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Electronic Spectra of Perylene and Coronene Evaporated Films as a Function of Their Crystallinity

Yusuke Kamura,* Ichimin Shirotani, Koichi Ohno,# Kazuhiko Seki, and Hiroo Inokuchi**

The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106

#College of General Education, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153

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The absorption spectra of evaporated thin films of perylene and coronene have been studied as a function of their crystallinity. The amorphous films deposited on a low-temperature substrate *in vacuo* gave rise to "molecular" spectra which are very different from those of the polycrystalline films. The absorption spectra of amorphous films gradually changed with an increase in the substrate temperature to become similar to those of the polycrystalline films.

It has been found that the spectral responses of the evaporated thin films of polycyclic aromatic compounds depend on the temperature of their substrate during vacuum evaporation.[1–6] This behavior has been interpreted as being due to the difference in molecular aggregation in the films; that is, the evaporation of aromatics onto a high-temperature substrate yields oriented polycrystalline films, while evaporation onto a substrate kept at a low temperature gives rise to amorphous ones.

In a previous paper, we have reported[4,5] the absorption spectra and their pressure dependences of naphthacene and pentacene evaporated films. The Davydov splitting of the 0–0 band in their oriented polycrystalline films was found at atmospheric pressure, and the magnitude of this splitting increased with increasing pressure; on the other hand, no Davydov splitting could be observed in amorphous films, and the pressure-induced spectral red shifts were found to be slightly larger than those in the polycrystalline state.

Further, it was found that naphthacene and pentacene in the amorphous state are much more unstable and reactive than in the polycrystalline state under illumination and also under heat treatment in air.[4]

By means of a polarizing microscope, just after the evaporation a very dark image was observed for the naphthacene and pentacene amorphous films with a crossed nicol condition.[3] In a few days, however, several bright microcrystallites appeared in the dark background, their number increasing day by day. The change in the absorption spectrum due to crystallization was not measured because of the interference of a chemical reaction in the film.

In this paper, we will present the results of some studies of the electronic spectra of the perylene and coronene evaporated films as a function of the crystallinity and will also discuss the relation between the electronic states and the structures of the films.

Experimental

Synthesized perylene and synthesized coronene were purified by recrystallization and sublimation. Their thin films were prepared by evaporation onto a quartz substrate kept at room temperature (RT-film) or a low temperature (~170 K) (LT-film) in a vacuum of 10^{-4} Torr. The thickness of the films was monitored by means of a quartz-crystal oscillator and was estimated to be about 6×10^2 Å. The absorption spectra of the films were measured with a Cary 14 spectrophotometer.

The absorption spectra of the RT-film were measured at room temperature. The temperature dependence of the spectra of the LT-film was studied from 170 to 300 K *in vacuo*. The change in the X-ray diffraction patterns and also that in the absorption spectra of LT-films were investigated at room temperature. Further, the structures of these films were studied with a polarizing microscope.

In order to confirm the orientation of molecules in the film, and also in order to assign the absorption spectra, some additional experiments were carried out: the quartz substrate was inclined with respect to the incident light beam so that the transition with their polarization vector perpendicular to the plane of the substrate could be observed in the absorption spectra.

Results and Discussion

Absorption Spectra of Perylene and Coronene LT-films. We have already reported some findings on the absorption spectra of the naphthacene and pentacene evaporated films.[4] The characteristic absorption bands in the RT-film (oriented microcrystalline film) disappear in the LT-film (amorphous film); The absorption spectra in the LT-films resemble those of the corresponding free molecules in solution. Figures 1 and 2 show the absorption spectra of the LT- and RT-films and an ethanol solution for perylene and coronene respectively. The spectra of the LT-films at 170 K were similar to the molecular spectra in solution, but they were very different from those of the RT-films. These findings are similar to those for naphthacene and pentacene.[4]

Figure 3 shows the temperature dependence of the absorption spectra of the coronene LT-film. Its absorption bands gradually changed with an increase in the temperature. The absorption spectrum in the LT-film at room temperature agrees approximately with that of the RT-film. As is shown in Fig. 4, the absorption band of the perylene LT-film at room temperature was not similar to that of the RT-film.

By means of a polarizing microscope, a very dark image was observed for naphthacene and pentacene LT-films at room temperature using crossed nicols. However, in the case of perylene and coronene LT-

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* Present address: Hatano Research Institute, F.D.S.C., Ochiai, Hatano-shi 257.

** Present address: Institute for Molecular Science, Okazaki 444.

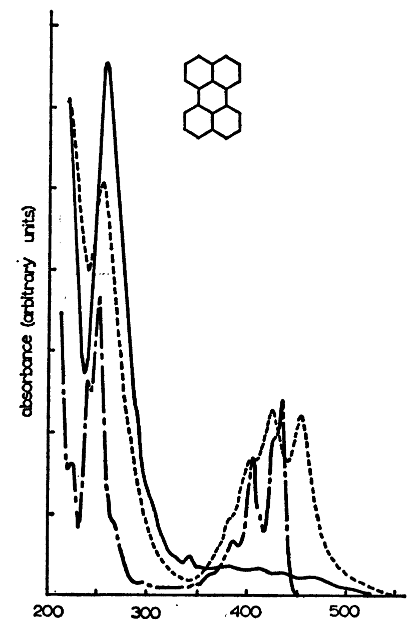

Fig. 1. Absorption spectra of perylene.
——: RT-film, ----: LT-film at 170 K, –––: ethanol solution.

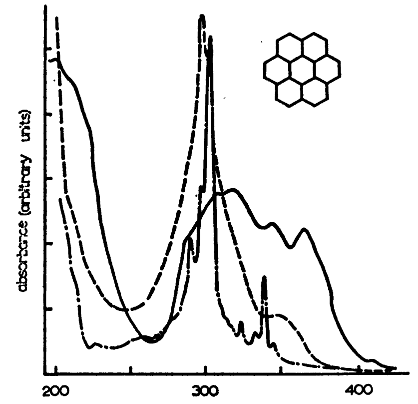

Fig. 2. Absorption spectra of coronene.
——: RT-film, ----: LT-film at 170 K, –––: ethanol solution.

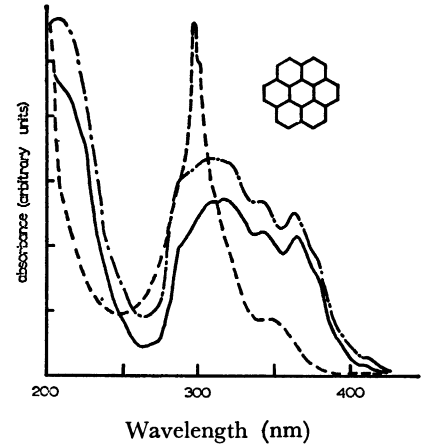

Fig. 3. Absorption spectra of coronene.
----: LT-film at 170 K, –––: annealed LT-film at 300 K, ——: RT-film.

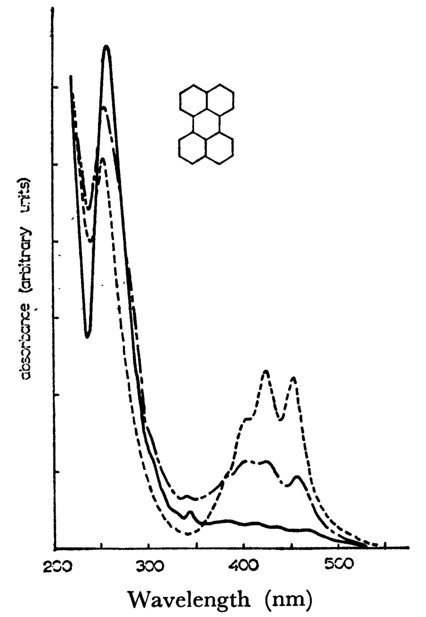

Fig. 4. Absorption spectra of perylene.
----: LT-film at 170 K, –––: annealed LT-film at 300 K, ——: RT-film.

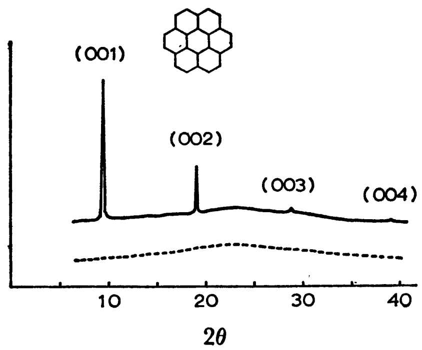

Fig. 5. X-Ray diffraction patterns of coronene evaporated films at room temperature.
——: RT-film, ----: LT-film.

films at room temperature, a large number of bright crystallites were found against a dark background, and the number increased with the time.

From these facts we may conclude that the amorphous state in their LT-films undergoes a crystallization process with a change in the temperature and also with time.

Figure 5 shows the X-ray diffraction patterns of the LT- and RT-films of coronene at room temperature. The sharp peaks corresponding to the (00*l*) plane[7] were found for the RT-film, but no peaks could be observed for the LT-film. Similar results, in Fig. 6, were also found in perylene films.[8] As has been mentioned above, though LT-films at room temperature are partially crystallized, it should be noted that the sharp X-ray diffraction lines could not be found. This may be interpreted as follows: in the annealed films the crystallites are not oriented, and the thickness of the films is not sufficient for diffraction patterns to be observed.

The absorption bands of the naphthacene and pentacene LT-films are gradually changed with the

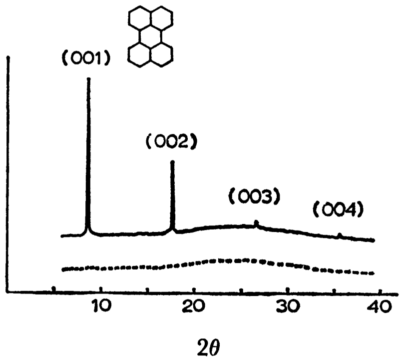

Fig. 6. X-Ray diffraction patterns of perylene evaporated films at room temperature.
——: RT-film, ----: LT-film.

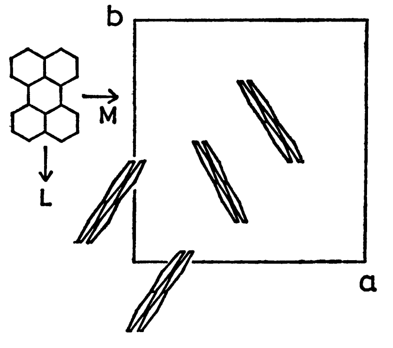

Fig. 7. Projection of perylene molecule onto the ab plane.

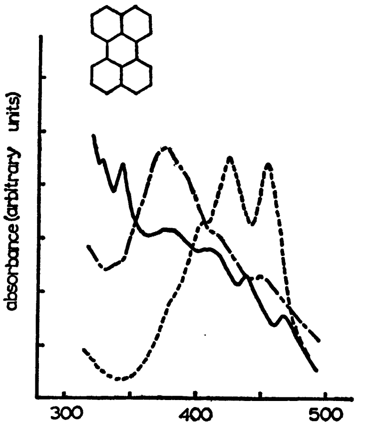

Fig. 8. Absorption spectra of perylene evaporated films.
——: Incident light with respect to the normal of the substrate is perpendicular, — —: incident light with respect to the normal of the substrate is set about 75°, ----: LT-film.

passage of time at room temperature. Although the formation of microcrystals is observed in the LT-films, this spectral change arises mainly from the chemical reaction.[4]

Amorphous films of coronene and perylene, however, were easily annealed. In particular, the rate of the crystallization of amorphous coronene was very rapid. On the other hand, amorphous naphthacene and pentacene crystallized very slowly. These results suggest that the various effects of annealing on the amorphous organic films may be related to the difference in molecular shape.

Molecular Orientation in the Evaporated Films. The absorption spectra of the perylene single crystal has been studied in terms of the Davydov splitting of the exciton states by Tanaka.[9,10] The spectra were observed through the ab plane of the crystal, and the a-axis and b-axis polarization components were resolved. The absorption spectrum was found to be in good agreement with our spectrum of the RT-film when the plane of the substrate was set perpendicular to the incident light beam (Fig. 1). In our oriented microcrystalline film, however, only the bands of the b-axis polarization component could be found at 460 and 440 nm for the first electronic transition band between 400—500 nm. This is reasonable, since the b-axis polarization component in this spectral region is much larger than the a-axis one in the single crystal ab-plane spectra obtained by Tanaka. It has been shown that the first electronic transition band has its polarization vector along the long axis (L-axis) of the molecule.[9,10] As may be seen from Fig. 7,[8] the L-axis is almost perpendicular to the ab plane, whereas the short molecular axis (M-axis) is nearly parallel to the ab plane. Therefore, the L-axis polarized transitions in the crystals can be expected to be of a much reduced intensity in the ab-plane spectra in comparison with those observed for the LT-film and the solution. In fact, this can be seen from Fig. 1, where the 250—260 nm bands have been assigned as an M-axis transition;[9,10] therefore, they are considered to be slightly emphasized in the spectrum of the RT-film. The weakened L-axis transition bands, however, may be expected to appear when the ab planes of the single crystal on the oriented microcrystals are inclined nearly parallel to the direction of the incident-light beam. An additional experiment for the RT-film of perylene, where the angle of the incident light with respect to the normal of the substrate was set at about 75° (Fig. 8), clearly revealed the ac polarization component of the exciton states, which should be much more polarized along the crystal c'-axis normal to the ab plane. The peaks at 405 and 445 nm observed in this spectrum were found to be in good agreement with those observed in the c-axis polarization component of the ab-plane crystal spectra. From the arguments given above, one can conclude that the perylene RT-film should be regarded as oriented microcrystalline films in which the crystallites are oriented with their ab planes parallel to the substrate planes. This is consistent with the orientation of the crystallites determined by X-ray diffraction in the previous subsection.

The spectral behavior of the evaporated films of coronene is very similar to that found for perylene. The absorption spectrum of the LT-film is shown in Fig. 2; it is found to agree well with the solution spectra. The most prominent band at about 300 nm in this spectrum of the LT-film may be assigned to a $^1A_{1g} \rightarrow {}^1E_{1u}$ transition, as in the case of the analogue in the solution spectra.[11] The absorption spectrum of the coronene RT-film, when the incident light beam was

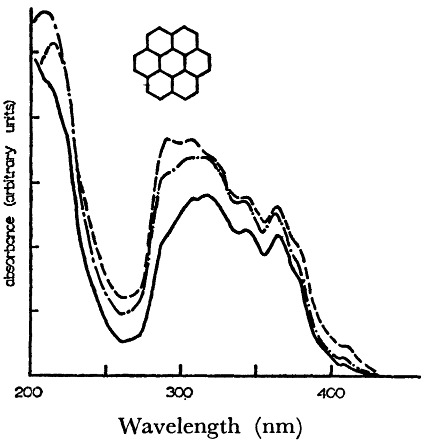

Fig. 9. Absorption spectra of coronene RT-film. ——: Incident light with respect to the normal of the substrate is perpendicular, – – –: incident light with respect to the normal of the substrate is set about 45°, ----: incident light with respect to the normal of the substrate is set about 60°.

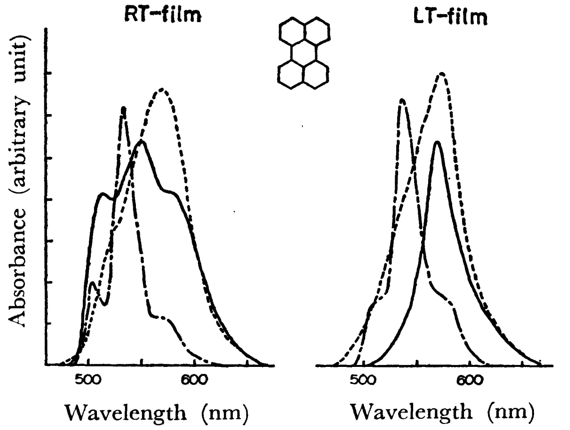

Fig. 10. Fluorescence spectra of perylene RT- (left side) and LT- (right side) films. – – –: At liquid helium temperature, ——: at liquid nitrogen temperature, ----: at room temperature.

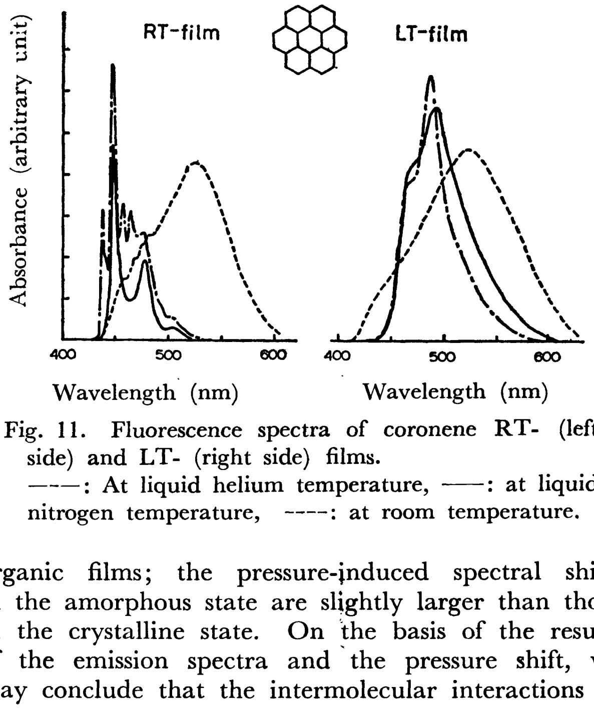

Fig. 11. Fluorescence spectra of coronene RT- (left side) and LT- (right side) films. – – –: At liquid helium temperature, ——: at liquid nitrogen temperature, ----: at room temperature.

set perpendicular to the substrate, was found to be in good agreement with the ab-plane absorption spectra of the single crystals obtained by Tanaka.[11] His analysis showed that the bands between 280 and 320 nm could be assigned in terms of the Davydov splitting of the exciton states arising from a $^1E_{1u}$ state of the molecule. From our additional experiment, the band at 290 nm in the RT-film spectra increases in intensity on a decrease in the incident light angle with respect to the normal of the substrate: 0°, 45°, and 60° (Fig. 9), in this order. One can therefore assign the band at 290 nm to one of the ac polarization components of the exciton states arising from the $^1E_{1u}$ state, which should be much more polarized along the crystal c′-axis normal to the ab plane. This assignment of the 290 nm band is consistent with that made by Tanaka.[11] From the assignments given above, we can also conclude, for the coronene evaporated films, that the LT-film should be regarded as an amorphous film in which the orientation of the molecules is disordered, and that the RT-film is composed of a large number of crystals oriented with their ab planes parallel to the substrate.

Fluorescence Spectra of Perylene and Coronene Evaporated Films. Figure 10 shows the temperature dependence of the fluorescence spectra of the perylene RT- and LT-films. The fluorescence spectra of RT-film were similar to those of the α-type of perylene single crystal.[9] A broad emission band was observed in both films at room temperature. Judging from the results of the fluorescence of the perylene crystal,[9] the broad emission may arise from the excimer emission. This emission in the RT-film disappeared at the temperature of liquid nitrogen, where a monomer-like emission was observed. On the other hand, the excimer emission appeared in the LT-film at 77 K. This shows that the short-range molecular interaction in the amorphous state is rather stronger than that in the crystalline state. In a previous paper,[5] we have reported the pressure shift of the vibronic band in organic films; the pressure-induced spectral shifts in the amorphous state are slightly larger than those in the crystalline state. On the basis of the results of the emission spectra and the pressure shift, we may conclude that the intermolecular interactions in organic amorphous films are never weak in comparison with those in crystalline films. Figure 11 shows the temperature dependence of the fluorescence spectra of the coronene RT- and LT-films. Both the RT- and the LT-films of coronene showed an excimer-type emission at room temperature. However, at very low temperatures the excimer-type emission band could not be found in the fluorescence spectrum of the RT-film. In contrast, the LT-film showed an excimer-type emission at any temperature between room temperature and 4.2 K. It may, therefore, be suggested that, in the LT-film, the excited dimer state is rather more favorable than in the RT-film, where the emission spectrum may be affected by energy transfer through the exciton states.

Crystallization Processes in the Disordered Aggregates by Annealing. As has been mentioned in the previous subsections, the LT-films of coronene and perylene undergo some annealing processes at room temperature, while for naphthacene and pentacene the LT-films are considered to be in amorphous states when they are left at room temperature for a few days. The absorption spectrum of the annealed LT-film coronene became very similar to that of the RT-film (Fig. 3). In connection with the results in the previous subsection, this may lead us to conclude that the annealed LT-film of coronene is in a microcrystalline state. Whether the annealed LT-film is oriented or not may be ascertained as follows. Since the absorption peaks in the spectrum of the annealed LT-film agree well with those of the RT-film and also with those of single crystals, the crystallites in the annealed LT-film may be considered as single crystals in which the arrangement and orientation of coronene molecules are almost perfect. Therefore, the diffuse X-ray diffraction pattern observed for the annealed LT-film may not be accounted for a disorder of the molecular orientation and arrangement in the microcrystals. As can be seen from Fig. 3, the 290 nm band for the annealed LT-film is slightly more intense than that for the RT-film. Furthermore, the spectra of the annealed LT-film were found to be independent of the incident-light angle. These facts indicate that the orientation of the crystallites is almost at random in the annealed LT-film. This may be the reason why the X-ray diffraction pattern was found to be still diffuse for the annealed LT-film.

The absorption spectrum of the annealed LT-film of perylene is shown in Fig. 4, together with those of the LT-film and the RT-film. For perylene, the absorption spectrum of the annealed LT-film did not become similar to that of the RT-film, but remained rather similar to that of the LT-film. The spectral peaks found in the L-axis transition bands for the annealed LT-film correspond well to those of the LT-film. The spectral intensities for these bands, however, were weakened in the annealed LT-film. These facts mean that the molecular orientation in the crystallites found through the microscope for the annealed LT-film is disordered to some extent and that the L-axis of the perylene molecules in the annealed LT-film is slightly oriented on average perpendicular to the plane of the substrate. Furthermore, the M-axis transition band at 250 nm for the annealed LT-film is found to be more intense than that observed for the LT-film; the M-axes of the perylene molecules in the annealed LT-film may also be slightly oriented on average parallel to the plane of the substrate. Since, for the annealed LT-film, crystallites were actually observed with a microscope, the molecules in the crystallites may be arranged in a way similar to that of the perfect crystals, especially for such a large disc-like-shaped planar molecule as perylene. One may, therefore, suggest that the annealed LT-film of perylene is composed of imperfect crystallites in which the orientation of the molecules within the molecular plane is disordered to some extent.

The various effects of annealing at room temperature on the LT-films may be related to the difference in their molecular shape. As was seen in the previous subsection, the fluorescence spectra of the LT-films and also of the annealed LT-films of perylene and coronene were found to be of the excimer type. This means that the molecules in the films are stacked in a similar way, with their planes parallel to one another. In the perfect crystals the molecules are regularly stacked. If such a stacking structure is well distributed in the LT-films of coronene and perylene, the rate-determining step lies in the molecular re-orientation within the crystal lattice. On the basis of this assumption the behavior of the annealed LT-films of coronene and perylene can be explained as follows. Since a coronene molecule has an almost disc-like shape, rotational motion along the normal-axis of the molecular plane may proceed in the aggregates without any serious change in the arrangements of the neighboring molecules; it follows that the LT-film of coronene may be almost perfectly annealed into a microcrystalline film. Since the perylene molecule is not so perfect in disc shape as coronene, rotational motion occurs less readily and may result in the imperfect crystal growth found in the annealed LT-film. On the other hand, for long-plate-like molecules, for example, naphthacene and pentacene, such a rotational motion may be inhibited because the re-orientation of the molecular axes should be quite difficult without the exclusion of neighboring molecules. One can, therefore, understand that the properties of the LT-films of naphthacene and pentacene are retained even if the films are left at room temperature for a few days.

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References

1) H. Inokuchi, H. Kuroda, and H. Akamatu, This Bulletin, **34**, 749 (1961).

2) Y. Maruyama, T. Iwaki, T. Kajiwara, I. Shirotani, and H. Inokuchi, *ibid.*, **43**, 1259 (1970).

3) Y. Maruyama and N. Iwasaki, *Chem. Phys. Lett.*, **24**, 26 (1974).

4) Y. Kamura, I. Shirotani, H. Inokuchi, and Y. Maruyama, *Chem. Lett.*, **1974**, 627.

5) I. Shirotani, Y. Kamura, and H. Inokuchi, *Mol. Cryst. Liq. Cryst.*, **28**, 345 (1974).

6) Y. Kamura, K. Seki, and H. Inokuchi, *Chem. Phys. Lett.*, **30**, 35 (1975).

7) J. M. Robertson and J. G. White, *J. Chem. Soc.*, **1945**, 607.

8) D. M. Donaldson, J. M. Robertson, and J. G. White, *Proc. Roy. Soc.*, **A220**, 311 (1953).

9) J. Tanaka, This Bulletin, **36**, 1237 (1963).

10) J. Tanaka, T. Kishi, and M. Tanaka, *ibid.*, **47**, 2376 (1974).

11) J. Tanaka, *ibid.*, **38**, 86 (1964).