values for the intervals S , E and M in Fig. 2 of 60 s, 5 K and 10 K, respectively.

In order to obtain a continuous heat capacity curve, an attempt was made to circumvent the transient interval E . We have tried to achieve this by cooling the sample over the same interval E after completion of the previous

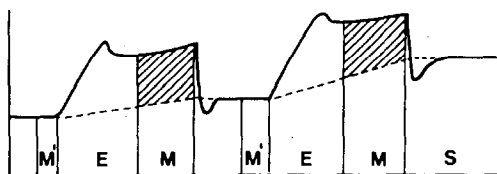


Fig. 2. Display of a typical measurement cycle.

cycle. However, this resulted in a saw-tooth shaped curve instead of a continuous one. This indicates that the DSC loses a great deal of its stability when cooling and heating are alternated.

The total measuring period ($E + M$) was chosen to ensure that the curvature of the baseline still permitted linear interpolation. When a transition was encountered or melting took place, the starting temperature was chosen such that the total effect was included in one interval. The values sampled over 1 K intervals were converted to J K^{-1} by calibration. The calibration was done by measuring a sapphire disk of 12.85 mg and converting the data to heat capacity values, using high precision adiabatic data from the literature [6]. The conversion factor thus obtained at 1 K intervals over the temperature range 300–450 K turned out to be only slightly temperature dependent. A computer program was written, which completely automates the procedure described above.

RESULTS AND DISCUSSION

The experimental data of these compounds that did not show a transition or melting were fitted to a third degree polynomial according to Forsythe [7]. The values of the coefficients of these fits as well as their standard deviations (S.D.) are presented in Table 1, which also includes the values of 1,4 dithiane and squaric acid, because these compounds showed a nearly linear behavior over an appreciable temperature interval. The smoothed data of these compounds are plotted in Fig. 3. The smoothed experimental results of the remaining compounds are reported in Table 2.

The values of the enthalpies of transition and melting as well as the temperatures at which they occur are given in Table 3, which includes, for comparison, literature data and the data concerning maleic anhydride and imidazole from our adiabatic work (see part II of this series [4]). Table 3 also lists values for the transition temperature and the melting temperature of fumaric acid dinitrile. During the experiments serious problems were encountered due to decomposition of the compound, which makes the data unreliable. This is why the data concerning heat capacities and enthalpies of transition and melting of this compound are not reported. Only few specific heat data are available in the literature. Table 1 includes relative deviations of our data compared to those from the literature averaged over the same temperature interval as used during the experiments. The overall agreement is good, except for succinic acid and s-trithiane. Concerning the former compound we feel that the high precision data of Van der Zee and Westrum [11] obtained by adiabatic calorimetry should be preferred.

s-Trithiane is a story of its own, there is a huge difference between the specific heat data found by Nadkarni and Schultz [12], also using a DSC technique, and our data. To illustrate this difference we recall the values

TABLE 1

Coefficients of a third degree polynomial fit in the temperature range 300–450 K

| Compound | A | B | C | $D \times 10^5$ | S.D. | Deviation compared to lit. data |
|--|------------|---------|----------|-----------------|------|---------------------------------|
| (a) Dicyanodiamide | -621.9 | 5.266 | -0.01263 | 1.0581 | 0.18 | 5% [8] |
| (b) Diglycollic anhydride | 4503.7 | -42.983 | 0.14006 | -14.9338 | 0.22 | |
| (c) 1,4 Dithiane | -4165.9 | 36.618 | -0.10507 | 10.2281 | 0.42 | |
| (d) Dithiooxamide | -1322.8 | 12.236 | -0.03512 | 3.4653 | 0.76 | |
| (e) Furane- α , α -dicarboxylic acid | -1075.0 | 9.476 | -0.02433 | 2.1845 | 0.74 | |
| (f) Hexamethylene-tetramine | -1886.4 | 16.187 | -0.04351 | 4.0576 | 0.26 | 3% [4] |
| (g) Oxamide | -551.7 | 4.534 | -0.01029 | 0.8183 | 0.33 | |
| (h) Squaric acid | 984.7 | -8.509 | 0.02642 | -2.5716 | 0.18 | 2% [10] |
| (i) Succinic acid | -3259.8 | 28.214 | -0.07837 | 7.4061 | 0.57 | 7% [11] |
| (j) Tetracyanoethylene | -402.4462 | 2.691 | -0.00024 | -0.1888 | 0.76 | |
| (k) Thiourea | -1159.5333 | 10.081 | -0.02720 | 2.4957 | 0.29 | |
| (l) 1,3,5 Trithiane | -1354.6782 | 11.573 | -0.03018 | 2.6980 | 0.39 | ^a |

^a See text.

found for the specific heat at 400 K: $C_p(s) = 29.5 \text{ J mole}^{-1} \text{ K}^{-1}$ (Nadkarni) and $C_p(s) = 185.5 \text{ J mole}^{-1} \text{ K}^{-1}$ (this work). We feel that the value found by Nadkarni et al. is definitely too low. This suggestion is corroborated by results obtained by Van Miltenburg [13] using high precision calorimetry. For instance the value found in this work for the specific heat at 355 K was: $C_p(s) = 185.92 \text{ J mole}^{-1} \text{ K}^{-1}$, whereas we found a value of $160.7 \text{ J mole}^{-1} \text{ K}^{-1}$ at the same temperature. We therefore consider our values to be the preferred ones.

Concerning the enthalpies of transition and melting, the only data available from the literature beyond the data from our adiabatic work are those about squaric acid and maleic anhydride. The enthalpy of transition of squaric acid reported in Table 3 was calculated from the relation $\Delta H_t = T\Delta S_{tr}$, and the ΔS_{tr} value found by Barth et al. [10]. Vilcu et al. [14] report a value of $8.79 \text{ kJ mole}^{-1}$ for the enthalpy of melting of maleic anhydride using a DTA method. We consider this value to be too low because Marchidan [14] found a value of $12.25 \text{ kJ mole}^{-1}$ which is more in accordance with the value we found of $13.55 \text{ kJ mole}^{-1}$ from our adiabatic work

TABLE 2

Smoothed experimental heat capacities

| T (K) | C_p (J K ⁻¹ mole ⁻¹) | T (K) | C_p (J K ⁻¹ mole ⁻¹) | T (K) | C_p (J K ⁻¹ mole ⁻¹) |
|-----------------------|--|------------|--|------------|--|
| <i>Cyanoacetamide</i> | | | | | |
| 300.0 | 111.1 | 345.0 | 173.6 | 385.0 | 204.1 |
| 305.0 | 115.7 | 350.0 | 373.0 | 390.0 | 757.3 |
| 310.0 | 118.2 | 355.0 | 284.1 | 395.0 | 3262.9 |
| 315.0 | 120.5 | 360.0 | 146.9 | 400.0 | 638.9 |
| 320.0 | 123.0 | 365.0 | 139.0 | 405.0 | 194.3 |
| 325.0 | 125.2 | 370.0 | 141.2 | 410.0 | 195.3 |
| 330.0 | 127.0 | 375.0 | 146.6 | 415.0 | 196.1 |
| 340.0 | 133.6 | 380.0 | 158.0 | 420.0 | 196.6 |
| <i>1,3-Dithiane</i> | | | | | |
| 300.0 | 113.9 | 325.0 | 487.2 | 350.0 | 174.9 |
| 305.0 | 132.1 | 330.0 | 2196.3 | 355.0 | 179.2 |
| 310.0 | 156.0 | 335.0 | 743.2 | 360.0 | 181.7 |
| 315.0 | 190.8 | 340.0 | 175.4 | 365.0 | 183.0 |
| 320.0 | 146.9 | 345.0 | 176.3 | 370.0 | 185.0 |
| <i>1,4-Dithiane</i> | | | | | |
| 300.0 | 129.8 | 335.0 | 157.4 | 370.0 | 183.4 |
| 305.0 | 136.0 | 340.0 | 161.0 | 375.0 | 189.0 |
| 310.0 | 140.1 | 345.0 | 163.8 | 380.0 | 223.8 |
| 315.0 | 143.7 | 350.0 | 167.3 | 385.0 | 6118.9 |
| 320.0 | 147.8 | 355.0 | 171.0 | 390.0 | 201.9 |
| 325.0 | 151.6 | 360.0 | 175.3 | 395.0 | 201.7 |
| 330.0 | 155.2 | 365.0 | 180.1 | 400.0 | 202.7 |
| <i>Pyrazole</i> | | | | | |
| 300.0 | 87.9 | 330.0 | 124.4 | 360.0 | 150.4 |
| 305.0 | 93.1 | 335.0 | 410.6 | 365.0 | 151.5 |
| 310.0 | 96.7 | 340.0 | 4318.5 | 370.0 | 151.4 |
| 315.0 | 101.1 | 345.0 | 146.9 | 375.0 | 152.6 |
| 320.0 | 106.3 | 350.0 | 149.8 | 380.0 | 153.8 |
| 325.0 | 111.4 | 355.0 | 149.0 | 385.0 | 154.9 |
| <i>Squaric acid</i> | | | | | |
| 315.0 | 121.6 | 385.0 | 159.0 | 445.0 | 162.7 |
| 320.0 | 124.1 | 390.0 | 154.6 | 450.0 | 163.4 |
| 325.0 | 126.6 | 395.0 | 153.5 | 455.0 | 165.3 |
| 330.0 | 129.2 | 400.0 | 153.7 | 460.0 | 166.2 |
| 335.0 | 132.01 | 405.0 | 154.4 | 465.0 | 167.7 |
| 340.0 | 134.32 | 410.0 | 154.9 | 475.0 | 169.7 |
| 345.0 | 137.9 | 415.0 | 156.4 | 480.0 | 170.8 |
| 350.0 | 139.9 | 420.0 | 157.6 | 490.0 | 172.5 |
| 355.0 | 142.3 | 425.0 | 158.7 | 495.0 | 172.6 |
| 360.0 | 145.1 | 430.0 | 159.5 | 500.0 | 172.3 |
| 365.0 | 148.0 | 435.0 | 160.7 | 505.0 | 172.2 |
| 370.0 | 151.3 | 440.0 | 161.7 | 510.0 | 173.4 |
| 375.0 | 156.0 | | | | |

TABLE 2 (continued)

| T (K) | C_p ($J K^{-1} mole^{-1}$) | T (K) | C_p ($J K^{-1} mole^{-1}$) | T (K) | C_p ($J K^{-1} mole^{-1}$) |
|-------------------------|-----------------------------------|------------|-----------------------------------|------------|-----------------------------------|
| <i>Maleic anhydride</i> | | | | | |
| 310.0 | 123.2 | 330.0 | 3210.6 | 345.0 | 164.9 |
| 315.0 | 127.4 | 335.0 | 175.7 | 350.0 | 166.2 |
| 320.0 | 131.5 | 340.0 | 175.9 | 355.0 | 167.9 |
| <i>Imidazole</i> | | | | | |
| 310.0 | 94.4 | 340.0 | 110.1 | 365.0 | 966.1 |
| 315.0 | 97.2 | 345.0 | 113.6 | 370.0 | 1892.5 |
| 320.0 | 99.8 | 350.0 | 119.4 | 375.0 | 159.5 |
| 325.0 | 102.6 | 355.0 | 126.2 | 380.0 | 162.6 |
| 335.0 | 107.5 | 360.0 | 181.9 | 385.0 | 166.2 |

[4] as well as in this work of $13.6 \text{ kJ mole}^{-1}$. Both the results on the heat capacity measurements and the enthalpies of transition and melting have shown that the sampling technique provides a reliable and fast method for the determination of the heat capacities and related phenomena.

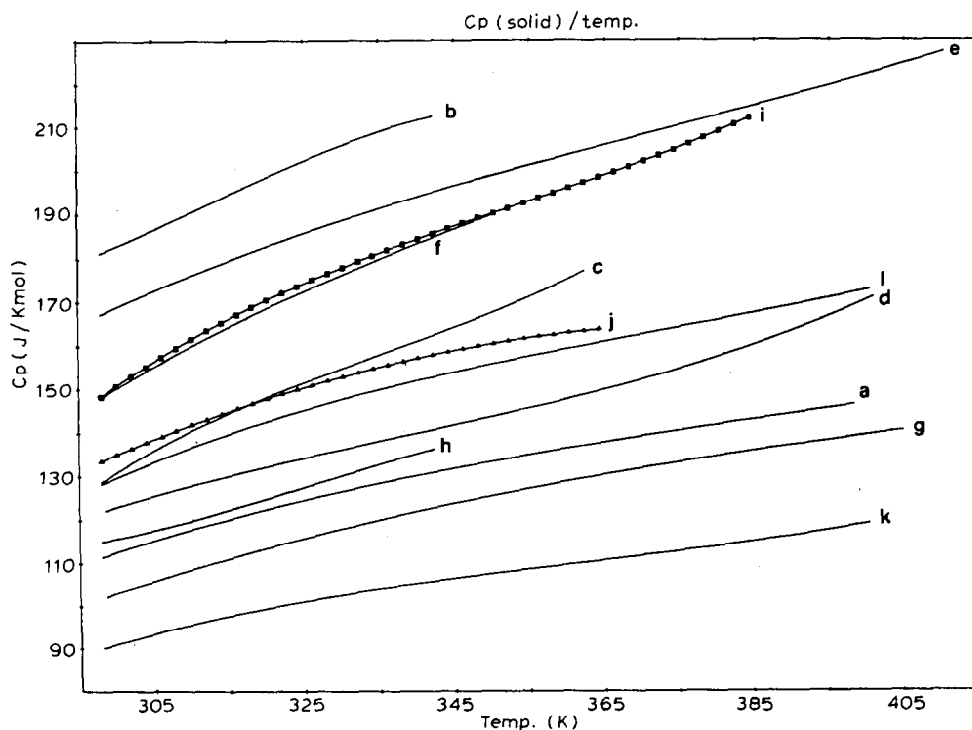


Fig. 3. Smoothed C_p curves vs. temperature of the substances in Table 1. The letters identifying the curves correspond to those in Table 1.

TABLE 3
Temperatures and enthalpies of transition and melting

| Compound | T_{trs} (K) | T_{fus} (K) | ΔH_{trs} (kJ mole ⁻¹) | ΔH_{fus} (kJ mole ⁻¹) | T_{trs} (lit.) (K) | T_{fus} (lit.) (K) | ΔH_{trs} (lit.) (kJ mole ⁻¹) | ΔH_{fus} (lit.) (kJ mole ⁻¹) |
|-----------------------|------------------|------------------|--|--|-------------------------|-------------------------|---|---|
| Cyanoacetamide | 346.5 | 387.3 | 1.2 | 21.7 | | | | |
| 1,3-Dithiane | 316.4 | 327.2 | 0.8 | 14.4 | | | | |
| 1,4-Dithiane | | 384.6 | | 21.6 | | | | |
| Fumaric acid dinitril | 318.9 | 370.0 | | | | | | |
| Pyrazole | | 333.1 | | 13.8 | | | | |
| Squaric acid | 372.2 | | 0.3 | | 373.57 [10] | | 0.35 [10] | 13.55 [4] 8.79 [14] |
| Maleic anhydride | | 325.3 | | 13.6 | | 325.72 [4] | | 12.25 [14] 12.82 [4] |
| Imidazole | | 361.9 | | 12.8 | | 362.69 [4] | | |

ACKNOWLEDGEMENTS

We thank the Dutch Organization of Pure Research (Z.W.O.) for financial support, and Prof. A.F. Peerdeman for critically reading the manuscript.

REFERENCES

- 1 A.I. Kitaigorodsky, *Molecular Crystals and Molecules*, Academic Press, New York, 1963.
- 2 D.E. Williams, *Acta Crystallogr.*, Sect. A, 28 (1972) 629.
- 3 H.G.M. De Wit, C.G. De Kruif and J.C. Van Miltenburg, *J. Chem. Thermodyn.*, in press.
- 4 H.G.M. De Wit, C.G. De Kruif and J.C. Van Miltenburg, *J. Chem. Thermodyn.*, in press.
- 5 S.C. Mraw and D.F. Naas, *J. Chem. Thermodyn.*, 11 (1979) 567.
- 6 D.C. Gwinning and G.T. Furukawa, *J. Am. Chem. Soc.*, 75 (1953) 522.
- 7 G.E. Forsythe, *Soc. Ind. Appl. Math.*, *J. Num. Anal.*, 5 (1972) 74.
- 8 Landold Bernstein, *Zahlenwerte und Funktionen*, Band II, Teil IV, Springer, Berlin, 1961.
- 9 S.S. Chang and E.F. Westrum, *Phys. Chem.*, 64 (1960) 1547.
- 10 E. Barth, J. Helwig, H. Maier, H. Müses and J. Petersson, *Z. Phys. Chem.*, Abt. B, 34 (1979) 393.
- 11 C. Van der Zee and E.F. Westrum, *J. Chem. Thermodyn.* 2 (1970) 681.
- 12 V. Nadkarni and J. Schultz, *J. Mater. Sci.*, 8 (1973) 525.
- 13 J.C. Van Miltenburg, unpublished results.
- 14 R. Vilcu, S.T. Perisanu and I. Giocazanu, *Bul. Inst. Politeh. Gheorghe Gheorghiu-Dej Bucuresti*, Ser. Chem. Metal., XL (2) (1978) and refs. cited therein.