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LOW TEMPERATURE HEAT CAPACITIES OF 1,1'-BIPHENYL AND 1,1'-BIPHENYL-d_{10}[†]

Tooru ATAKE,* Kazuya SAITO, and Hideaki CHIHARA
Chemical Thermodynamics Laboratory and Department of Chemistry, Faculty of
Science, Osaka University, Toyonaka, Osaka 560

Heat capacities of 1,1'-biphenyl-d_{10} were measured between 3 and 300 K and phase transitions were located at 20.2 and 36.8 K with entropies of transition, 0.009 and 0.128 $J \cdot K^{-1} \cdot mol^{-1}$, respectively. Remeasurements of heat capacities of 1,1'-biphenyl-h_{10} below 20 K showed that an anomaly at 11 K previously reported was a false one which probably was due to a defect in germanium thermometer scale. Revised thermodynamic properties relating to phase transitions are given.

The molecular conformation of biphenyl, regarding the twisting degree of freedom of its two phenyl rings, depends strongly on the environment. While the structure is of the twisted symmetry D_2 in the liquid or in the gaseous state, it becomes statistically planar (D_{2h}) in the crystalline state (C_{2h}^5-$P2_1/a$, Z=2)[1-5] at room temperature. On cooling, however, the molecule resumes the D_2 symmetry below a soft-mode phase transition at 40 K.

Since Cailleau et al.[6-8] discovered the incommensurability in biphenyl-d_{10}, many studies on biphenyl by calorimetric,[9,10] optical,[11-13] and other[14-19] techniques have been reported. We also started thermodynamic studies on biphenyl-h_{10}, a part of which has been published preliminarily[10] and then extended the studies to the deuterated analogue (d_{10}). In the mean time, an error was uncovered about the earlier measurements on the h_{10} specimen below 13.81 K, and therefore we have remeasured the heat capacities of h_{10} compound below 20 K in higher precision.

This note presents the low temperature heat capacities of a d_{10} sample and also describes the erratum for our earlier calorimetry on an h_{10} sample.

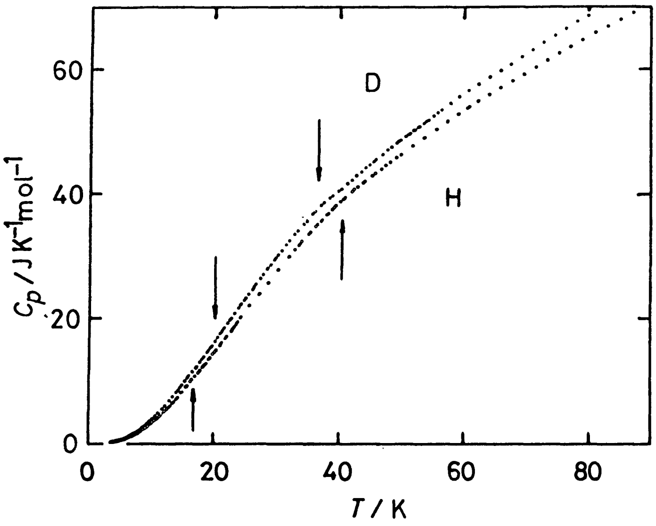

Fig. 1. The low temperature molar heat capacities of biphenyl-h_{10} (○) and -d_{10} (●). The locations of phase transitions are indicated by vertical arrows.

The apparatus and the procedure for the adiabatic heat capacity measurements on biphenyl-d_{10} were the same as for the previous experiments on the h_{10} sample[10,20-23] and we shall not describe them here.

Deuterated biphenyl (99 %) was purchased from Merck Sharp & Dohme Canada Ltd.,

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and was purified by fractional sublimation in vacuum. The isotope purity of the specimen was confirmed as 99 % by the high resolution NMR technique and the chemical purity of the sample used for the calorimetry was better than 99.9 %, which was determined by gas-chromatography. Before calorimeter loading, the specimen was melted and recrystallized again in helium gas and then pulverized gently. The powdered sample loaded into the calorimeter vessel weighed 14.9825 g (0.091206 mol) after correction for the buoyancy effect. The calorimeter vessel was degassed and sealed off after adding a small amount of helium gas (7 kPa at room temperature) for heat exchange. The d_{10} sample contributed about 70 % to the total heat capacity including the calorimeter vessel at 20 K and about 50 % at 50 K. After each heat input, thermal equilibrium within the calorimeter vessel was attained in a few minutes below 20 K and in ten minutes at about 50 K.

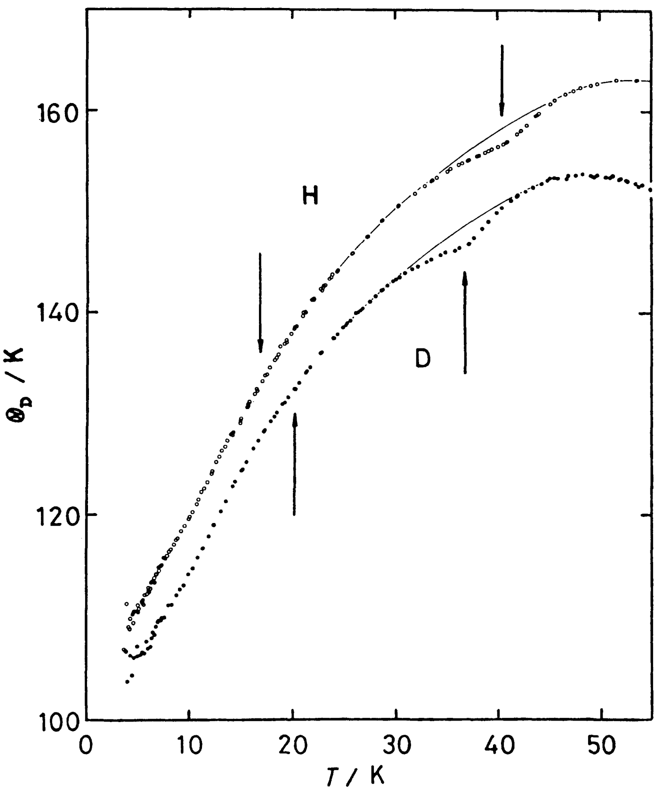

Fig. 2. Debye characteristic temperatures corresponding to the heat capacities of biphenyl-h_{10} (○) and -d_{10} (●), assuming 9*N* degrees of freedom.

The heat capacity of the d_{10} sample was measured from 3 to 300 K, part of which is shown in Fig. 1 together with the earlier data of the h_{10} sample.[10)] There are two successive phase transitions at 20.2 K and 36.8 K. The anomalies are more clearly seen by plotting the Debye characteristic temperatures corresponding to the heat capacities as given in Fig. 2. The larger anomaly due to the soft-mode phase transition is very broad extending from 28 to 44 K with a maximum at 36.8 K, the shape of which is very similar to that of h_{10} sample. By assuming normal portion as shown by the solid line in Fig. 2, excess heat capacities are separated as shown in Fig. 3. The anomaly due to the commensurate-incommensurate transition (so-called lock-in transition) is even smaller and also broad but it is certainly located with a maximum at 20.2 K, which was observed consistently in three separate series of measurements as shown in Fig. 4. Thus, there exist two successive phase transitions in biphenyl-d_{10}; the thermodynamic properties of the phase transitions are summarized in Table 1.

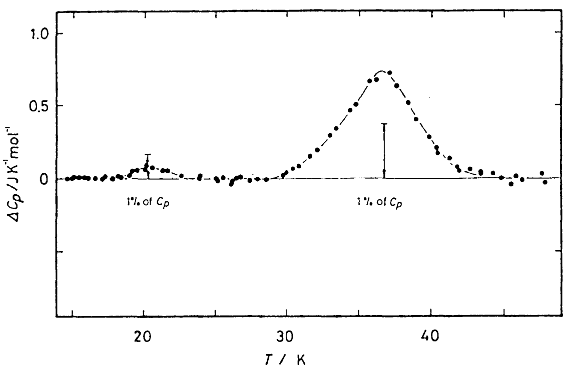

Fig. 3. Excess heat capacities of biphenyl-d_{10}.

The location and the smallness of the anomaly due to the lock-in transition at 20.2 K, which have been established for the d_{10} compound by the present experiments, cast some doubt about an anomaly in the h_{10} compound reported previously[10)] because the value of the entropy of 'anomaly' at 11.0 K in the h_{10} compound is very large compared with the present results on the d_{10} compound and also because a similar anomaly has been observed on the d_{10} compound as well at 11.0 K as seen in Fig. 2. Thus, the 'anomaly' at 11.0 K might be of an instrumental origin of some kind. In fact, it is in a temperature region in which calorimetry is least sensitive. Below 20 K, sensitivity of a platinum resistance thermometer and of thermocouples used for adiabatic control becomes as low as to be barely tolerable while the heat capacity of a specimen decreases as T^3. Another problem lies in the temperature scale; the IPTS-68 is defined on a platinum resistance thermometer only above 13.81 K, below which there is some difficulty in realizing the thermodynamic temperature scale on a germanium resistance thermometer commonly used in calorimetry.[22-24]

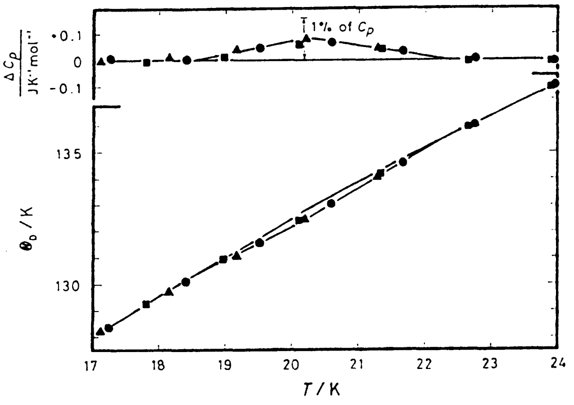

Fig. 4. The lock-in transition of biphenyl-d_{10}. Each series of measurements is represented by a different symbol.

Such a situation described above prompted us to construct an improved calorimeter, by making use of which remeasurements on the h_{10} compound should be made in higher precision to search for the lock-in anomaly.

Thus, the h_{10} sample was melted in the new vessel in helium gas atmosphere, and therefore a large amount of sample could be loaded (24.9569 g = 0.161836 mol), which contributed about 90 % to the total heat capacity at 10 K and about 85 % at 20 K. The melted sample was cooled gradually down to room temperature for solidification and then the vessel was degassed and sealed off without any additional helium gas for heat exchange. A KARMA heater, a germanium thermometer, and thermocouples for adiabatic control were mounted on the calorimeter thereafter in the usual way. The thermal contact between the sample and the calorimeter vessel was satisfactory; after each heat input, thermal equilibrium within the calorimeter vessel was attained in a few minutes below 20 K. For the adiabatic control, Au+0.07%Fe vs. Chromel thermocouples (diameter 0.1 mm) were used; its thermal emf was several times higher than that of the Chromel vs. Constantan thermocouples used in the earlier measurements. The working thermometer was a calibrated germanium thermometer purchased from SI Inc. U.S.A. (model N2D), which had been calibrated on the 1962 ^{3}He vapor pressure scale and on the 1965 provisional helium acoustical scale. Other components of cryostat/calorimeter assembly were the same as used previously.

Now, remeasurements on the h_{10} compound were made to search for the lock-in transition and to see if the 'anomaly' at 11 K was a real one in higher resolution of meas-

Table 1. Thermodynamic properties of the phase transitions in biphenyl-h_{10} and -d_{10}.

	h_{10}		d_{10}	
T_{max} / K	16.8 ± 0.1	40.4 ± 0.2	20.2 ± 0.1	36.8 ± 0.2
anomalous region / K	15.3 - 18.3	30 - 47	18.5 - 22.5	28 - 44
ΔH_{trs} / J·mol^{-1}	0.15 ± 0.02	5.02 ± 0.08	0.18 ± 0.04	4.61 ± 0.08
ΔS_{trs} / J·K^{-1}·mol^{-1}	0.009 ± 0.001	0.129 ± 0.003	0.009 ± 0.002	0.128 ± 0.003

urements. The lock-in transition was located at about 16.8 K as shown in Fig. 5 but there was no corresponding anomaly at 11 K. The revised thermodynamic properties of the phase transitions are given in Table 1.

The major difference between the h_{10} and the d_{10} compounds is that the region of incommensurate phase is narrower in the d_{10} compound. As Table 1 shows, the entropies of transition in the two compounds are equal to each other, assuming that the two compounds undergo transitions of the same mechanism. Detailed analysis of the results will be published elsewhere.[24)]

A remark should be made about the origin of a false anomaly at 11 K reported previously. Because the thermometer used in the present remeasurements is different from the previous one and the temperature scale used is also different, we are inclined to believe that the effect was due to difficulty in fixing the germanium scale, i.e. its smooth connection to the platinum scale. More detailed investigation into this problem is under way.

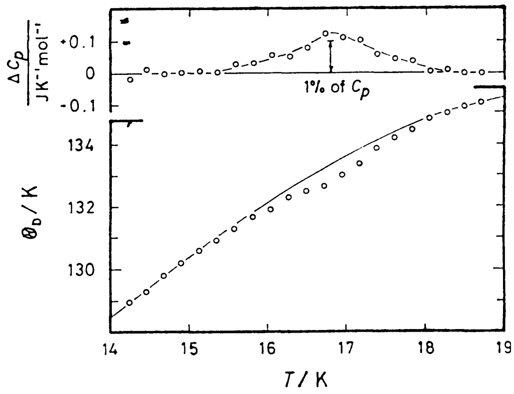

Fig. 5. Shape of the lock-in transition of biphenyl-h_{10} (data of a typical run).

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