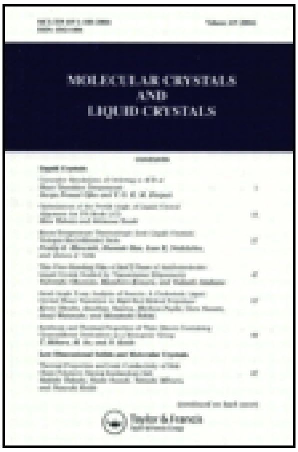

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# Dynamic Behavior of N-(2,4-Dinitrophenyl)-o-Anisidine Crystals

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# DYNAMIC BEHAVIOR OF *N*-(2,4-DINITROPHENYL)-*o*-ANISIDINE CRYSTALS

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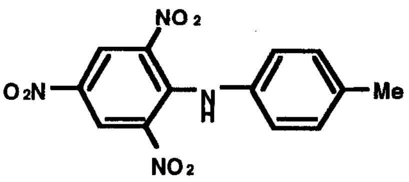
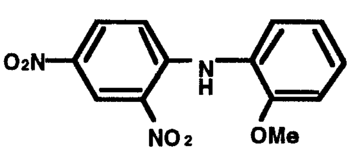
Abstract *N*-Picryl-*p*-toluidine (**I**) and *N*-(2,4-dinitrophenyl)-*o*-anisidine (**II**) crystallize in two modifications, orange and red forms. The orange forms of both compounds transform to the red forms on heating, while the red forms do not change thermally. The thermal transformation of **I** from the orange form (**Io**) to the red (**Ir**) takes place through the liquid phase. In the case of **II**, the transformation from the orange form (**IIo**) to the red (**IIr**) occurred in the solid state over the wide temperature range, 110 ~ 158°C. In order to investigate the mechanism of the phase transformation between these polymorphs, we carried out the observation on the hot-stage with the microscope, the X-ray structure analysis, measurement of temperature dependent powder diffractions, and calorimetry. We also investigated the preliminary study on the structure at high temperature.

## INTRODUCTION

*N*-Picryl-*p*-toluidine (I) and *N*-(2,4-dinitrophenyl)-*o*-anisidine (II) crystallize in two modifications, orange and red forms.[1,2] The condition to crystallize in each form is very subtle, so that it is by chance which form can be obtained from solution. We often observed the coexistence of two forms. The orange forms of both compounds transform to the red forms on heating, while the red forms do not change thermally. In order to investigate the mechanism of the phase transformation between these polymorphs, we carried out the observation on the hot-stage with the microscope, the X-ray structure analysis, measurement of temperature dependent powder diffractions, and calorimetry. We also investigated the preliminary study on the structure at high temperature.



**I**



**II**

## CRYSTAL AND MOLECULAR STRUCTURES

Crystal structures of polymorphic forms have been determined in order to study the relationships between a polymorphism and molecular interactions. Crystal data are listed in Table I. The molecular and crystal structures of the orange form (**Io**) and the red form (**Ir**) of **I** are shown in Figure 1. The molecular structures of **Io** and **Ir** are very similar to each other. Intramolecular NH···O hydrogen bond is formed between anilino and nitro groups. The dihedral angles between two phenyl rings are 59.8° and 58.0° for **Io** and **Ir**, respectively.

TABLE I Crystal Data

| | Io | Ir | IIo | IIr |
|---|---|---|---|---|
| | $C_{13}H_{10}N_4O_6$ | $C_{13}H_{10}N_4O_6$ | $C_{13}H_{11}N_3O_5$ | $C_{13}H_{11}N_3O_5$ |
| FW | 318.17 | 318.17 | 289.25 | 289.25 |
| Color | Orange | Red | Orange | Red |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/a$ | $P2_1/c$ | $P2/a$ | $P2_1$ |
| $a$/Å | 16.475(3) | 13.107(4) | 21.561(5) | 15.693(2) |
| $b$ | 6.007(1) | 17.739(4) | 4.219(1) | 10.981(3) |
| $c$ | 15.203(3) | 6.090(2) | 16.749(5) | 3.842(1) |
| $\beta$ /° | 114.12(1) | 102.16(3) | 122.30(1) | 98.39(2) |
| V/Å$^3$ | 1373.2(4) | 1384.2(8) | 1287.7(6) | 655.0(2) |
| Z | 4 | 4 | 4 | 2 |
| Dx /gcm$^{-3}$ | 1.539 | 1.527 | 1.492 | 1.467 |
| Radiation | MoKα | MoKα | MoKα | MoKα |
| Observed | 2188 | 1434 | 1842 | 886 |
| R | 0.052 | 0.106 | 0.060 | 0.079 |
| mp /℃ | 163.0-164.0 | 167.0-168.0 | 157.5-158.5 | 166.5-167.5 |
| tp * /℃ | 163-167 | | 110-158 | |

* Transition point from the orange to the red form.

The molecular and crystal structures of the orange form (**IIo**) and the red form (**IIr**) of **II** are shown in Figure 2. It was revealed from the structure analysis that the molecule of **IIo** is a rotational isomer of **IIr**. In **IIr**, the NH group is hydrogen-bonded to nitro and methoxy groups bifurcately, while in **IIo** the NH group is hydrogen-bonded only to the nitro group because of an intramolecular rotation of the o-methoxyphenyl group by about 60°. The dihedral angles between two phenyl rings are 63.9° and 50.5° for **IIo** and **IIr**, respectively. In the crystals of **IIo** and **IIr**, molecules are arranged approximately perpendicularly to the shortest axes, the b and c, respectively.

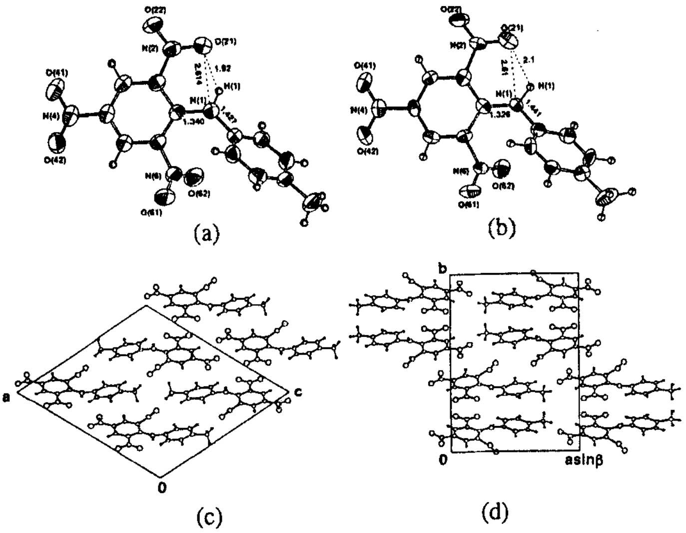


FIGURE 1 The molecular structures of *N*-picryl-*p*-toluidine of (a) the orange form (**Io**) and (b) the red form (**Ir**). (c) Projection of the crystal structure of **Io** viewed along the b axis. (d) Projection of the crystal structure of **Ir** viewed along the c axis.

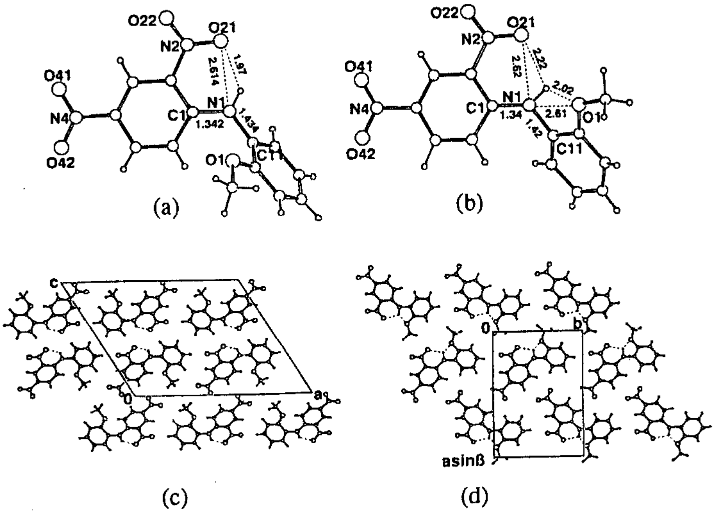


FIGURE 2 The molecular structures of *N*-(2,4-dinitrophenyl)-*o*-anisidine of (a) the orange form (**IIo**) and (b) the red form (**IIr**). (c) Projection of the crystal structure of **IIo** viewed along the b axis. (d) Projection of the crystal structure of **IIr** viewed along the c axis.

## THERMAL BEHAVIOR OF I

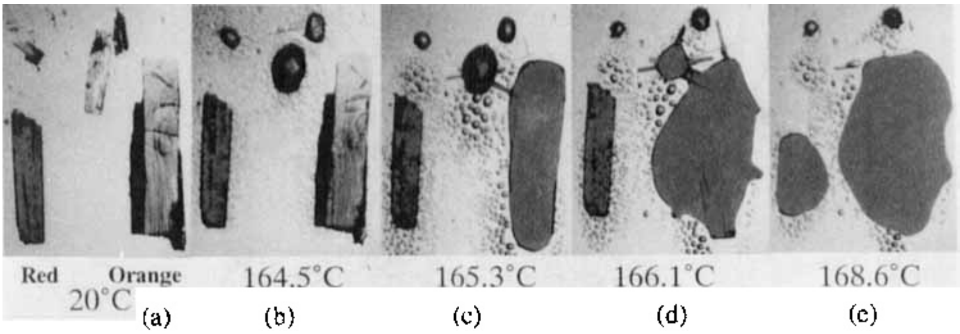
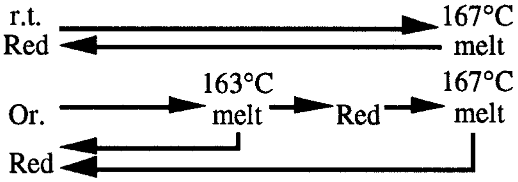


FIGURE 3 The microscopic photographs of the crystals of **I** on the hot stage. (a) Some orange crystals (**Io**) at the right and a red crystal (**Ir**) at the left hand side at the temperature of 20℃. (b) A part of the **Io** began to melt at 164.5℃. (c) The small red crystals began to grow from the molten samples. (d) The red crystals have grown in the molten sample at 166.1℃. (e) The crystal of **Ir** and the grown red crystals have melted at 168.1℃ which corresponding to the melting point of **Ir**. See Color Plate I.



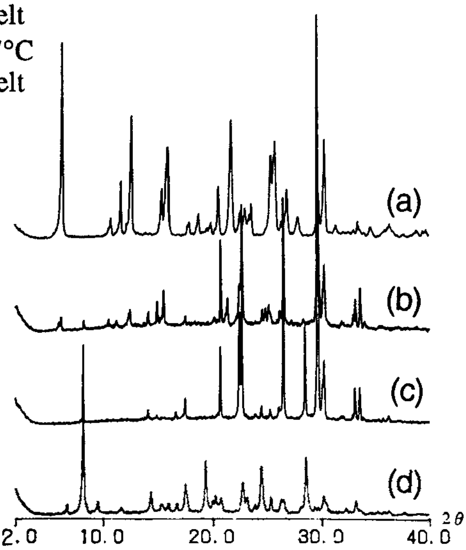


FIGURE 4 The temperature dependent powder diffraction of **I**. (a) The diffraction pattern of **Io** at the room temperature. (b) The diffraction peaks of **Io** are weakened and new peaks are arisen at 164℃ (c) Only the new peaks are remained at 165℃. (d) The diffraction pattern of **Ir** at 164.5℃.

Thermal behavior of the crystals of Io on the hot stage ovserved by the microscope was shown in Figure 3. Crystals of **Io** melted at 163-164℃, with changing thier color from orange to red. After **Io** has melted completely, the red crystals began to grow from the red molten samples as shown in Figure 3(c) and re-melted at 167℃, which coincides with the melting point of **Ir**. It has been confirmed from the measurement of the powder X-ray diffraction that the red crystals growing from the molten samples are the same as those of **Ir** crystallized from the solution as shown in Figure 4. In the case of **I**, the thermal transformation from the orange form to the red takes place through the liquid phase. On cooling from the liquid phase, only **Ir** was obtained, and hence **Io** was crystallized only from the solutions. Crystals of **Ir** melted at 167℃ without showing any change during heating.

## THERMAL BEHAVIOR OF II

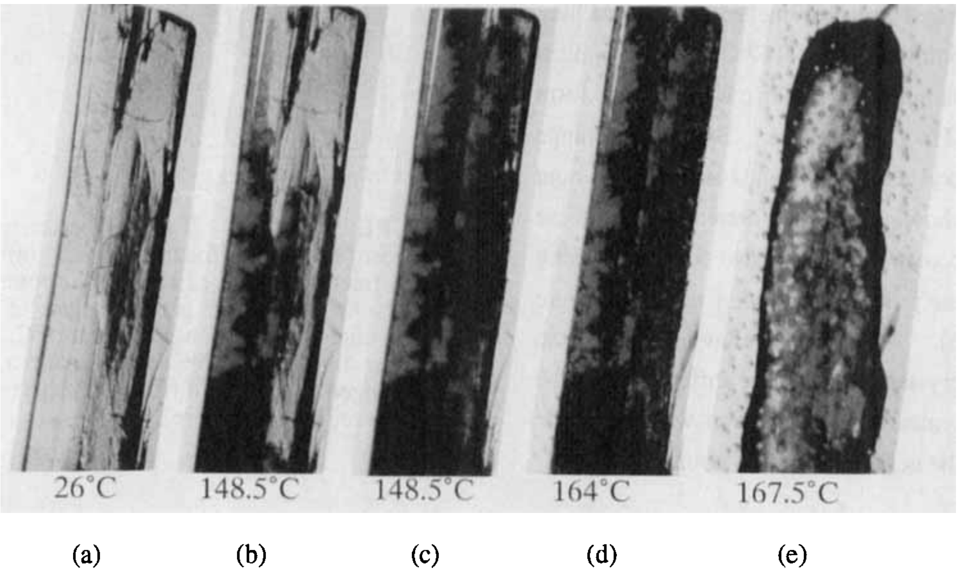
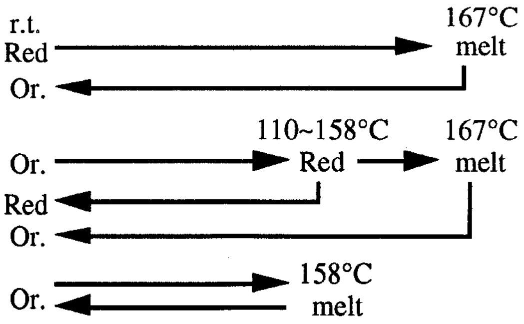


FIGURE 5 The thermal behavior of the single crystal of **IIo** on the hot stage. (a) At the room temperature. (b) Some part of the crystal began to change to the red at 148.5℃. The transformation progressed along the needle axis. (c) After a few seconds, the whole crystal has changed to the red. (d) The crystal did not melt at 164℃, beyond the melting point of **IIo**. (e) The crystal has melted at 167.5°C which coincide to the melting point of **IIr**. See Color Plate II.

In the case of *N*-(2,4-dinitrophenyl)-*o*-anisidine, the transformation from the orange form (**IIo**) to the red (**IIr**) occurred in the solid state over the wide temperature range, 110-158℃ depending on specimen, as shown in Figure 5. At the high temperature the transformation



had completed within a few seconds, but it takes a long time (several hours or days) at the low temperature. These red crystals did not return to the orange form after cooling to the room temperature. Thus this transformation is irreversible in the solid state. The red crystals obtained by the thermal transformation melted at the melting point of **IIr** (167℃). The molten samples recrystallize to an orange form (**IIo**) on cooling. But some orange crystals (**IIo**) melted at 158℃ without showing the transformation. All these conversions were also confirmed using the powder diffraction method (Figure 6). Thermal behavior for these crystals seems to be different from the typical phase transition which indicate the definite transition point.

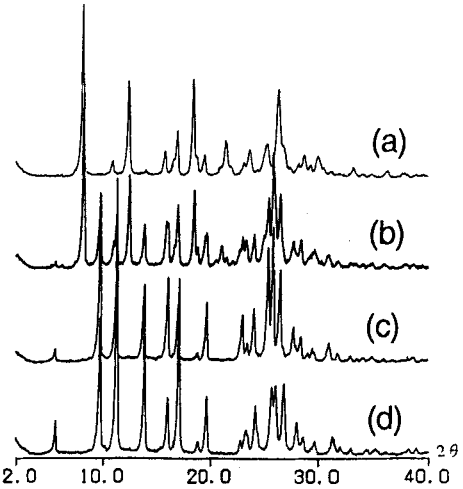


FIGURE 6 The temperature dependent powder diffraction of **II**. (a) The diffraction pattern of **IIo** at the room temperature. (b) The pattern began to change after 20 minutes holding at 115℃. (c) After 4 hours at 115℃, whole pattern has changed. (d) The diffraction pattern of **IIr** at room temperature.

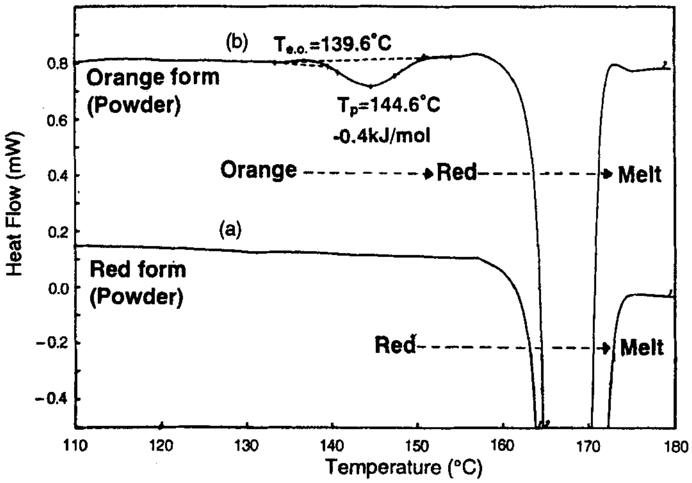


FIGURE 7 The DSC curves of **II** at the heating rate of 10℃/min. (a) **IIr**. The large endotherm at 168℃ corresponds to the melting point. (b) **IIo**. A small endotherm corresponding to the rearrangement to **IIr** was observed at 144℃.

Figure 7 shows the Differential Scanning Calorimetry, DSC, of the ground powder sample of **IIo** and **IIr**. For **IIr** only a large endotherm corresponding to the melting was observed, while for **IIo** a small endotherm corresponding to the rearrangement to **IIr** was observed at 144°C. After this point a large endotherm was observed, which agrees with the melting of **IIr**. Shapes and temperatures of a small endotherm depend on the heating rate. If the rate is slower, peaks become broader. We found from DSC measurements that the ground orange crystals always undergo the transformation. From the observation on the hot-stage with a microscope, some orange single crystals melted without showing the transformation. Therefore it is concluded that the transformation depends on the condition of the crystals. The transformation will start at defects in the crystals and be accelerated by grinding.

## THERMAL REARRANGEMENT OF IIo TO IIr

When some single crystals of **IIo** were kept at 120°C for several hours, half of the each crystal became red as shown in Figure 8. The red region of the crystal remained at room temperature. X-ray oscillation patterns of the orange, the red and the boundary parts were measured using a Weissenberg-type diffractometer with the Imaging Plate. Oscillation photographs of each part that are taken by oscillating the needle axis of the

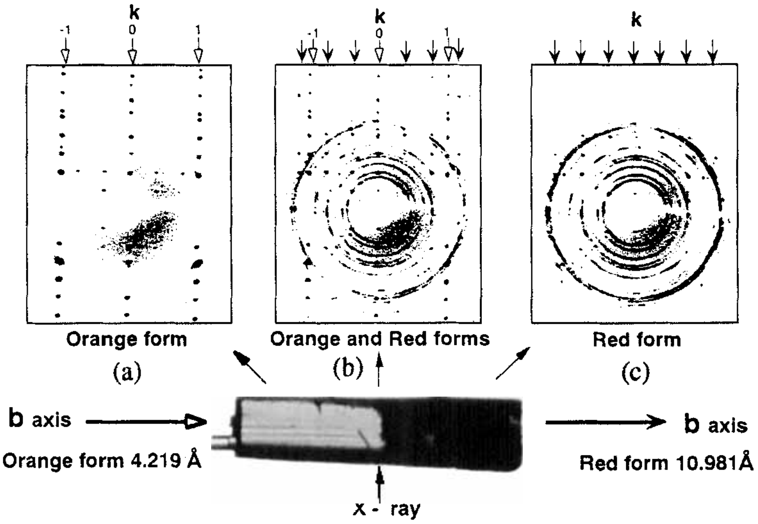


FIGURE 8 A partially transformed crystal of **IIo**. The oscillation photographs of (a) the orange part, (b) the boundary part, and (c) red part. See Color Plate III.

crystal are also shown in Figure 8. An oscillation photograph of the orange part shows that the oscillation axis, the needle axis of the crystal, is the b axis of **IIo**. The red part gave powder diffraction rings showing the preferred orientation. Some sharp Bragg spots were overlapped in this photograph which indicate an existence of the region of a single crystal. In the boundary region, two kinds of Bragg spots, which were recorded at orange and red parts, were observed together. From the symmetry and the period of these spots, oscillation axis of a single crystal region in the red part was revealed to be the b axis of **IIr**. This observation means that the b axis of **IIo**, the needle axis of the crystal before the transfromation, gradually changes to the b axis of **IIr** during the transformation from **IIo** to **IIr**. We examined the same experiments for several crystals and the transformation **IIo** to **IIr** always proceeded retaining the orientation of the b axis. We took other photographs with rotatiing the crystals perpendicularly to the needle axis. The correspondence of the a and c axes between the two forms was different among each specimen. The relationship of the crystal structures of **IIo** and **IIr** viewed along the b axis was shown in Figure 9, where the relationships of the a and c axes of **IIo** and **IIr** were also illustrated according to the observed orientations.

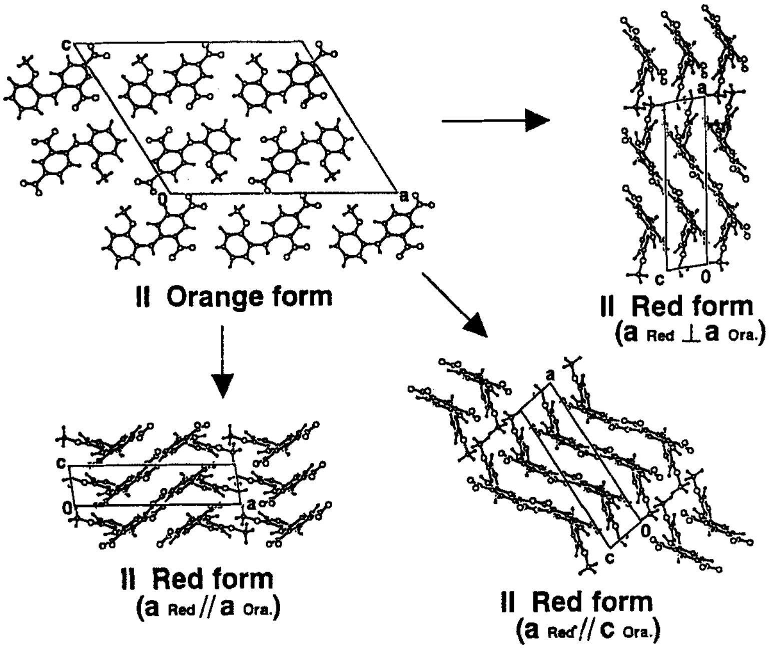


FIGURE 9 The crystal structures of **IIo** and **IIr** viewed along the b axis. The relationships of the a and c axes of each projections are according to the observed orientations from the oscillation photographs of the partially transformed crystals.

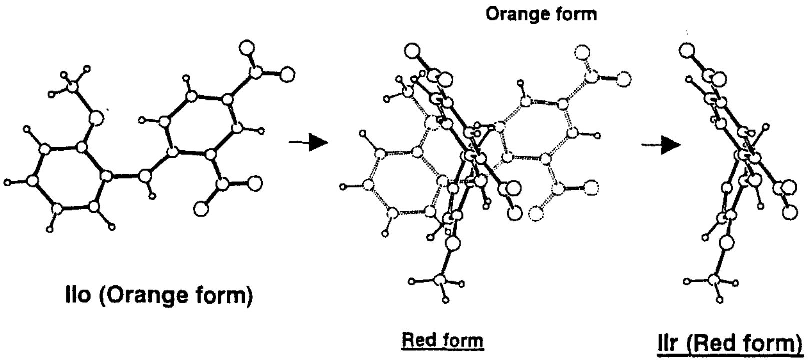


FIGURE 10 The plausible motion of one molecule during the conversion for **IIo** (left) to **IIr** (right).

The molecular planes of **IIo** are approximately perpendicular to the b axis, while those of **IIr** are approximately parallel to the b axis. If the solid-phase transformation from **IIo** to **IIr** occurs retaining the b axis as a needle axis, the whole molecules should rotate by about 90° together with an intramolecular rotation of the o-methoxyphenyl group. In Figure 10, a motion of one molecule is depicted in the course of the phase transformation. The conversion from **IIo** (the left) to **IIr** (the right) may be performed by twisting and then the molecule may stand up like the figure. However, such motion needs a large space, so that this rearrangement may occur at defects in a crystal and destroy the crystal to be a polycrystalline.

## STRUCTURE ANALYSIS OF IIo AT HIGH TEMPERATURE

We expect to catch some intermediate state of the phase transformation of **IIo** from the structure analysis at high temperature. The diffraction data were measured by the Imaging-Plate diffractometer equipped with the $N_2$-gas-stream high-temperature apparatus. Because the transition point has a wide temperature range depending on the specimen, data were recorded at several temperatures up to 130℃. Table II shows the crystal data. Each data set was measured within 2 hours using same specimen. In order to study the time-dependent variation, 3 and 2 sets of data were measured every 3 hours at 120 and 130℃, respectively.

TABLE II Crystal data of **IIo** at several temperatures.

| Temp.(℃) | 24 | 50 | 75 | 100 | 120 | 130 |
|---|---|---|---|---|---|---|
| *a* /Å | 21.538 | 21.555 | 21.514 | 21.592 | 21.554 | 21.594 |
| *b* | 4.228 | 4.253 | 4.272 | 4.310 | 4.328 | 4.344 |
| *c* | 16.743 | 16.736 | 16.655 | 16.714 | 16.694 | 16.716 |
| β /° | 122.29 | 122.28 | 122.22 | 122.21 | 122.12 | 122.08 |
| No. observed | 1612 | 1652 | 1601 | 1517 | 1370 | 1289 |
| R | 0.084 | 0.090 | 0.091 | 0.092 | 0.090 | 0.089 |

The crystal structures were successfully refined using each data set. The structure was revealed to be an orange form even at the 130℃. Thus the phase transformation did not occur in this case. However the cell parameters changed anisotropically during the heating. The b axis simply elongated while the a and c axes did not show significant changes. This lengthening corresponds to the widening of the distance between molecular planes which arrange vertically to the b axis. Anisotropic temperature factors obtained at 130℃ also showed a large movement perpendicular to the molecular plane. These results may partially support our plausible mechanism proposed above.

## ACKNOWLEDGMENT

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