The Effect of High Magnetic Field on the Crystal Growth of Benzophenone

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The crystal growth of benzophenone was observed under high magnetic fields. In the presence of a magnetic field (8 T) the benzophenone crystal, which was diamagnetic, aligned in such a way that its crystal *c*-axis was perpendicular to the direction of the magnetic field. This phenomenon seemed attributable to the anisotropic diamagnetic susceptibility of the crystal.

Recently effects of high magnetic fields have received increased experimental and theoretical attention.[1-7] As for magnetic orientation, few were reported. Torbet et al.[1] and Yamagishi et al.[2] reported that giant fibrin fibers, obtained by the polymerization of fibrinogen monomers, aligned when the reaction was carried out in the presence of high magnetic fields (1-11 T). Co-polymers composed of *p*-hydroxybenzoic acid and poly (ethyleneterephthalate), which had a liquid crystal-like chromophore, aligned when heated in the presence of a magnetic field (6 T).[3] However, the magnetic field effects on the crystal growth of diamagnetic compounds have not studied in detail yet. In this Letter the crystal growth of a diamagnetic organic compound (i.e., benzophenone) was examined in detail under the high magnetic field (8 T).

Benzophenone (Tokyokasei, GR grade) and *n*-hexane (Nacalai, GR grade) were used as supplied.

Magnetic fields were applied by using a superconducting magnet (Oxford Instruments, Spectromag 1000, B_{max} = 9 T). Its bore (50 ϕ × 370 mm) was installed horizontally. The details were described elsewhere.[6]

The benzophenone was crystallized from a hot *n*-hexane solution (ca. 60 °C). A glass vessel (38 mm in width × 50 mm in length × 25 mm in height) containing the *n*-hexane solution (0.44 mol dm^{-3}, ca. 15 ml) of benzophenone was placed in the bore of the superconducting magnet. The temperature in the bore was kept at about 9 °C. The crystals were grown for 5 h in the presence of a magnetic field. The vessel was then taken out from the bore and the solvent was immediately removed in order to minimize the growth of the crystal at outside of the magnetic field. The crystallization at zero field was carried out similarly and simultaneously.

Crystal structure and orientation of the benzophenone crystal were determined by using a X-ray diffraction apparatus (Mac Science, MXC 3).

Figures 1 (a) and (b) show the crystals of benzophenone grown from a hot *n*-hexane solution, obtained in the absence and presence of a magnetic field (8 T), respectively. Their crystal form was needles and their length was 5 ~ 10 mm. At zero field the direction of the needles was aligned randomly. In the presence of the high magnetic field the direction of the long axis of the needles tended to align perpendicular to the direction of the magnetic field. Orientation of the needles was observed at the magnetic field higher than ca. 2 T. The degree of the orientation of the needles depended only on the intensity of the magnetic field and did not depend on the gradient of the magnetic field.

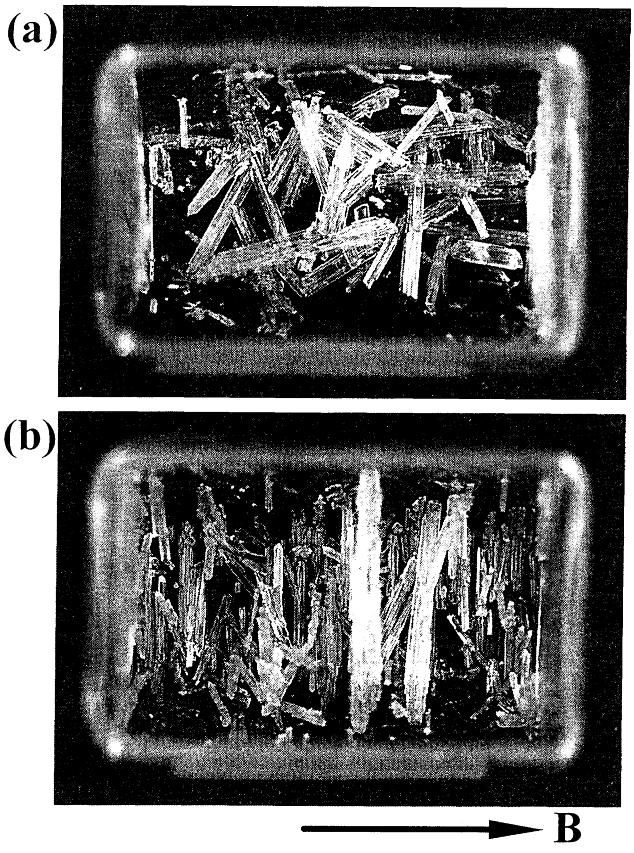

Figure 1. The benzophenone crystals obtained in the absence and presence of a magnetic field. (a) 0 T, (b) 8 T.

The crystals grown under the high magnetic field (8 T) were analyzed with a X-ray diffraction technique. (1) The crystal structure of benzophenone was orthorhombic (*a* = 10.28 Å, *b* = 12.11 Å, *c* = 7.98 Å, *z* =4) as shown in Figure 2. These values are in good agreement with the reported ones (*a* = 10.30 Å, *b* = 12.15 Å, *c* = 8.00 Å, *z* =4),[7,8] indicating that the magnetic field did not affect the crystal structure at all. (2) Furthermore, the long axis of the needles was identified with the *c*-axis of the unit cell. The relationship between the direction of the magnetic field and other crystal axes was unclear, since the long axis of the needle was the unique axis that could be determined experimentally at the present time.

Magnetic orientation of a crystal is considered to be caused by its anisotropic magnetic susceptibilities. The magnetic field-induced difference in the Gibbs free energy ΔG, which results from the difference between two magnetic susceptibilities along each axis of the unit cell, is given by eq. (1),[9]

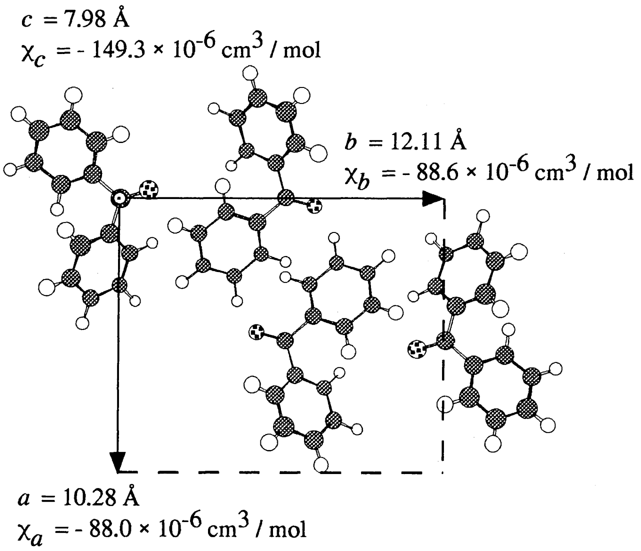

Figure 2. The schematic representation of the structure of benzophenone crystal. χ values were cited from reference 10.

$$\Delta(\Delta G) = -\frac{1}{2}\frac{1}{\mu_0}\left(\chi_i - \chi_j\right) B^2 \qquad (1)$$

where χ_i and χ_j are the molar magnetic susceptibilities along i and j axes of the cell, respectively, μ_0 and B are the magnetic permeability and the intensity of the magnetic field, respectively. When $\Delta(\Delta G)$ becomes equivalent to the thermal energy, the orientation of a crystal takes place.

In the case of the benzophenone crystal, the anisotropic magnetic susceptibilities along each axis of the unit cell are reported.[10] The molar magnetic susceptibilities along a-, b-, and c- axes are $- 4\pi \times 8.80 \times 10^{-11}$, $- 4\pi \times 8.86 \times 10^{-11}$, and $- 4\pi \times 14.93 \times 10^{-11}$ m^3mol^{-1}, respectively. This large anisotropy arises from the fact that the two phenyl groups of benzophenone are nearly parallel with the ab plane as shown in Figure 2. The difference between two Gibbs free energies $\Delta(\Delta G)$ becomes maximum when $\chi_i = \chi_c$ and $\chi_j = \chi_a$. At 8 T, the difference in the Gibbs energy $\Delta(\Delta G)$ for one mole of benzophenone is estimated to be 1.96×10^{-2} J mol^{-1}. The value for one unit cell is calculated to be 1.30×10^{-25} J. This value is much smaller than the thermal energy, since the thermal energy at 282 K (9 °C) is estimated to be 3.89×10^{-21} J. When n unit cells are aligned along the c-axis, however, $\Delta(\Delta G)$ of the aggregate can become comparable with the thermal energy, and then the orientation of the microcrystals takes place, which results in the orientation of macrocrystals. n is estimated to be about 3×10^4.

Furthermore, magnetic orientation of inorganic diamagnetic crystals (i.e., potassium chlorate and barium chloride) was also observed, when crystallized from aqueous solutions. In these cases, flat plates (ca. 0.1 mm in thickness × 5 mm in width × 5 mm in height) were aligned in such a way that the normal of the plate was parallel to the magnetic field.

In conclusion, the magnetic orientation of benzophenone crystals is attributable to its magnetic anisotropy. Magnetic orientation of organic and inorganic diamagnetic crystals seems to occur commonly when the crystals have large anisotropic diamagnetic susceptibilities.

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