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# THERMODYNAMIC STUDY OF THE INCOMMENSURATE PHASE TRANSITIONS IN CRYSTALLINE BIS(4-CHLOROPHENYL)SULFONE

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## SUMMARY

The temperature dependence of heat capacity of bis(4-chlorophenyl)sulfone (BCPS) was measured by AC calorimetry between liquid nitrogen and room temperatures. The existence was confirmed of the normal-incommensurate phase transition of the second-order at 146 K. Also detected at about 115 K was the anomaly probably due to another phase transition, which was predicted as a lock-in transition from the NQR experiments by Corbero *et al.* The nature of the transition(s) is discussed on the basis of the magnitude of the anomalies.

## INTRODUCTION

Flexibility of molecules has attracted much attention of a number of chemists in the field of molecular structure because it presents such questions in a simplified form, *e.g.* the nature of a chemical bonding, competing intermolecular interactions, *etc.* Among such molecules, one of the most famous is biphenyl of which the conformation depends on the substituent(s) and/or the circumstance (ref. 1). In recent years, the phase transition associated with the molecular conformational change was discovered in crystalline biphenyl (ref. 2). The discovery greatly extended the area of researchers who are interested in the molecular flexibility to those of solid state sciences. The homologues of biphenyl, *i.e.* *p*-terphenyl, *p*-quaterphenyl and substituted biphenyls enabled the systematic study of the effects of the molecular flexibility on the mechanism of the phase transition (refs. 3-8). The molecular crystal, which undergoes phase transitions having some relation with the intramolecular degree(s) of freedom, has seldom been reported except for the cases mentioned above.

The title compound, BCPS, is one of the molecules on which the study of the molecular conformation was conducted (ref. 9). The crystal and the molecular structures are shown in Fig. 1 (refs. 10 & 11). The molecule has two chlorophenyl groups connected to the central sulfur atom by a bond, the length of which is within the range of that of C-S single-bond. Thus, the molecule has the "soft" internal degrees of freedom. This is clearly demonstrated by the fact that there is more Raman lines in the lattice mode region than the expected (ref. 12). The crystal structure was separately determined by the

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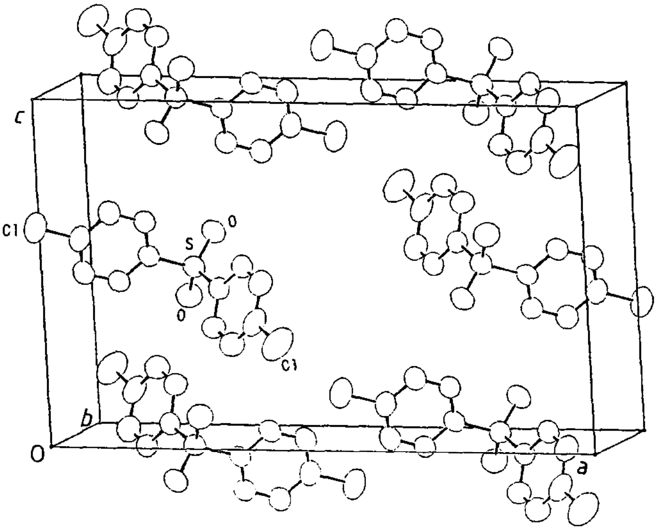

Fig. 1. Crystal structure of BCPS.

X-ray (refs. 10 & 13) and the neutron (ref. 14) diffraction experiments at room temperature. The crystal belongs to the space group I2/a and a unit cell contains four molecules. The molecules are located on the two-fold axis and arranged antiferroelectrically along the a- and c-axes as shown in Fig. 1.

Recently, Corbero *et al.* (ref. 15) suggested the existence of successive phase transitions at about 150 and 110 K from their $^{35}$Cl-NQR experiments, contrary to the earlier report of NQR data (ref. 16). They also suggested the nature of the transitions as the normal-incommensurate and the incommensurate-commensurate (so-called "lock-in") transitions, *i.e.* the transition sequence is normal-incommensurate-commensurate phases (ref. 15). The successive reports (refs. 17 & 18) proposed the mechanism of the transition as twist of the phenyl groups similar to the case of biphenyl on the basis of the smallness of the anomaly in the temperature dependence of the NQR lines. Nakayama *et al.* (ref. 19) detected in the Raman spectra of the a(bb)c polarization a soft-mode, which followed the relation $\omega \propto (T_c - T)^{\gamma}$ with $T_c$ = 141 K and $\gamma$ = 0.39. No anomaly was detected around 110 K. Very recently, Kasano *et al.* (ref. 20) confirmed the incommensurate nature the phase below the 150 K-transition by X-ray diffractometry. The modulation wavevector characterizing the incommensurate phase is $\boldsymbol{q} = \boldsymbol{a}^{*} + (1/5 + \delta)\cdot \boldsymbol{b}^{*}$, where the superscripts * indicates the reciprocal lattice vector and $\delta$ the small misfit parameter. No significant anomaly was observed in the intensity of the satellite reflection nor $\delta$, though the intensity was linearly dependent of $T$ above 110 K and showed the deviation from the linearity below 110 K. They detected no manifestation of lock-in.

Rerat and Rerat (ref. 21) studied the stable arrangement of two BCPS molecules through calculation taking into account of the permanent dipole and van der Waals interaction. The most stable arrangement was that two molecules had the common two-fold axis as along the b-axis in the crystal.

BCPS is a candidate which offers a strong coupling between the intra- and the inter-molecular degrees of freedom, as described above. Moreover, the fact that the molecular crystal which have incommensurate phases are rare makes BCPS very interesting. For BCPS, Novoselova *et al.* (ref. 22) reported the results of adiabatic calorimetry between 14 and 330 K. They, however, missed anomalies due to the phase transitions. Hence there exists no thermodynamic study on the phase transitions though their existence has been demonstrated by the spectroscopic and the structural studies. In this report, the result of AC calorimetry on crystalline BCPS is described and, by comparing the behavior with that of biphenyl (ref. 23), some similarities and differences are pointed out.

## EXPERIMENTAL

BCPS was purchased from Tokyo Kasei Kogyo Co., Ltd. and recrystallized from hot benzene solution. A sample crystal with the dimension of 2.0 x 1.5 x 0.05 $mm^3$ was used for the measurements. The temperature dependence of the heat capacity was measured using a laboratory-made AC calorimeter (ref. 24) at the measurement frequency of 1.40 Hz. The surface of the crystal facing to the heat source (a halogen lamp) was blackened with graphite spray. The amplitude of the temperature oscillation was about $10^{-2}$ K. The measured results were found to have precision of 0.2 per cent and to agree with the data by adiabatic calorimetry (ref. 22) within 2 per cent between 100 and 250 K. The temperature dependence of the inverse of the amplitude of the temperature oscillation was converted into the absolute scale (ref. 25) referring to the data which were measured by adiabatic calorimetry by Novoselova *et al.* (ref. 22). The heat capacity of the thermocouple attached to the sample was smaller than 2 per cent of the sample heat capacity.

## RESULTS AND DISCUSSION

The results of a typical run are shown in Fig. 2. Small anomalies can be recognized around 115 and 150 K. Since the locations of the anomalies are reasonably close to those reported in the NQR experiments (refs. 15, 17 & 18), the higher and the lower anomalies are attributed to the normal-incommensurate and the lock-in phase transitions, respectively. It is, however, necessary to note that the shape and the location of the lower anomaly depended on the direction of the measurement (cooling or heating) and/or the thermal history while no such phenomena were encountered in the case of the higher anomaly.

These behavior is considered as the indication of the fact that the normal-incommensurate transition is of the higher-order and the lock-in transition the first-order.

In order to obtain the thermodynamic quantities such as entropy of transition, we need to subtract the "normal" portion of heat capacity from the measured values. Since no sufficient data on the molecular and the lattice vibration is available at present, we draw the smooth interpolating curve as the normal portion as shown in Fig. 2 with solid line. The excess heat capacity thus separated are plotted in Fig. 3. The scatter of the points demonstrates the smallness of the anomalies.

The excess heat capacity due to the normal-incommensurate phase transition has long tail below the transition temperature and is identified as typical of the second-order phase transition. The transition temperature is determined as (146 ± 1) K. The enthalpy and the entropy of transition are determined as (41 ± 2) $J \cdot mol^{-1}$ and (0.30 ± 0.02) $J \cdot K^{-1} \cdot mol^{-1}$, respectively by graphical integration of the anomaly. The value of the entropy of transition is much smaller than $R \cdot \ln 2$ and consistent with the displacive nature associated with the soft-mode (ref. 19) though the value is larger by factor 2 than that in biphenyl (ref. 23). The smallness of the anomaly indicates the similarity in the crystal structure above and below the transition (ref. 18).

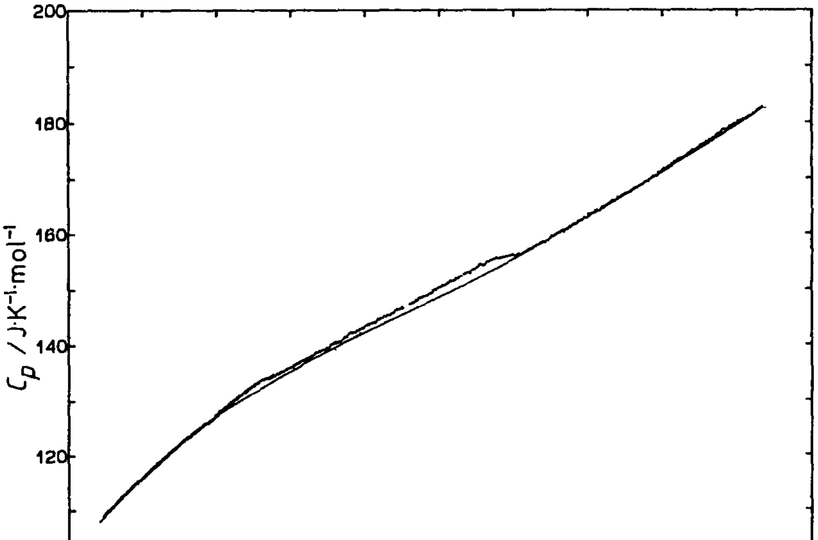

Fig. 2. Measured heat capacity of BCPS. Solid line shows the assumed normal portion.

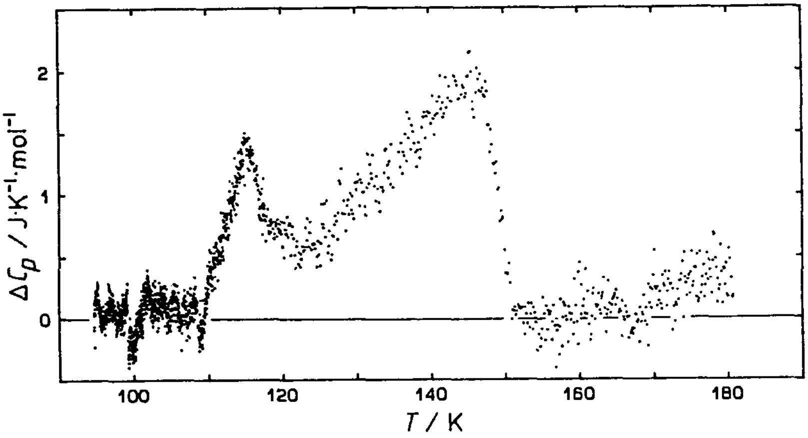

Fig. 3. Excess heat capacity of BCPS.

Since the excess heat capacity due to the lock-in transition depends on some factors as described above, it is impossible to discuss its nature in detail. In addition to the difficulty, there is the experimental difficulty concerning the first-order nature of the transition, *i.e.* the usual method of AC calorimetry is impossible to measure a latent heat due to the first-order phase transition. It is, however, considered that the anomaly detected in the present results gives the lower limit of the change in thermodynamic quantities due to the phase transition. Thus we make some comments on the excess heat capacity in Fig. 3. The anomaly due to the lock-in transition lies on the tail of that due to the normal-incommensurate phase transition. Such a situation was also reported for $K_2SeO_4$ (ref. 26). The maximum of the excess heat capacity in Fig. 3 is at about 114 K. The graphical integration yields 6 J·mol$^{-1}$ and 0.05 J·K$^{-1}$·mol$^{-1}$ for the enthalpy and the entropy of transition, respectively. It is noted that no significant deviation from the normal condition of AC calorimetry was detected around 114 K in this run. Thus the latent heat due to the lock-in transition will be rather small.

Now it is interesting to compare the behaviors of BCPS and biphenyl (refs. 2 & 23). The similarity that each substance have incommensurate phase(s) at low temperature must be, first of all, pointed out. The nature of the incommensurate modulation in biphenyl is the periodic change in the twist angle of the phenyl groups around the molecular long axis (ref. 2). In the case of BCPS, the nature of the modulation has not been clarified until now though the similar type of the twist of chlorophenyl groups was suggested (ref. 18). The structural study will reveal the point. The other similarity is, hence, that the phase transition in each case seems to have much relation with the intramolecular degree(s) of freedom. Indeed the soft-mode which drives the phase transition in biphenyl is a coupled branch between the acoustic and the internal twisting degrees of freedom (refs. 2 & 27).

There also exists, however, large differences between two; they concern with one-particle properties. The first is whether the molecule is polar or not. The molecule of biphenyl is, of course, non-polar. Thus, the intermolecular interaction is regarded as rather weak van der Waals interaction. On the other hand, BCPS has some electric dipole moment as easily understood from the molecular structure. The crystal structure of BCPS reflects the interaction between the electric dipoles. This fact will be responsible for, in part, the different phase behaviors between the two systems. The second difference is also in a one-particle property, *i.e.* the potential curve for internal rotation of phenyl groups. The potential curve in biphenyl is determined by two competing effects, the delocalization of $\pi$-electrons and the steric repulsion between *ortho* hydrogens. The minimum of the potential energy thus exists at about 42 °. In room temperature phase, the biphenyl molecule is planar, in contrast to that in gaseous state and in the low temperature phases. Hence, the phase transition in biphenyl (and also in *p*-terphenyl and in *p*-quaterphenyl) results from the competition between the inter- and the intra-molecular interactions. On the other hand, the potential curve in the BCPS molecule is primarily determined by the steric repulsion because the effect of the conjugation through the d-orbital of the central sulfur atom is little. The energy calculation using non-bonded interatomic potentials of Buckingham type (ref. 28) yields flat curve within 1 $kJ \cdot mol^{-1}$ by about 20° twist, irrespective of the twisting modes of $A_2$ or $B_2$ symmetry species as shown in Fig. 4; here the molecular symmetry is assumed as $C_{2v}$ and the coordination of the central sulfur atom as that of the ideal tetrahedron. Therefore, the

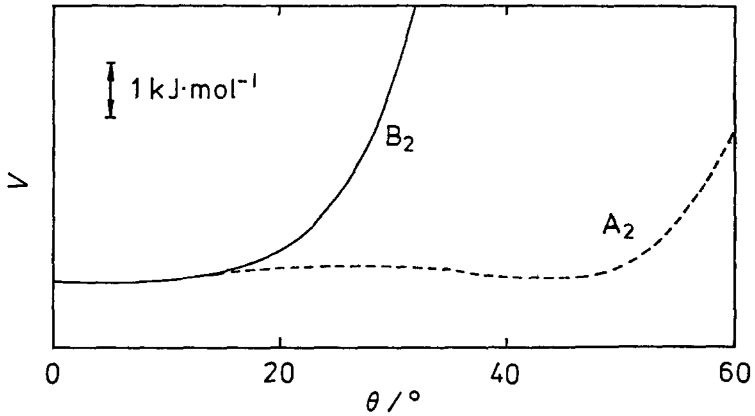

Fig. 4. Calculated potential energy for twisting of the phenyl groups in BCPS molecule as a function of the angle. The molecular symmetry is assumed as $C_{2v}$.

orientation of the chlorophenyl groups in BCPS crystal should be described as if it is solely determined by the intermolecular interactions. These will be the key differences to solve the problem why the phase behavior is different for rather similar systems, BCPS and biphenyl.

After completion of this series of measurements, Nakayama (ref. 29) privately informed the results of the re-experiment of $^{35}$Cl-NQR. The results showed some differences from those reported by Corbero *et al.* (refs. 15 & 17) and Pusiol *et al.* (ref. 18). No lock-in transition was observed, in agreement with the Raman (refs. 12 & 19) and the X-ray (ref. 20) studies. Moreover, at 4.2 K four lines were observed, implying the existence of the four non-equivalent chlorine sites. Nakayama (ref. 29) also suggested there was another phase transition at about 60 K. These diverging results concerning phase relation (refs. 12, 15, 17-20, 29) may be attributed to the difference in the procedure of sample preparation, and, from the different point of view, can be regarded as the indication of the fact that incommensurate systems appear as a result of subtle balance between competing interactions and that there are, therefore, many metastable states having similar Gibbs energy (ref. 30).

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