

HEAT CAPACITIES OF DIPHENYL, *p*-TERPHENYL AND *p*-QUATERPHENYL FROM 180 K TO THEIR MELTING POINTS

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The heat capacities of diphenyl, *p*-terphenyl and *p*-quaterphenyl from 180 K to their melting points were measured with a Perkin–Elmer DSC 1B scanning calorimeter. Anomalies were observed in the heat capacity curves for *p*-terphenyl (from 400 K to the melting point) and *p*-quaterphenyl (from 190 to 260 K, and from 450 to 540 K). It is assumed that the anomalies near the melting points of the compounds under consideration could be related both to modification of the motion of the phenyl rings (external or/and internal) and to change in the motion of the molecules as a whole (diffusion phase).

The molecules of linear polyphenyls, either free or contained in crystals, are known to be not exactly planar. The changes in the molecular configurations result in phase transitions at about 40 K [1, 2], 190 K [3, 4] and 250 K [5, 6] in diphenyl (DPh), *p*-terphenyl (*p*-TPh) and *p*-quaterphenyl (*p*-QPh), respectively. In the high-temperature phase, polyphenyl molecules are reported to be pseudo-planar, but with an unusually large vibrational amplitude of the phenyl rings around the long molecular axis [7]. In the low-temperature phase, the molecules become non-planar and the vibrational amplitude of the phenyl rings decreases to a normal value [8].

The phase transition in diphenyl is regarded as a gradual process [1]. Starting from the statistically planar high-temperature molecular configuration, the two phenyl rings rotate in opposite directions when the temperature decreases below the phase transition. The equilibrium angle between the planes of the rings gradually increases from 0° at 40 K to about 10° at 4.2 K [2]. In the low-temperature modification of *p*-terphenyl the outer rings of the molecule are twisted as a pair with respect to the central ring [8]. The planar configuration revealed by X-ray diffraction for *p*-terphenyl molecules in the high-temperature phase is the statistical average, which arises from the jumps of the central ring between two possible positions [9]. The phase transition in *p*-quaterphenyl, like that in diphenyl, is continuous and occurs over a temperature range of about 40 K [6].

NMR investigations and theoretical calculations of the potential energy with the atom-atom potential method indicate that the reorientation of the central ring of the *p*-terphenyl molecule around the long molecular axis takes place between two potential energy minima of different depths [10]. Reorientation of the central ring of the molecule is correlated with the motion of its closest neighbours, and the shape of the potential energy curve depends on temperature.

It is generally believed that the phase transitions in the polyphenyls are of the second-order type. However, by using simple thermal analysis Cullick and Gerkin [11] found that a first-order phase transition took place at 42.5 K in diphenyl. Unfortunately, relatively few calorimetric studies of these polyphenyls have been carried out and these have concerned the low-temperature region (except for [12]). Dworkin and Cailleau [13] did not observe any specific heat anomalies for diphenyl in the temperature range 10–50 K. On the other hand, Atake and Chihara [14] detected two broad anomalies, at 11 K and 40.4 K, in the C_p curve of diphenyl. The heat capacity measurements on *p*-terphenyl in the temperature range 150–220 K revealed an anomaly at 193.3 K [4].

Although the phase transitions in polyphenyls have received considerable attention, almost all the studies concerned the low-temperature region. Therefore, it was interesting to investigate the phase relations in polyphenyls at increased temperatures, up to the melting points, and especially the measurements of the spin-lattice relaxation time T_1 for *p*-terphenyl and *p*-quaterphenyl indicated the possibility of phase transitions at higher temperatures [10, 15].

Experimental

Diphenyl was purified by twofold sublimation under a vacuum, the initial sublimation step being carried out through activated carbon. *p*-Terphenyl and *p*-quaterphenyl were sublimed only once under a vacuum. Diphenyl and *p*-terphenyl were eventually purified by zone melting; approximately 100 zone passes were made.

The thermal and heat capacity measurements were performed with a Perkin-Elmer DSC 1B apparatus, the masses of samples being 10–20 mg for the heat capacity measurements, and 5–10 mg for DSC. The samples in the form of pressed pellets were sealed in standard aluminium pans. The heat capacity measurements were made on two samples of each compound (two runs were made for each sample) at heating (or cooling) rates of 2 and 4 K min⁻¹. The plots of heat capacity vs. temperature were derived from the results of at least four runs. The standard deviation of C_p measurements was ± 2.5 J K⁻¹ mole⁻¹.

There is quite good agreement between our results for diphenyl and those reported by Huffman et al. [12].

The IR spectrum of *p*-terphenyl in a pressed KBr pellet was recorded by using a Perkin-Elmer model 621 spectrophotometer over the range 400–4000 cm⁻¹ at room temperature.

Results

The heat capacity results for diphenyl, *p*-terphenyl and *p*-quaterphenyl are shown in Fig. 1, together with the expected temperature-dependence of C_p for the compounds under consideration. The expected temperature-dependence of C_p for diphenyl and *p*-terphenyl was calculated according to Einstein's formula:

$$C_v = \sum_{i=1}^N \frac{(h\omega_i)^2}{kT^2} \frac{\exp\left(-\frac{h\omega_i}{kT}\right)}{\left[\exp\left(-\frac{h\omega_i}{kT}\right) - 1\right]^2} \quad (1)$$

where C_v is the heat capacity at constant volume, and ω_i the frequency of the external or internal mode. The values of the heat capacity at constant pressure C_p were calculated by using the empirical Lord's equation, $C_p = C_v + aTC_v^2$, and assuming that $a = 3 \cdot 10^{-7}$ mole J $^{-1}$.

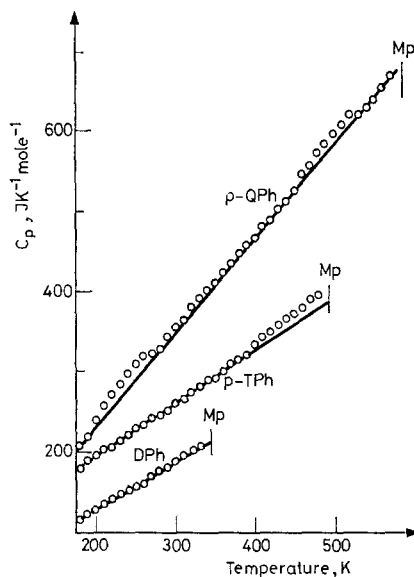


Fig. 1. Temperature-dependence of the heat capacity (C_p) for diphenyl (DPh), *p*-terphenyl (*p*-TPh) and *p*-quaterphenyl (*p*-QPh), plotted from a representative selection of the experimental results (open circles). Solid lines denote the expected temperature-dependences of C_p , calculated by using Einstein's and Lord's formulas for DPh and *p*-TPh and via the polynomial $C_p = -15.458 + 1.27936 T - 0.000158 T^2$ for *p*-QPh

The frequency data for diphenyl were taken as follows: 59 values of intramolecular vibrations from the Raman [16] and IR spectra [17] recorded at room temperature, and 10 modes in the phonon region from an inelastic neutron scattering study at 308 K [18].

The frequency data for *p*-terphenyl were taken as follows: 49 values from the Raman spectrum [6] recorded at 200 K, 11 intramolecular vibrations from the IR spectrum recorded by us at room temperature (450, 573, 673, 690, 750, 913, 1075, 1338, 1380, 1402 and 1943 cm $^{-1}$), and 11 low-frequency modes from refs [19, 20].

All the frequencies used in the C_p calculations were taken from the spectral data obtained for the high-temperature phases of polyphenyls.

Table 1

Temperatures and enthalpies of fusion and solid–solid transitions of diphenyl (DPh), *p*-terphenyl (*p*-TPh) and *p*-quaterphenyl (*p*-QPh)

Compound	Fusion		Transition		Ref.
	T_f , K	ΔH_f , kJ mole ⁻¹	T_t , K	ΔH_t , kJ mole ⁻¹	
DPh	343.3±0.3	19.9±0.6			this work
	344.1±0.2	18.8±0.5			21
<i>p</i> -TPh	493.1±0.3	41.6±0.8	400 to p.m.		this work
	486.3	35.5±1.3			21
			193.3	0.091	4
<i>p</i> -QPh	586.7±0.3	57.6±0.9	190 to 260	approx. 1.1	this work
			450 to 540	approx. 1.0	this work
	587.2	37.8±1.1			21
			230 to 270		6

The expected temperature behaviour of C_p for *p*-quaterphenyl cannot be calculated in the same manner as that for diphenyl and *p*-terphenyl, due to the lack of adequate spectral data. Thus, we estimated the possible course of C_p for *p*-quaterphenyl via the polynomial $C_p = -15.458 + 1.27936 T - 0.000158 T^2$, where the values of coefficients were calculated by the least squares method using our C_p data in the regions 180–190 K, 300–440 K and 530–560 K.

Inspection of Fig. 1 reveals that the heat capacity results for diphenyl are in good agreement with the normal temperature-dependence of C_p as expected on the basis of phonon occupation. However, in *p*-terphenyl a distinct deviation of the experimental C_p values from those expected takes place, starting at about 400 K up to the melting point.

No anomalies in the C_p values for *p*-terphenyl were observed at about 190 K, i.e. at the phase transition temperature as reported by other authors, probably due to the low sensitivity of the DSC 1B calorimeter.

Two broad maxima were observed in the temperature-dependence of the heat capacity for *p*-quaterphenyl: the first in the range 190–260 K, and second between 450 and 540 K. The former is evidently related to the well-known phase transition revealed in *p*-quaterphenyl by spectroscopic investigations [6], while the latter can be regarded as the next phase transition in *p*-quaterphenyl.

The temperatures and the enthalpies of fusion and transitions of the three polyphenyls are collected in Table 1. We note a disagreement between our measurement of the enthalpy of fusion for *p*-quaterphenyl and that reported by Smith [21]. The reason for this difference is not known.

Conclusions

Although the present results do not provide any direct support for the phase transition in *p*-terphenyl above 400 K, we believe that the anomalous increase in the heat capacity of *p*-terphenyl above 400 K cannot be accounted for by a pure thermal effect. Instead, the marked maximum in the temperature-dependence of the heat capacity for *p*-quaterphenyl as observed above 450 K, relates undoubtedly to the new phase transition, which has not been described previously.

The calorimetric measurements reported here do not provide any indications as to the nature of these phase transitions, but in our opinion changes in the molecular motion mechanism take place in both *p*-terphenyl and *p*-quaterphenyl near their melting points. The changes could be related both to modification of the phenyl ring motion (external or/and internal rings) and to the freedom of some translational motions in the crystal lattice (diffusion or nematic phase). The nature of these phase transitions will be discussed in detail elsewhere after completion of NMR measurements.

References

1. P. S. FRIEDMAN, R. KOPELMAN and P. N. PRASAD, Chem. Phys. Lett., 24 (1974) 15.
2. A. BREE and M. EDELSON, Chem. Phys. Lett., 46 (1977) 500.
3. A. GIRARD, H. CAILLEAU, Y. MARQUETON and C. ECOLIVET, Chem. Phys. Lett., 54 (1978) 479.
4. H. CAILLEAU and A. DWORKIN, Mol. Cryst. Liq. Cryst., 50 (1979) 217.
5. J. L. BAUDOUR, Y. DELUGEARD and P. RIVET, Acta Cryst., B34 (1978) 625.
6. B. A. BOLTON and P. N. PRASAD, Chem. Phys., 35 (1978) 331.
7. H. CAILLEAU, J. L. BAUDOUR and C. M. E. ZEYEN, Acta Cryst., B35 (1979) 426.
8. J. L. BAUDOUR, Y. DELUGEARD and H. CAILLEAU, Acta Cryst., B32 (1976) 150.
9. J. L. BAUDOUR, H. CAILLEAU and W. B. YELON, Acta Cryst., B33 (1977) 1773.
10. J. WAŚICKI, Ph.D. Thesis, A. Mickiewicz University, Poznań, 1980.
11. A. CULLIK and R. E. GERKIN, Chem. Phys., 23 (1977) 217.
12. H. M. HUFFMAN, G. S. PARKS and A. C. DANIELS, J. Am. Chem. Soc., 52 (1930) 1547.
13. A. DWORKIN and H. CAILLEAU, J. Phys. Paris, Lett., 41 1980 L83.
14. T. ATAKE and H. CHIHARA, Solid State Commun., 35 (1980) 131.
15. J. WAŚICKI, Z. PAJAK and N. PIŚLEWSKI, Institute of Nuclear Physics Kraków, Report, No 1174/PL (1982) 208.
16. A. BREE, C. Y. EANG and L. RABENECK, Spectrochim. Acta, A27 (1971) 1293.
17. A. BREE, M. EDELSON and R. A. KYDD, Spectrochim. Acta, A31 (1975) 1569.
18. K. KREBS, S. SANDRONI and G. ZERBI, J. Chem. Phys., 40 (1964) 3502.
19. B. WYNCKE, F. BREHAT and A. HADNI, J. Phys. Paris, 38 (1977) 1171.
20. P. A. REYNOLDS and J. W. WHITE, J. Chem. Soc., Faraday Trans. II, 68 (1972) 1434.
21. G. W. SMITH, Mol. Cryst. Liq. Cryst., 49 (1979) 207.

ZUSAMMENFASSUNG — Die Wärmekapazitäten von Diphenyl, *p*-Terphenyl und *p*-Quaterphenyl wurden im Bereich von 180 K bis zum Schmelzpunkt der Verbindungen mit einem Perkin—Elmer DSC 1B Scanning-Kalorimeter gemessen. Anomalien der Wärmekapazitätskurven wurden bei *p*-Terphenyl (von 400 K bis zum Schmelzpunkt) und bei *p*-Quaterphenyl

(von 190—260 K und von 450—540 K) beobachtet. Es wird angenommen, daß die Anomalien nahe der Schmelzpunkte der betreffenden Verbindungen auf Veränderungen der Bewegung der Phenylringe (äußere und/oder innere) und der Moleküle an sich (Diffusionsphase) zurückzuführen sind.

Резюме — С помощью дифференциального сканирующего калориметра Перкин-Эльмер ДСК 1Б была измерена теплоёмкость бифенила, п-терфенила и п-кватерфенила от 180 К до их точек плавления. На кривых теплоёмкости наблюдались аномалии для п-терфенила от 400 К до температуры плавления, для п-кватерфенила — от 190 до 260 К и от 450 до 540 К. Предположено, что наблюдаемые аномалии около точек плавления обусловлены изменением движения фенильных колец (внешним или внутренним), а также изменением движения молекул в целом (диффузионная фаза).