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CROSSOVER OF THE LOW TEMPERATURE HEAT CAPACITIES OF BIPHENYL AND p-TERPHENYL†

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Heat capacities of biphenyl, p-terphenyl, and their deuterated analogues were measured between 3 and 300 K. As the temperature decreases, the heat capacity of biphenyl decreases less steeply than that of p-terphenyl, and they cross each other at 12 K. A simple model calculation of lattice vibration shows that the crossover is due to the greater twisting flexibility of phenyl rings in biphenyl.

Since Cailleau et al.[1,2] discovered the incommensurate structure in crystalline biphenyl, particular attention has been focused on the phase transitions in the first several members of a series of p-polyphenyls (biphenyl, p-terphenyl, and p-quaterphenyl).[3] While these molecules in the gaseous state are of twisted conformation with respect to the torsional angle between the phenyl rings, they crystallize in planar conformation at least on the average at room temperature. On cooling, however, the crystals undergo a phase transition below which the molecules resume twisted conformation.

An order-disorder type of mechanism has been indicated by several experiments[4-9] for the transitions of p-terphenyl at 193.5 K and of p-quaterphenyl at 233.0 K, which are consistent with our thermodynamic studies.[10]

In the case of biphenyl, on the other hand, a displacive type of phase transition occurs at a very low temperature (40.4 K), associated with a soft-mode.[11,12] Furthermore, the new phase is incommensurate[1,2] in both $\mathfrak{a}^*$ and $\mathfrak{b}^*$ directions, and the "lock-in" transition for the $\mathfrak{a}^*$ direction exists at 16.8 K.[13] Recently, such abnormal behavior of crystalline biphenyl has attracted much attention[14-18] and led us to study their thermodynamic properties.[10,13]

In the course of such studies, we obtained an interesting result that the heat capacity curve of biphenyl crosses that of p-terphenyl at about 12 K. This paper presents the low-temperature results on these two substances which we will attempt to relate to the torsional degree of freedom of the phenyl rings that is especially active in the case of biphenyl.

The samples of biphenyl and p-terphenyl used for the calorimetry were purchased from Nakarai Chemicals, Ltd., and their deuterated analogues from Merck Sharp & Dohme Canada, Ltd. (isotope purity of 99% for biphenyl-d_{10} and 98% for p-terphenyl-d_{14}). The specimens were further purified by fractional sublimation in vacuum to the final chemical purity of better than 99.9% as confirmed by gas-chromatography. The adiabatic heat capacity measurements were made in the same way as in

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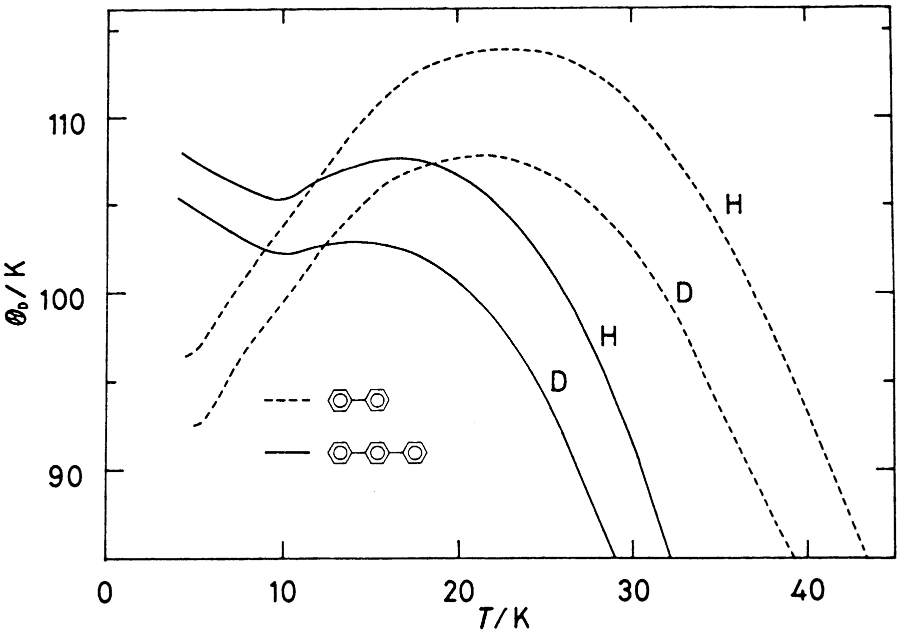

Fig. 1. Debye characteristic temperatures corresponding to the measured heat capacities of biphenyl, p-terphenyl and their deuterated analogues, assuming $6N$ degrees of freedom.

the previous experiments.[13,19] The experimental details will be described elsewhere.[10]

Figure 1 shows the heat capacity results in the form of the Debye temperature for $6N$ degrees of freedom. Below about 20 K, the heat capacity of biphenyl decreases less steeply than that of p-terphenyl as the temperature decreases, and they cross each other at about 12 K. The situation is the same for their deuterated analogues.

Since biphenyl and p-terphenyl have a similar crystal structure and their intermolecular interaction is also similar, one would expect the relative values of their heat capacities are primarily determined by the relative molecular mass, i.e. p-terphenyl would have a consistently larger heat capacity than biphenyl at sufficiently low temperatures where vibrations are considered to be more or less harmonic. Therefore, there must be some motional mode or modes in biphenyl for which the force constant is much smaller than for the corresponding mode(s) in p-terphenyl. We suspected that the torsional mode about the central C-C bond in biphenyl would be the candidate of such a mode in view that the twisted conformation in p-terphenyl has been established below its order-disorder transition in contrast with biphenyl in which the incommensurate structure in the $\mathfrak{b}^*$ direction continues to exist even below 16.8 K.

We then tried to rationalize the observed crossover by a simple model calculation of lattice vibration spectra. For biphenyl, we adopted the average crystal structure at 22 K,[20] ignoring the incommensurability[21] which plays an important role only in the very low temperature region where the contribution of "phason" becomes dominant.[22] The structure of p-terphenyl at 113 K was corrected for thermal expansivity down to 22 K by the method of linear extrapolation.[4,6] The atom-atom pair potential parameters (for C-C, C-H, and H-H) Williams[23] obtained for benzene crystal[24] were used. The interactions were summed over molecules within the radius, 1 nm. Lattice vibration was calculated in the harmonic approximation for 512 points picked up uniformly in the first Brillouin zone. The results of calculation are shown in Figs. 2 and 3. If one ignores the torsional degree(s) of freedom about the bond(s) connecting the phenyl rings, p-terphenyl shows larger heat capacities than biphenyl at all temperatures, as expected from the mass difference. We then attempted to introduce a much greater flexibility in the biphenyl molecule, as compared with the p-terphenyl molecule, with regard to the twisting of phenyl rings by using the same intramolecular contribution, which would lead to a frequency of 60 cm^{-1}, to the overall twisting force constant as in an isolated molecule; the overall force constant includes intermolecular part. The corresponding force constant for p-terphenyl was assumed to be so large that the torsional modes begin to contribute to its heat capacities only at sufficiently high temperatures. If we do it, biphenyl comes to show higher density of states in the low frequency region. On the other hand, p-terpheny has higher density between 25 cm^{-1} and 45 cm^{-1} due to its larger mass. Figure 3 shows the Debye temperature curves calculated from the spectra of Fig. 2 and the greater torsional flexibility in biphenyl is reflected in the crossover in the heat capacities at about 12 K. Now, we conclude qualitatively that the crossover can be attributed to the twisting mode contribution of phenyl rings in biphenyl.

Our interpretation must have a certain consequence at still lower temperatures. Thus, in the low-temperature limit, the heat capacity of p-terphenyl must become

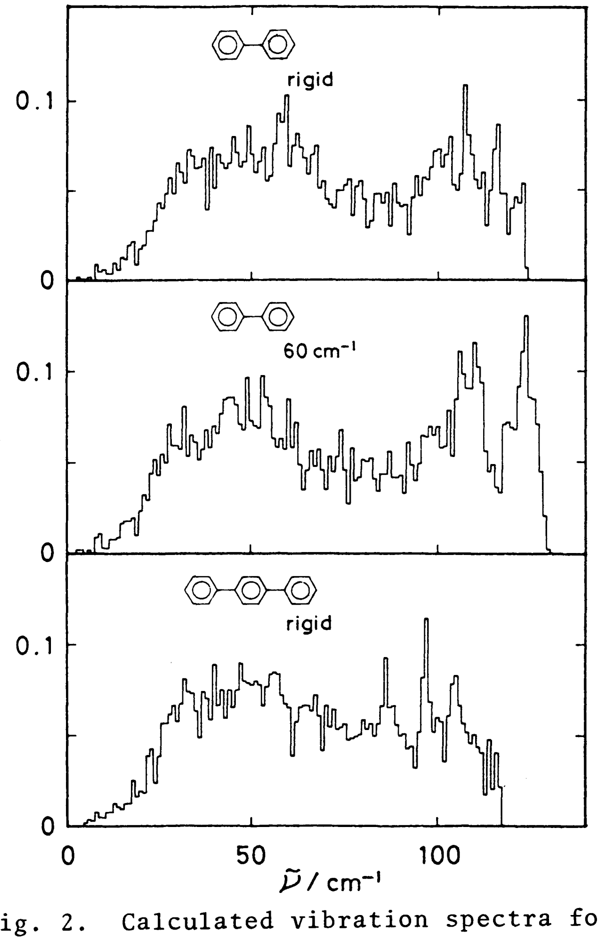

Fig. 2. Calculated vibration spectra for rigid biphenyl, flexible biphenyl, and rigid p-terphenyl.

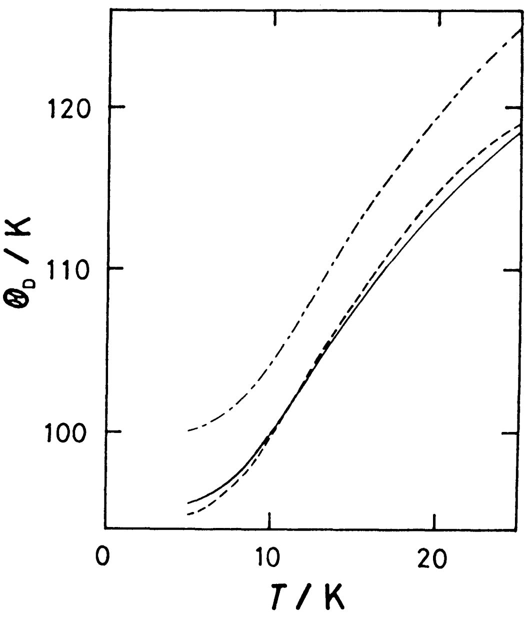

Fig. 3. Calculated Debye characteristic temperatures assuming 6N degrees of freedom. Solid curve; rigid p-terphenyl. Broken curve; flexible biphenyl. Dot-dash curve; rigid biphenyl.

larger than that of biphenyl because flexibility in biphenyl must cease to affect its heat capacity below a certain temperature region where the kinetic energy of torsional motion is not large enough to change the conformation. If the incommensurability is related to the flexibility for the torsional motion in biphenyl, the "lock-in" transition for the $\mathfrak{b}^*$ direction might exist near there.

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