Crystal Growth of *trans*-Azobenzene in a Magnetic Field of 80 kOe

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The crystal growth of *trans*-azobenzene (diamagnetism) has been investigated in a magnetic field of 80 kOe. The crystallographic axes are determined by X-ray diffraction and compared with the magnetic axes. The crystals grow so that the magnetic χ_3 axis is parallel to the direction of the field. The orientation is explained by the magnetic anisotropy ($\chi_2 < \chi_1 < \chi_3$) of the crystals. Since the magnetic energy has a minimum in the χ_3 direction, the crystals containing a considerable number of unit cells can be stabilized by rotating in this direction against thermal disordering.

1. Introduction

It has been known that diamagnetic liquid crystals and proteins are oriented in magnetic fields. Liquid crystals have orientational order along the directors, and the orientation in magnetic fields is characterized by the Freedericksz transition. Proteins, such as fibrinogen and lysozyme, have higher-order structures with large molecular weights of ∼100 000, and the orientation takes place on polymerization and crystallization.[1−4] From these findings, the magnetic orientation seems to be a phenomenon inherent in ordered structures of large molecular aggregates.

How about crystals of diamagnetic organic molecules in magnetic fields? Although the component molecules are of low molecular weights, crystals have rigid and ordered structures, and the orientation is therefore expected. We have found orientation of the crystallization of benzophenone under a field of 80 kOe,[5] and a similar observation has been reported for the microcrystals of 4-alkoxy-4′-cyanobiphenyls in thin films cast under a field of 9 kOe.[6]

The present paper deals with the orientation of the crystal growth of *trans*-azobenzene (diamagnetism) in a magnetic field of 80 kOe. The crystallographic axes are determined by X-ray diffraction and compared with the magnetic axes. The relationship between the orientation of the crystal growth and the magnetic axes is discussed.

2. Experimental Methods

trans-Azobenzene (Nacalai Tesque, >99%) was dissolved in hot ethanol (Japan Alcohol Trading, >99%) to prepare 0.36 mol dm^{-3} solution. The crystals were obtained after the solution (10 cm^3) was allowed to stand in a glass cell (50 mm × 35 mm × 25 mm). The temperature of the cell was kept at 281 K by passing water from a circulator (Advantec LP-3100) around it.

The magnetic fields up to 80 kOe were applied by a superconducting magnet (Oxford Spectromag 1000). The field direction was horizontal.

The orientation of the crystals was followed by a fiberscope (Olympus R100-095-090-50) and a camera (Olympus SC35-15) in the magnet and recorded by a camera (Nikon Nikomat FTN) after taking the glass cell out of the magnet.

The X-ray diffraction measurements were performed on a four-circle diffractometer (Mac Science MXC 3) with Cu Kα radiation (1.540 50 Å) at 293 K. The cell dimensions were determined by a least-squares analysis of 31 reflections. A single crystal (0.5 mm × 0.6 mm × 0.05 mm) was used for data collection.

3. Results

3.1. Orientation of Crystals. The *trans*-azobenzene crystals, shown in Figure 1a, are obtained in a magnetic field of 80 kOe after standing for 5 h. The crystals are of a form of tabular rhombuses with their rhombic planes lying horizontal, as shown in Figure 1b. The typical crystal dimensions are 5 mm × 2 mm × 0.5 mm. The crystals are oriented so that their diagonal lines bisecting the acute angle of the rhombuses are perpendicular to the direction of the field. The orientation is observed in fields of >20 kOe.

The growing process of the crystals is followed at 80 kOe. The crystals of lengths of 1 mm, which are at the limit of observation in the present experiment, separate out perpendicularly to the direction of the field after standing for 3 min.

The crystals, shown in Figure 1c, are obtained in zero field. The crystal form and dimensions are the same as in the field of 80 kOe, but the crystals are oriented randomly.

3.2. Crystallographic and Magnetic Axes. The crystallographic axes are determined for the crystals growing in a magnetic field of 80 kOe. The crystal system is monoclinic. The cell dimensions are $a = 15.2146(24)$, $b = 5.7823(9)$, $c = 12.1677(11)$ Å, $\beta = 112.430(10)°$ with $Z = 4$. These data are in agreement with the previous ones of $a = 15.219(4)$, $b = 5.7855(8)$, $c = 12.177(4)$ Å, $\beta = 112.42(2)°$ with $Z = 4$.[7] The field is not found to affect the cell dimensions. With respect to the orientation of the crystals, the plane of the tabular rhombus is the (100) plane and its diagonal line bisecting the obtuse angle is the *b* axis (Figure 1b).

The magnetic susceptibilities are reported to be $\chi_1 = -87.5 \times 10^{-6}$, $\chi_2 = -130.2 \times 10^{-6}$, $\chi_3 = -83.1 \times 10^{-6}$ cm^3 mol^{-1}.[8] The χ_1 and χ_3 axes coincide with *c* and *b* axes, respectively, while the χ_2 axis lies in the (010) plane (Figure 1b).[9] It is clear, after determination of the crystallographic axes, that the crystals are oriented so that the χ_3 axis is parallel to the direction of the field.
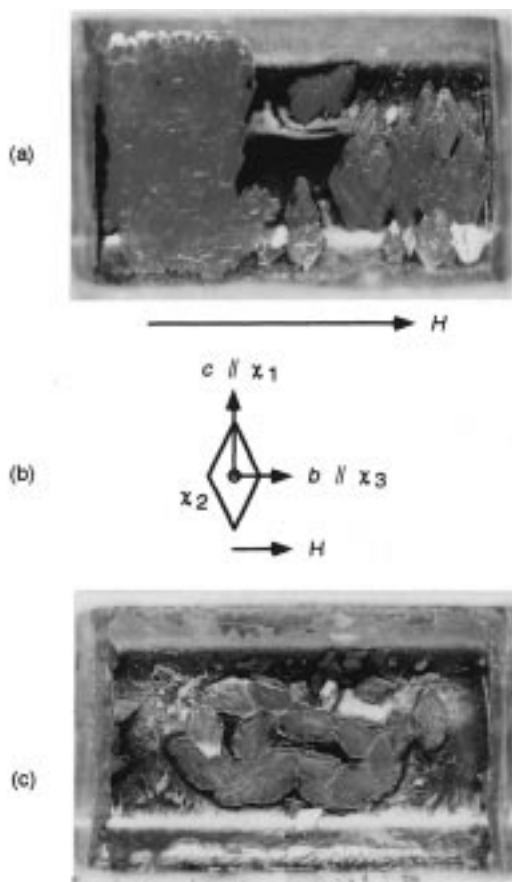
Figure 1. Photographs of *trans*-azobenzene crystals growing in (a) 80 kOe and (c) zero fields for 5 h. Solution is removed for observation's sake. (b) Schematic diagram of orientation of *trans*-azobenzene crystals in a 80 kOe field. Field direction is shown with an arrow.
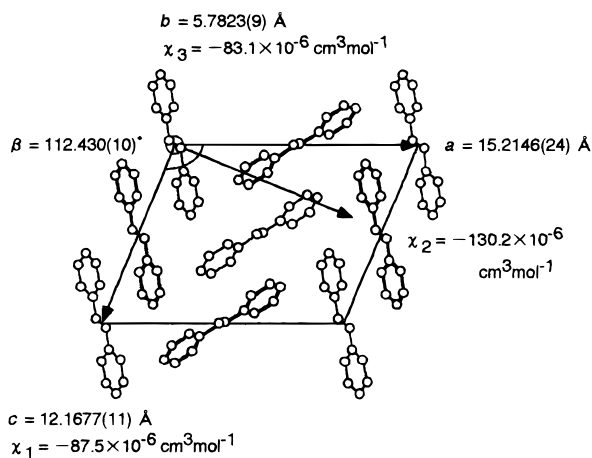

Figure 2. Projection of molecular arrangement along a monoclinic *b* axis for *trans*-azobenzene crystals. Molecules having their centers at $y = 0$ and $y = 1/2$ are drawn with thin and thick lines, respectively.

4. Discussion

4.1. Crystal Structure. The magnetic anisotropy of the crystal is considered to result from the arrangement of the molecules. For the *trans*-azobenzene crystal (see Figure 2),[7] four molecules are arranged in the unit cell with space group $P2_1/c$.[10] The arrangement remains practically unchanged when the molecules are rotated by π about the axis that lies perpendicular to the *c* axis in the (010) plane. These crystallographic data show that the magnetic χ_1 and χ_3 axes coincide with the crystallographic *c* and *b* axes, respectively, and that

the magnetic χ_2 axis is perpendicular to the crystallographic *c* axis. Furthermore, the benzene rings occupy a larger area on the projection along the χ_2 axis than along the χ_1 or χ_3 axis. In benzene (diamagnetism), the magnetic anisotropy is large; the susceptibility normal to its plane is much less than in its plane $(K_{\parallel} - K_{\perp} = 59.7 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1})$.[11] This explains, for the *trans*-azobenzene crystal, that the susceptibility χ_2 is a minimum among the susceptibilities χ_1, χ_2, and χ_3, which is consistent with the magnetic data: $\chi_1 = -87.5 \times 10^{-6}$, $\chi_2 = -130.2 \times 10^{-6}$, $\chi_3 = -83.1 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$.[8]

4.2. Magnetic Anisotropy Energy. When a crystal composed of *n* moles of molecules is placed in a magnetic field *H*, the magnetic anisotropy energy is given by

$$E(\alpha, \beta, \gamma) = -(n/2)(\chi_X \cos^2 \alpha + \chi_Y \cos^2 \beta + \chi_Z \cos^2 \gamma)H^2$$

X, *Y*, and *Z* are the principal magnetic axes fixed to the crystal. χ_X, χ_Y, and χ_Z are the principal (molar) magnetic susceptibilities along the *X*, *Y*, and *Z* axes, respectively. α, β, and γ are the angles between the *H* direction and the *X*, *Y*, and *Z* axes, respectively. For a crystal of lower than cubic symmetry, the susceptibilities χ_X, χ_Y, and χ_Z are different. In the case of $\chi_X < \chi_Y < \chi_Z$, the magnetic energy $E(\alpha, \beta, \gamma)$ has a minimum value to stabilize the crystal in the *Z* direction ($\alpha = \beta = \pi/2$, $\gamma = 0$). As the crystal grows larger with a larger *n* value, the difference of the magnetic energies $E(\alpha, \beta, \gamma) - E(\pi/2, \pi/2, 0)$ between any direction and the *Z* direction becomes larger. When the difference of the magnetic energies is larger than the thermal energy, the crystal will be oriented so that the *Z* axis is parallel to the *H* direction.

Owing to gravity, the *trans*-azobenzene crystals grow with the plane of the tabular rhombus lying horizontal. Thus, the χ_2 axis is vertical and perpendicular to the magnetic field. This gives the constraint that the field acts in the $\chi_1\chi_3$ plane. Since the susceptibilities are in the order of $\chi_2 < \chi_1 < \chi_3$, the magnetic energy is a minimum and the crystals are stabilized when the χ_3 axis is parallel to the direction of the field. The present observation shows that the crystals are oriented to satisfy the requirement of the magnetic energy. The difference of the magnetic energies between the χ_1 and χ_3 directions at 80 kOe is calculated to be 1.4×10^{-3} J mol^{-1} from the difference of the susceptibilities of 4.4×10^{-6} cm^3 mol^{-1}. The thermal energy at 281 K is 3.9×10^{-21} J. Since the unit cell contains four molecules, the number of the unit cells required for the orientation of the crystals against thermal disordering can be estimated to be $>4.2 \times 10^5$.

4.3. Comparison with Benzophenone Crystals. The orientation of the benzophenone crystals has been found in the magnetic field of 80 kOe.[5] The space group is $P2_12_12_1$, and the cell dimensions are $a = 10.30$, $b = 12.15$, $c = 8.00$ Å with $Z = 4$.[12] The magnetic susceptibilities are $\chi_a = -88.0 \times 10^{-6}$, $\chi_b = -88.6 \times 10^{-6}$, $\chi_c = -149.3 \times 10^{-6}$ cm^3 mol^{-1}.[8] The crystals are columns elongated along the *c* axis. The crystals grow so that the *c* axis is perpendicular to the direction of the field. The directions of the *a* and *b* axes in the field are not determined. Since $\chi_c < \chi_a \sim \chi_b$, the magnetic energy has a maximum and the crystals are unstable in the *c* direction. It will make the crystals rotate so that the *c* axis is perpendicular to the field. The magnetic orientation can be explained in terms of stabilization by minimization of the magnetic energy for both the *trans*-azobenzene and the benzophenone crystals.

However, the magnitude of the magnetic anisotropy is not similar between the *trans*-azobenzene and the benzophenone crystals. The difference of 4.4×10^{-6} cm^3 mol^{-1} between the susceptibilities χ_3 and χ_1 for the *trans*-azobenzene crystals is 1

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order of magnitude smaller than that of 61.0×10^{-6} cm^3 mol^{-1} between the susceptibilities $\chi_a \sim \chi_b$ and χ_c for the benzophenone crystals. It is noteworthy that the magnetic orientation results from the smaller magnetic anisotropy of 4.4×10^{-6} cm^3 mol^{-1} for the *trans*-azobenzene crystals.

5. Conclusions

The *trans*-azobenzene crystals grow so that the magnetic χ_3 axis is parallel to the direction of the field. The orientation is explained by the magnetic anisotropy ($\chi_2 < \chi_1 < \chi_3$) of the crystals.

References and Notes

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(9) The present unit cell is chosen in the same way as that of the crystallographic data[7] but is different from that of the magnetic data;[8] the present *a* and *c* axes correspond, respectively, to the *c* and *a* axes of the magnetic data.

(10) The center of each molecule lies at the center of symmetry of the lattice; there are two nonequivalent pairs, and one-half of each kind of molecule comprises one asymmetric unit.

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