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COMPUTATION OF HEAT CAPACITIES OF SOLID STATE BENZENE, *p*-OLIGOPHENYLENES AND POLY-*p*-PHENYLENE

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Abstract

Heat capacities (C_p) of solid benzene, biphenyl, *p*-terphenyl, *p*-quaterphenyl, and poly-*p*-phenylene were analyzed using the ATHAS Scheme of computation. The calculated heat capacities based on approximate vibrational spectra of solid benzene and the series of oligomers containing additional phenylene groups were compared to experimental data newly measured and from the literature to identify possible additional large-amplitude motion. The skeletal heat capacity was fitted to the Tarasov equation to obtain the one- and three-dimensional vibration frequencies Θ_1 and Θ_3 using a new optimization approach. Their relationship to the number of phenylene groups n is: $\Theta_1=426.0-150.3/n$; and $\Theta_3=55.4+81.8/n$. Except for benzene, the quantitative thermal analyses do not show significant contributions from large-amplitude motion below the melting temperatures.

Keywords: benzene, biphenyl, heat capacity, poly-*p*-phenylene, *p*-quaterphenyl, *p*-terphenyl

Introduction

Using the ATHAS, the Advanced THermal Analysis System, a data bank has been collected with information on thermodynamic properties of currently nearly 250 linear macro-molecules and small molecules [1]. Recently, heat capacities of the solid states, mesophases, and liquids were collected for two series of oligomers of increasing chain lengths. The first consisted of paraffins up to polyethylene [2], the second of perfluoroparaffns leading to polytetrafluoroethylene [3]. It was found that the same group vibrations could be used to compute the heat capacities of oligomers and polymers, and the skeletal vibrations could be represented for molecules of more than a few atoms by simple functions of the chain length, n. For the paraffins and polyethylene a gradual increase in heat capacity beyond that of the vibrational contribution was found below the melting temperature. This increase in C_p could be attributed to large-amplitude motion, leading to a small amount of conformational disorder [2]. The perfluoroparaffins, in contrast, gain most of their conformational disorder in first-order transitions far below ultimate melting (isotropization) [3]. The behavior of phenylene groups is quite different from the smaller and more flexible CH_2 groups. The connecting bonds between phenylene

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groups have a bond angle of 180°, i.e. there is no deflection of the chain on rotation (no flexibility). In fact poly-*p*-phenylene is not a flexible polymer and decomposes at about 800 K before melting. Rotation of the phenylene groups about their backbone axis is, however, possible and the special effect this causes for the heat capacity is discussed.

In the present paper the connection between measured and calculated heat capacities of solid state of a homologous series of *p*-oligomers containing phenylene groups is estimated using the ATHAS computation scheme. The calculation of the heat capacities of solids have been made using data from literature on benzene [4], *p*-biphenyl, *p*-terphenyl, *p*-quaterphenyl [5–11], poly-*p*-phenylene [1] and also from new measurements from our laboratory [12]. The calculations are based on approximate vibrational spectra for the group vibrations and on skeletal spectra obtained by fitting the experimental heat capacities to the Tarasov equation [13]. The parameters Θ_1 and Θ_3 of the Tarasov equation were found using a new optimization approach [14, 15]. The agreement between calculated and experimented heat capacities is, as usual, better than ±3%. Except for benzene, the analyzed materials can be treated as a homologous series with Θ_1 and Θ_3 changing predictably with the molecular size. Further improvement of the Tarasov equation for ring structures are under consideration [12].

Calculation of the heat capacity for the solids

The computations of heat capacities for solids are based on the ATHAS scheme [16]. First, the low-temperature experimental heat capacities at constant pressure C_p(exp) from 5–300 K are converted to heat capacities at constant volume C_v using the Nernst-Lindemann approximation [17, 18]. The experimental heat capacities C_v(exp) can, next, be separated into contributions from the group vibration C_v(gr) and from the skeletal vibrations C_v(sk). The contribution C_v(gr) is computed using frequencies obtained from normal mode calculations fitted to results from infrared and Raman spectroscopy. After subtracting the heat capacity contributions of the group vibrations from the experimental C_v(exp), C_v(sk) remains. The C_v(sk) is then fitted to the Tarasov function at sufficiently low temperatures to obtain the two characteristic temperatures (frequencies) Θ_1 and Θ_3. The temperature Θ_1 represents the upper frequency limit of the intramolecular vibrations, Θ_3, the upper frequency limit of the intermolecular vibrations.

Once Θ_1 and Θ_3 are established, a heat capacity that corresponds only to the vibrational motion can be calculated with confidence for any temperature. In reverse, the calculated C_v(sk) is added to C_v(gr) to give the total heat capacity C_v(tot). By conversion to constant pressure, C_p(tot) is obtained for comparison with C_p(exp).

For each member of the series of *p*-oligomers the number of normal modes of vibration is 3N. These were separated into group vibrations (N_{gr}) and skeletal vibrations (N_{sk}) based on the chemical structure. For example, solid benzene with $N=12$ atoms has 36 normal modes of vibrations, which split into 30 group vibrations and 6 skeletal vibrations (3 of translational and 3 of rotational types of the molecule as a whole) [19]. For the other members of the *p*-oligophenyls, each additional C_6H_4 group adds 25 group vibrations and 5 skeletal vibrations as derived in [20]. In previous calculations for polymers with phenylene groups, we added two low frequency modes to the group vibrations with frequencies of 60–90 K to match the poly-*p*-phenylene normal mode calculations [21]. In the present calculations these were added to the skeletal modes and fitted to the Tarasov function. The approximate group vibration frequencies have been taken from normal mode analyses for C_6H_6 [19] and for C_6H_4 as of poly-*p*-phenylene [21] as listed in Tables 1 and 2.

Table 1 Group vibration of benzene

Vibrational mode*	Frequency/K	N_{gr}
C–H stretch (2,7A, 7B, 13, 20A, 20B)	4405	6
C–H bend, C–C stretch (14)	2430	1
C–H bend, C–C stretch (8A, 8B)	2290	2
C–H bend, C–C stretch (19A, 19B)	2140	2
C–H bend, C–C stretch (3)	1870	1
C–H bend (9A, 9B)	1695	2
C–H bend (15)	1680	1
C–H bend/ring motion (18A, 18B)	1490	2
C–H wag/ring motion (5)	1460	1
ring breathing (12)	1450	1
ring deformation (1)	1430	1
C–H wag/ring motion (17A, 17B)	1420	2
C–H wag/ring motion (10A, 10B)	1220	2
C–H wag/ring motion (4)	990	1
C–H wag/ring motion (11)	965	1
C–C–C bend (6A, 6B)	870	2
C–H wag/C–C–C bend (16A, 16B)	580	2

* The number in parentheses correspond to the mode assignment in [19] the designation of the atomic motions is approximate, see also [20].

Results

The experimental results of the transition behavior and heat capacities of *p*-terphenyl and *p*-quaterphenyl were obtained by DSC and adiabatic calorimetry and in the process of being reported [12]. These data were combined with all information on *p*-oligophenyls available in literature [4–11] for computation. The low-temperature experimental heat capacity contributions to the skeletal heat capacities from 5–200 K were fitted to the Tarasov function as outlined above. Table 3 presents the Θ values. Next, the vibrational heat capacities (C_p) were calculated for the whole range of temperatures (0.1–1000 K) using the parameters from Table 3. The comparison of experimental and calculated heat capacities for the solids is presented in Fig. 1. The average and RMS errors between the experimental and calculated heat

Table 2 Group vibration of phenylene

Vibrational mode*	Frequency/K	N_{gr}
2, 7B, 13, 20B	4425	4
8A	2352–2389	1
8B	2369–2379; 2284–2369	0.3; 0.7
19A	2172; 2172–2251; 2251	0.26; 0.55; 0.19
14	2071; 2071–2136	0.44; 0.56
3	1910; 1910–1966; 1966	0.29; 0.50; 0.21
7A	1838–1854	1
19B	1824–1854	1
9A	1621	1
15	1546	1
18A	1480–1512	1
12	1392; 1392–1464; 1464	0.22; 0.55; 0.23
17A	1382	1
5	1359	1
10A	1200	1
17B	1136–1207	1
1	1162–1217; 932–1162; 926–932	0.33; 0.56; 0.11
4	1016–1093	1
6A	866–892	1
16A	659–770; 770–806	0.56; 0.44
6B	636–662; 439–636; 433–439	0.30; 0.59; 0.11
16B	577	1

* The numbers correspond to those in [19], approximate motion can be taken from Table 1, see also [20]. The vibrations 5, 7A, 17B, 9B, 10B, 11, 18B and 20A are most reduced in frequency due to the substitution in the 1, 4 positions; the last 5 are for this reason taken as additional skeletal vibrations.

Table 3 Parameters used for the C_p calculation

Sample	N_{gr}	N_{sk}	T_m/	Θ_1/	Θ_3/	$A_0\times10^{-3}$/
				K		K mol J^{-1}
benzene	30	6	278.7	182.3	137	8.0
biphenyl	55	11	344.1	346.2	59.6	3.9
p-terphenyl	80	16	486.4	370.9	80.2	3.9
p-quaterphenyl	105	21	591.0	403.0	79.0	2.5
poly(*p*-phenylene)[b]	25	5	≈1000[a]	420.0	(54.0)	3.9

[a] from the extrapolation [22].

[b] Per repeating unit C_6H_4.

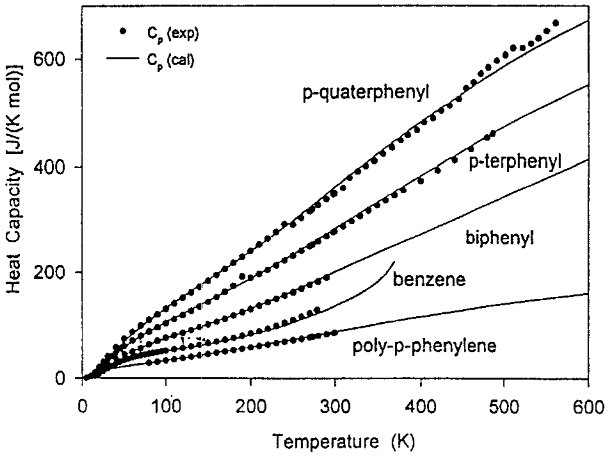

Fig. 1 Experimental and calculated heat capacities of solids for the series of *p*-oligophenyls

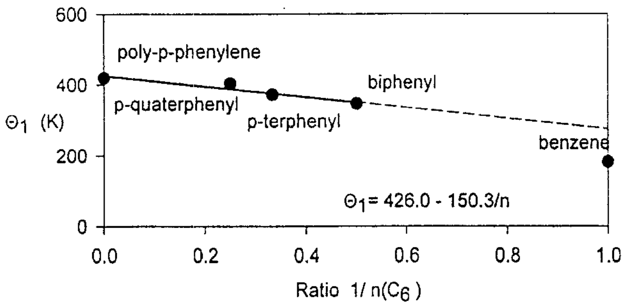

Fig. 2a Plot of Θ_1 *vs.* $1/n$. The lines correspond to the indicated equations

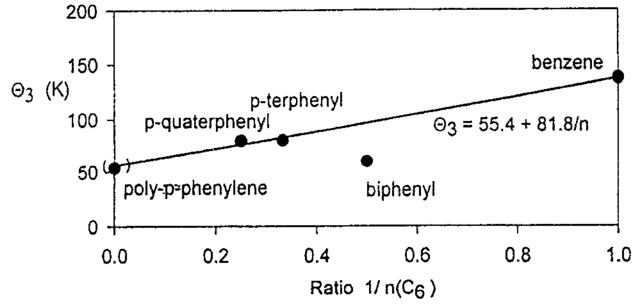

Fig. 2b Plot of Θ_3 *vs.* $1/n$. The lines correspond to the indicated equations

capacities of solid benzene to poly-*p*-phenylene are 0.1±3.2% between 5 and 300 K. Empirical relationships between characteristic parameters Θ_1 and Θ_3 and the fraction of phenyl groups in the molecule n are shown in Fig. 2. The correlation is:

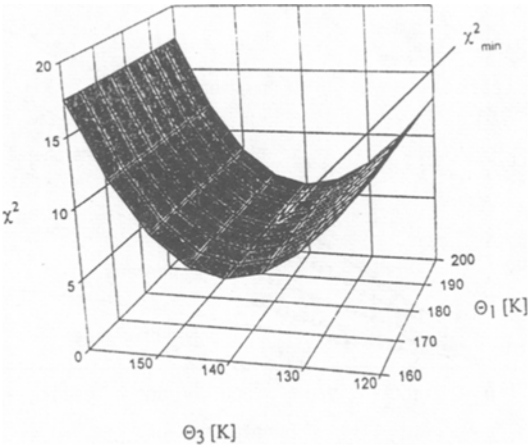

Fig. 3 Example plot of the fit of the experimental skeletal heat capacity to the Tarasov function; χ^2 is linked to the standard deviation σ_i by the equation given, which is a sum over all temperatures T_i:

$$\chi^2 = \sum\{[C_v(\mathrm{sk})_{\mathrm{exp}}(T_i) - C_v(\mathrm{sk})_{\mathrm{calc}}(T_i,\Theta_3,\Theta_1)]/\sigma_i\}^2$$

$\Theta_1 = 426.0-150.3/n$ and $\Theta_3 = 55.4+81.8/n$ for $n \geq 2$. Knowing Θ for all values of n, it is possible to predict heat capacities and all thermodynamic functions of the unmeasured members of the series *p*-oligophenyls.

Discussion

For all calculations, including the new fitting program for the characteristic temperatures Θ_1 and Θ_3, the commercial software Mathematica™ was used. In comparison to the previous calculations of the ATHAS [27], the calculation of the Debye functions were done using Spence's integral or Janquière's function, and the fitting program to the Tarasov equation was also improved [16, 17] (Fig. 3). The constant A_0 for the conversion of C_p to C_v [18] for benzene was adjusted to 8×10^{-3} J^{-1} K mol which was estimated from the thermodynamic relationship for the solid state, using experimental values for the expansivity ($\alpha=4.78\times10^{-4}$ K^{-1}) and for the compressibility ($\beta=8.37\times10^{-10}$ Pa^{-1}) [23]. The value of A_0 for *p*-quaterphenyl also deviates somewhat from the universal constant ($A_0=3.9\times10^{-3}$ J^{-1} K mol, Table 3). It was chosen for the best fitting of experimental and calculated C_p for the whole range of temperature. With these minor adjustments, a uniform treatment of all *p*-phenyl oligomers and poly-*p*-phenylene is possible (Fig. 1). Starting with $n=2$ the equations in Fig. 2 and Tables 1 and 2 for the group vibrations are sufficient for the calculations. The deviations for $n=1$ (and 2) indicate that these molecules are not sufficiently long (linear) to satisfy the Tarasov equation. The deviations of biphenyl from the other members of the series at low temperatures were noted already by Saito [5, 8, 11]. Similar deviations were observed for the homologous series of paraffins and perfluoroparaffins which needed about six chain atoms until a simple, functional relationship between n and Θ_1 and Θ_3 could be obtained [2, 3]. Advanced programming permitting simultaneous fitting of the experimental skeletal heat capacity to Θ_1, Θ_2, and Θ_3 may be more suitable for the short-chain oligomers [15]. The two-dimensional Debye function is well suited to represent two-dimensional structures with the characteristic temperature Θ_2. The corresponding Tarasov function has been used successfully in the past to distinguish between two- and three-dimensionally strongly bound solids [24].

Several discussions of the experimental results of transitions and heat capacities of the series of *p*-oligophenyls exist in the literature [4–11]. Earlier calculations of the heat capacities from benzene to *p*-quaterphenyl had made using the Debye or Einstein model [5–8]. The fittings involved, however, only short temperature ranges, using the functions empirically without microscopic interpretation. For benzene, the calculations of the heat capacity using Tarasov equation with Θ_1 and Θ_3 can be compared with the estimates from the three-dimensional Debye contribution. The differences are small. The Debye characteristic temperature is $\Theta_D = 155$ K, which is close to the low temperature limit of the Tarasov equation $(\Theta_1 \Theta_3^2)^{1/3} = 151$ K. This result indicates that the skeletal heat capacity of solid benzene can be approximated as well by the classical Debye function, as is typical for small molecules in the solid state.

All heat capacities, except for benzene, seem to show no systematic deviations from the vibrational heat capacity up to 300 or 450 K ($n=\infty$, 2 or $n=3$, 4, respectively, Fig. 1). This indicates no major increase in entropy beyond the vibrational contribution. It does not mean, however, that the phenylene and phenyl groups may not jump about their chain axes. After a 180° jump, an undistinguishable position is reached, negating any entropy contribution as long as the time in the intermediate rotation angles is negligible [24]. Only direct determination of the motion, as with solid state NMR, can resolve this problem. For benzene, the difference between experimental and calculated heat capacity starts at about 100 K and has been identified as a beginning jump-type reorientation about the six-fold axis normal to the plane of the benzene ring which changes with temperature to rotation, with the corresponding higher entropy [25]. Solid state NMR provided the supporting evidence [26].

The increase of Θ_1 in Fig. 2a appears reasonable if one considers that the intramolecular chain stiffness within the crystal increases with chain length. The values of Θ_3, in contrast, determined by the intermolecular interaction, decrease (Fig. 2b). One might expect such change from the increase in mass involved in vibrations of the molecules as a whole. This observation is, however, contrary to behavior of Θ_3 for the *n*-paraffin homologs [2]. One must note for the discussion of Θ_3 that the value for poly-*p*-phenylene is still uncertain since its experimental heat capacities start only at 80 K. It may, in addition, be necessary to amend the Tarasov equation to account for the ring-nature of the chain. Work in this direction is in progress [12].

It is now also possible to establish the enthalpy, entropy and free enthalpy from the heat capacities and the transition parameters. Results are listed in the WWW version of the ATHAS data bank [1] and will be discussed in detail in [12].

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