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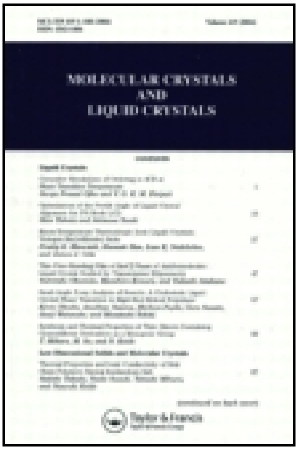

# Molecular Crystals and Liquid Crystals

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# Molecular and Crystal Structure of the α and β Forms of 9,10 - Phenanthrenequinone

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# Molecular and Crystal Structure of the α and β Forms of 9,10-Phenanthrenequinone

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9,10-Phenanthrenequinone was found to have at least two modifications. One of the forms, (α), belongs to the space group P2/c with $a = 16.450(2)$, $b = 7.988(1)$, $c = 7.738(1)$Å, $\beta = 103.60(2)°$, $Z = 4$ and has been refined to an $R$ factor of 0.069 on 391 non-zero reflections. Another form, (β), belongs to the space group $P\bar{1}$ with $a = 15.170(2)$, $b = 15.540(1)$, $c = 8.346(1)$Å, $\alpha = 83.51(1)$, $\beta = 76.57(1)$, $\theta = 31.21(1)°$, $Z = 4$ and has been refined to an $R$ factor of 0.092 on 2604 non-zero reflections. It was found that molecules in the β form were paired by approaching their carbonyl groups to each other at smaller distances than the sums of the van der Waals radii, while molecules in the α form were parallel to and separated at a distance of 3.60Å from each other in columns. There is some evidence for existence of other modifications in addition to the above two.

*Keywords: phenanthrenequinone, quinone, crystal structure, polymorphism, polymorphore*

## INTRODUCTION

We have recently studied the electronic spectra of various fundamental quinones, especially the phosphorescence spectra in the solid state. We purified crude quinones by various methods as many times as possible, in order to get rid of the quenching by impurities and to obtain intrinsic emissions. The 9,10-phenanthrenequinone (PHQ) crystal, which is one of the fundamental quinones, has seldom emitted phosphorescence in spite of its high purity. It was quite extraordinary in comparison with other quinones.

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The molecular and crystal structures of the fundamental quinones such as *p*- and *o*-benzoquinones,[1] naphthoquinone,[2] anthraquinone,[3] acenaphtenequinone,[4] and their derivatives[5] have been studied in detail, while those of PHQ have not been reported except for the crystal data[6] only. It was, therefore, presumed that there were some difficulties in the structural analysis of PHQ. As a result, a complicated polymorphism of PHQ was found.

## EXPERIMENTAL

Commercially available PHQ was purified by the zone refining method of 3000 passes, following recrystallization from the benzene solution. The purified crystals were clear orange and did not show any strange peak in the liquid chromatograms up to the sensitivity of ppm, supposing the equality of absorbances of materials at 256nm. This was used for obtaining various crystallines as an initial substance.

Single crystals of the α form of PHQ were obtained by vapour deposition on the inner wall of a glass tube from the melt or Bridgeman method. Single crystals of (α) obtained by vapour deposition were oblong tablets and those obtained by Bridgeman method could be cleaved to the cube. These two were identified by powder X-ray method and thermal analysis. However, these crystals were doubted to be twinned in the course of structure analysis. After many trials to obtain true single crystals, a small needle-shaped crystal was found among the oblong tablets, in the sublimation of the powder at 150°C in a glass tube evacuated by a rotary pump. It was the only true single crystal that we have found.

Single crystals of the β form of PHQ were obtained by slow cooling and vaporization of either chloroform or acetic acid solution. The crystals of (β) obtained from the chloroform solution were flat trapezoidal tablets and those obtained from the acetic acid solution were sexanglar tablets. These two kinds of crystals were identified by the powder X-ray method and thermal analysis.

The X-ray diffractions were measured by a Rigaku-Denki powder diffractometer and a Rigaku-Denki AFC-4 four-circle diffractometer. The intensities in single crystal diffractometry were collected with Cu Kα or Mo Kα radiation monochromatized by a graphite crystal at room temperature (scan speed = 4°/min).

A Shimadzu DT-30 thermal analyser was used for the differential thermal analysis (DTA) and the differential scanning calorimetry (DSC). The DTA and DSC curves were obtained for several milli-

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grams of PHQ powder by heating at a rate of 10°C/min in the flow of nitrogen gas (30ml/min). PHQ powders and $\alpha$ alumina, a reference, were shielded in the cell withstanding the inner pressure of ca. 3 atm because PHQ is easily sublimed near the melting point in the air. The transition temperature and heat were corrected to the melting points and the heat of fusion of the NBS-ICTA's indium and stunnum, respectively.

## STRUCTURE ANALYSIS OF FORM $\alpha$

Studies were carried out on the crystal of the dimension 0.5 × 0.01 × 0.03 mm$^3$ obtained by the above-mentioned sublimation. Reflections in the range $2\theta = 3°$ to $55°$ were measured by a $2\theta$-$\omega$ scan method with Mo K$\alpha$ radiation. The intensities in the high angle region were so weak that only 391 independent reflections could be used for the analysis. The crystal data are listed in Table I. The structure was solved by the MULTAN 72 system.[8] The position of the hydrogen atoms were given by the calculation. The structure parameters were refined by the block-diagonal least squares method. The final refinement converged to an R-value of 0.069. All calculations were performed by the UNICS III programs.[9]

The final atomic coordinates for ($\alpha$) are given in Table II.

As for the twinned crystals, an orthorhombic cell was erroneously taken: $a = 31.97$, $b = 7.729$, $c = 7.795$Å. It turned out that the

TABLE I

Crystal data of the $\alpha$ and $\beta$ forms of phenanthrenequinone.

| | $\alpha$-form | $\beta$-form | |
|---|---|---|---|
| Crystal system | Monoclinic | Triclinic | |
| Space group | $P2/c$ | $P\bar{1}$ | $P\bar{1}$ |
| Cell constants | | | (super lattice) |
| a(Å) | 16.450(2) | 15.170(2) | 29.24 |
| b(Å) | 7.988(1) | 15.540(1) | 10.43 |
| c(Å) | 7.738(1) | 8.346(1) | 12.95 |
| $\alpha$(°) | 90.00 | 83.51(1) | 89.70 |
| $\beta$(°) | 103.60(2) | 76.57(1) | 97.83 |
| $\gamma$(°) | 90.00 | 31.21(1) | 89.85 |
| Number of molecules in a cell | 4 | 4 | 16 |
| Density (calc.) (g.cm$^{-3}$) | 1.421 | 1.412 | |
| Density (obs.) (g.cm$^{-3}$) | 1.41 | 1.41 | |

TABLE II

Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) of the $\alpha$ form.

| ATOM | X | Y | Z | BEQV |
|---|---|---|---|---|
| OA | 780( 8) | 9298(14) | −1472(21) | 8.2 |
| C1A | 427(10) | 7921(21) | −1877(24) | 4.8 |
| C2A | 867(10) | 6345(21) | −1258(20) | 3.6 |
| C3A | 1648(10) | 6330(24) | −69(23) | 5.3 |
| C4A | 2024(10) | 4861(24) | 429(22) | 5.2 |
| C5A | 1605(10) | 3387(18) | −140(21) | 3.7 |
| C6A | 821(10) | 3373(17) | −1279(22) | 3.8 |
| C7A | 418( 8) | 4870(20) | −1880(19) | 3.2 |
| OB | 5783( 8) | 4350(15) | −2720(22) | 8.4 |
| C1B | 5441(10) | 3045(20) | −2646(28) | 5.9 |
| C2B | 5847(10) | 1411(21) | −2868(22) | 4.3 |
| C3B | 6632(10) | 1402(23) | −3216(21) | 4.2 |
| C4B | 7019( 9) | −69(25) | −3426(22) | 5.3 |
| C5B | 6601(11) | −1561(24) | −3317(23) | 5.6 |
| C6B | 5827(10) | −1603(18) | −2914(20) | 3.8 |
| C7B | 5403( 8) | −76(20) | −2719(18) | 3.2 |

relation $a^*\cos\beta = 0.5c^*$ is almost satisfied in the monoclinic crystal form. It is impossible to recognize whether the crystals are twinned or not from the x-ray diffraction in such a special condition.[10] The monoclinic crystals joined at the plane (100) in twinning.

## STRUCTURE DETERMINATION OF FORM β

Studies were carried out on a crystal of the dimension $0.6 \times 0.2 \times 0.1$ mm$^3$ obtained from the chloroform solution. 2935 independent reflections were collected in the range $2\theta = 3°$ to $120°$ with Cu K$\alpha$ radiation. 2604 reflections of these satisfied the equation $h + k = k + 1 = 1 + h = 2n$. The values of the Fo's for the rest were less than 2.0, excepting two reflections: $|Fo(\overline{17}\ 6\ 3)| = 85.10$ and $|Fo(\overline{17}\ 0\ 3)| = 37.46$. 2604 reflections were used for the analysis on the assumption that these exceptional two were due to some disorder in the lattice. The cell data are listed in Table I. The structure was solved by the same procedure to that in ($\alpha$) on the basis of this cell. The final R-value of 0.092 was obtained. Also, a structure which has a larger unit cell resulted from the analysis on the basis of all 2935 reflections. This unit cell contained four above cells and was regarded as a super lattice. The data for this lattice are also in Table I. Figure 1 shows one of the elemental cells in the super lattice. The final atomic coordinates of ($\beta$) are given in Table III.

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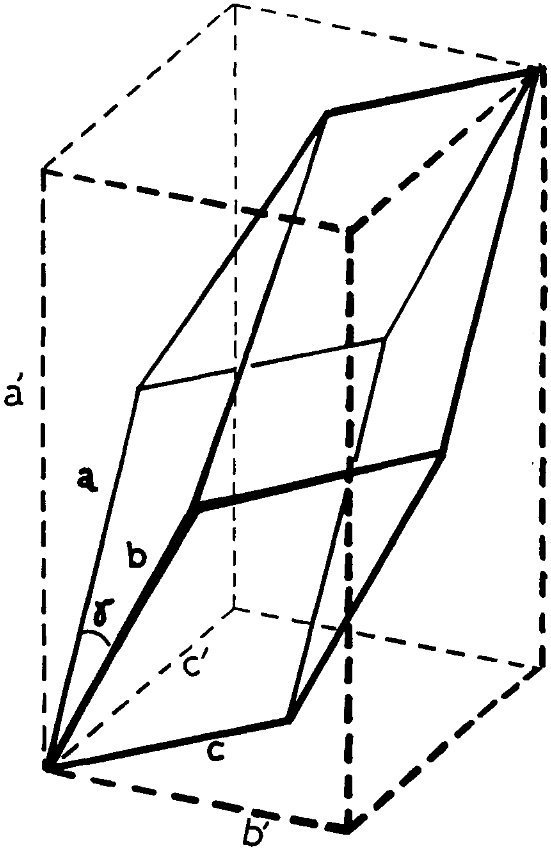

FIGURE 1 The elementary cell (solid line) and the super lattice (broken line) of the β form of the PHQ crystal.

## THERMAL ANALYSIS

Crystallization modes of samples used for thermal analysis are listed in Table IV. Endothermic transition peaks were observed for all samples in DTA. The crystals (1) and (2) transform at 186°C, (3) and (4) at 168°C, (5) at 173°C, and (6) at 159°C, respectively. Their heat of transition were 1.1, 1.1, 1.0, 0.9, 1.0 and 1.0 $\mathrm{Kjmol^{-1}}$, respectively. These transitions were monotropical and all the transformed solids melted at 208°C. That is, no transition peak was observed in DTA in cooling from the melting point and in the repeated DTA after that, except for the melting and the freezing. The solid phase which has

TABLE III

Atom coordinates ( × $10^4$) and temperature factors (Å$^2$ × $10^3$) of the β form.

| ATOM | X | Y | Z | BEQV |
|---|---|---|---|---|
| 1 O 2A | 1228( 6) | 4806( 6) | 3851( 7) | 4.1 |
| 2 O 1B | 21( 6) | 8885( 6) | 4844( 6) | 3.9 |
| 3 O 2B | 2940( 7) | 7373( 7) | 3055( 6) | 4.2 |
| 4 O 1A | 1565( 6) | 3083( 6) | 2292( 7) | 4.5 |
| 5 C13A | −1572( 8) | 7414( 8) | 3386( 8) | 2.7 |
| 6 C 8B | 3458( 8) | 6989( 7) | 7215( 8) | 2.6 |
| 7 C 7B | 1906( 8) | 7747( 7) | 8198( 7) | 2.5 |
| 8 C 8A | −2923( 8) | 8244( 8) | 2753( 8) | 2.6 |
| 9 C 2B | 727( 8) | 8393( 8) | 7397( 7) | 2.6 |
| 10 C13B | 3828( 8) | 6849( 7) | 5471( 8) | 2.7 |
| 11 C 2A | −1253( 8) | 5542( 8) | 1848( 7) | 2.7 |
| 12 C 1B | 1018( 8) | 8315( 8) | 5558( 8) | 2.8 |
| 13 C14A | 51( 8) | 5571( 8) | 3282( 8) | 2.7 |
| 14 C14B | 2654( 9) | 7484( 8) | 4573( 8) | 2.8 |
| 15 C 7A | −2781( 8) | 7306( 8) | 1990( 8) | 2.8 |
| 16 C 1A | 206( 8) | 4608( 8) | 2441( 8) | 2.9 |
| 17 C12B | 5332( 9) | 6092( 8) | 4548( 9) | 3.3 |
| 18 C12A | −1712( 9) | 8299( 9) | 4167( 9) | 3.4 |
| 19 C 6B | 1530( 9) | 7888( 9) | 9933( 8) | 3.4 |
| 20 C 3B | −761(10) | 9126( 9) | 8315( 9) | 3.9 |
| 21 C 9A | −4411( 9) | 9987( 8) | 2899( 9) | 3.6 |
| 22 C11B | 6460( 9) | 5478( 9) | 5533(10) | 3.9 |
| 23 C 9B | 4672(10) | 6329( 9) | 7985( 9) | 3.8 |
| 24 C10B | 6128( 9) | 5603( 9) | 7059(10) | 4.0 |
| 25 C 6A | −4130( 9) | 8111(10) | 1373( 9) | 4.1 |
| 26 C 3A | −1124(10) | 4648(10) | 1132( 9) | 4.0 |
| 27 C 5B | 38(10) | 8635(10) | 10846( 9) | 4.0 |
| 28 C10A | −4554( 9) | 10861( 9) | 3683(10) | 4.1 |
| 29 C11A | −3227(10) | 10038( 9) | 4299( 9) | 4.1 |
| 30 C 4B | −1099(10) | 9244(10) | 10048(10) | 4.4 |
| 31 C 4A | −2483(11) | 5491(12) | 560(10) | 4.7 |
| 32 C 5A | −3967(11) | 7212(11) | 675(10) | 4.8 |

TABLE IV

Modes of Crystallization

| Crystal | Mode of Crystallization |
|---|---|
| (1) | crystallized by the Bridgman method |
| (2) | slow vapour deposition above the melt |
| (3) | recrystallization from the chloroform solution |
| (4) | recrystallization from the acetic acid solution |
| (5) | recrystallization fron the benzene solution |
| (6) | quenched in liquid nitrogen for one hour after being rapidly solidified from melt |

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no transition between room temperature and the melting point is thought to be a quasistable phase, because it turned to another crystal state which showed a transition peak at 159°C in DTA after having been quenched in liquid nitrogen for one hour; it corresponds to (6).

## X-RAY POWDER DIFFRACTION

The patterns of x-ray powder diffraction were taken for the crystals listed in Table IV. The patterns of (1) and (2) were the same and those of (3) and (4) were also the same. These two kinds of patterns are not visually identical and correspond to (α) and (β), respectively. The interplanar spacing and the reflective intensities corresponding to some strong lines in the four types of crystals are listed in Table V, in which calculated *d*-spacings for (α) and (β) are also listed in parentheses. The observed and calculated *d*-spacings of (α) and (β) coincide within 0.007Å with each other. The pattern of (5) resembles that of (β), but the value of each *d*-spacing is slightly larger than that

TABLE V

Interplanar spacings corresponding to the some strong lines in the powder x-ray diffraction patterns (d > 3.1Å).

| α-form* | | β-form* | | (5)* | | γ-form* | |
|---|---|---|---|---|---|---|---|
| $d_{obs}$ | $I(d_{calc})$ | $d_{obs}$ | $I(d_{calc})$ | $d_{obs}$ | I | $d_{obs}$ | I |
| 8.029 | 100(8.00) | | | | | 8.169** | 58 |
| | | 7.971 | 14(7.96) | | | | |
| | | 7.363 | 100(7.33) | 7.375 | 100 | 7.326 | 83 |
| 7.149 | 79(7.15) | | | | | | |
| | | 6.445 | 38(6.48) | 6.511 | 19 | 6.521 | 38 |
| | | | | | | 5.571 | 17 |
| | | 5.161 | 31(5.13) | 5.225 | 19 | 5.231 | 23 |
| | | 4.527 | 18(4.52) | 4.557 | 16 | 4.553 | 18 |
| 4.439 | 47(4.43) | | | | | | |
| | | | | | | 4.475 | 27 |
| | | 4.250 | 41(4.25) | 4.289 | 34 | 4.270 | 63 |
| 4.002 | 27(4.00) | | | | | | |
| 3.762 | 30(3.76) | | | | | 3.576 | 21 |
| | | 3.675 | 46(3.67) | 3.696 | 55 | 3.691 | 60 |
| 3.485 | 67(3.48) | | | | | 3.521** | 63 |
| | | 3.249 | 49(3.24) | 3.269 | 84 | 3.264 | 100 |
| 3.127 | 24(3.13) | | | | | | |

*See Table IV. Patterns of (1) and (2) are the same and listed as α, and those of (3) and (4) are the same and listed as β. The γ form corresponds to (6).

**These are strong unique lines.

TABLE VI

Distance from atoms to the plane of the phenanthrene framework (Å).

| | α-form | β-form |
|---|---|---|
| atom | distance (σ) | distance (σ) |
| O1 | -0.07(2) | -0.07(1) |
| O2 | 0.08(2) | 0.06(1) |
| C1 | 0.00(1) | -0.02(1) |
| C2 | -0.02(2) | -0.01(1) |
| C3 | 0.02(2) | 0.02(1) |
| C4 | -0.02(2) | 0.04(2) |
| C5 | 0.00(1) | 0.02(1) |
| C6 | 0.01(1) | 0.00(1) |
| C7 | 0.01(1) | -0.01(1) |
| C8 | 0.00(1) | 0.01(1) |
| C9 | 0.01(1) | -0.00(1) |
| C10 | -0.01(1) | -0.02(1) |
| C11 | -0.02(2) | -0.03(1) |
| C12 | 0.00(1) | 0.01(1) |
| C13 | 0.01(1) | 0.03(1) |
| C14 | 0.01(1) | 0.03(1) |

of (β). The pattern of (6) includes many lines which are also found in (5), but the intense lines at 8.169 and 3.521Å are unique.

## DISCUSSION OF α AND β FORMS

The results of the X-ray structure analyses for (α) and (β) show that the crystal systems and space groups of the two crystal forms are different, which the molecular structures in them are quite equal.

Atomic displacements from the plane of the phenanthrene framework in (α) and (β) are listed in Table VI. It is seen from Table VI that the phenanthrene framework composes a complete plane in an experimental.error and two oxygens are slightly deviated to the opposite side from the plane. The bond lengths of the molecules in the α and β forms are shown in Figure 2, where the bond angles are omitted because the atoms in the molecule were almost on the same level. The bond lengths and bond angles were reasonable in comparison with other *o*-quinones[2,4] in both crystals.

Polymorphism of organic molecular crystals in classified into two kinds. One is that the molecular structures are different in different modifications and the other is that the molecular structures are equal even in different modifications. It is known that molecules are more

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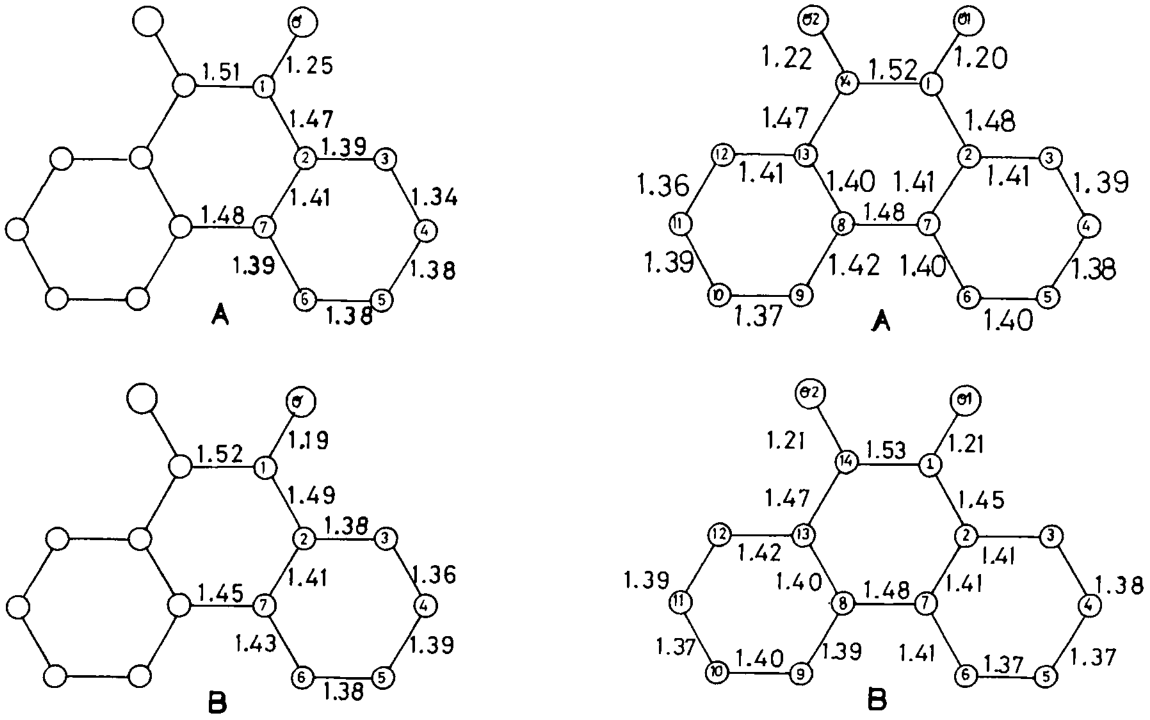

FIGURE 2 Atomic nomenclature and bond lengths (Å) of the molecules in the α and β forms of the PHQ crystal. Molecules A and B of the α form are on the left and those of the β form are on the right. It is supposed that the molecules of the α form are symmetrical.

or less spherical in shape in the latter crystals.[7] PHQ belongs to the latter case in spite of the planar molecule.

Both the crystal structures can be described conveniently in terms of columns of molecules. The projection along the *b* axis of the α form and that along the *c* axis of the β form are shown in Figure 3 and 4 respectively.

In Figure 3, the molecules are stacked parallel with each other, inclining in a column along the *c* axis, and their molecular planes are normal to the plane (010). The angle between molecular planes in neighboring columns is 49.6(3)°. The neighboring molecules in the column are arranged in the opposite direction of their α-diketone groups and their molecular planes are apart from each other about 3.6Å. Some of the shortest interatomic distances between neighboring molecules in (α) are listed in Table VII. Table VII shows that the hydrogen-hydrogen and the hydrogen-carbon distances are almost equal to the sums of their van der Waals radii (SVWR), and that the oxygen-oxygen and the oxygen-carbon distances are much larger than SVWR. This means that the dispersion forces between the phenanthrene frames are dominative to pack molecules in the α crystal.

On the other hand, molecules in (β) make a pair and the pairs are piled up along the direction (110) as seen in Figure 4. There are two

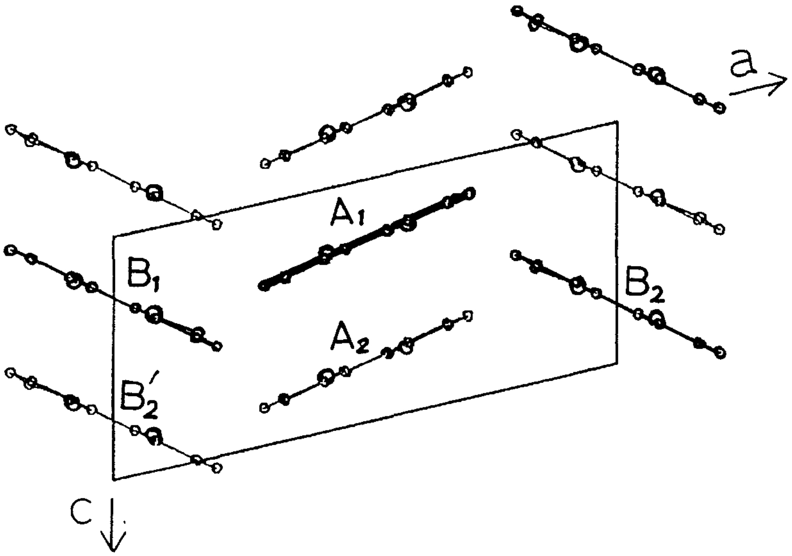

FIGURE 3 The projection along the *b* axis of the α form of the PHQ crystal.

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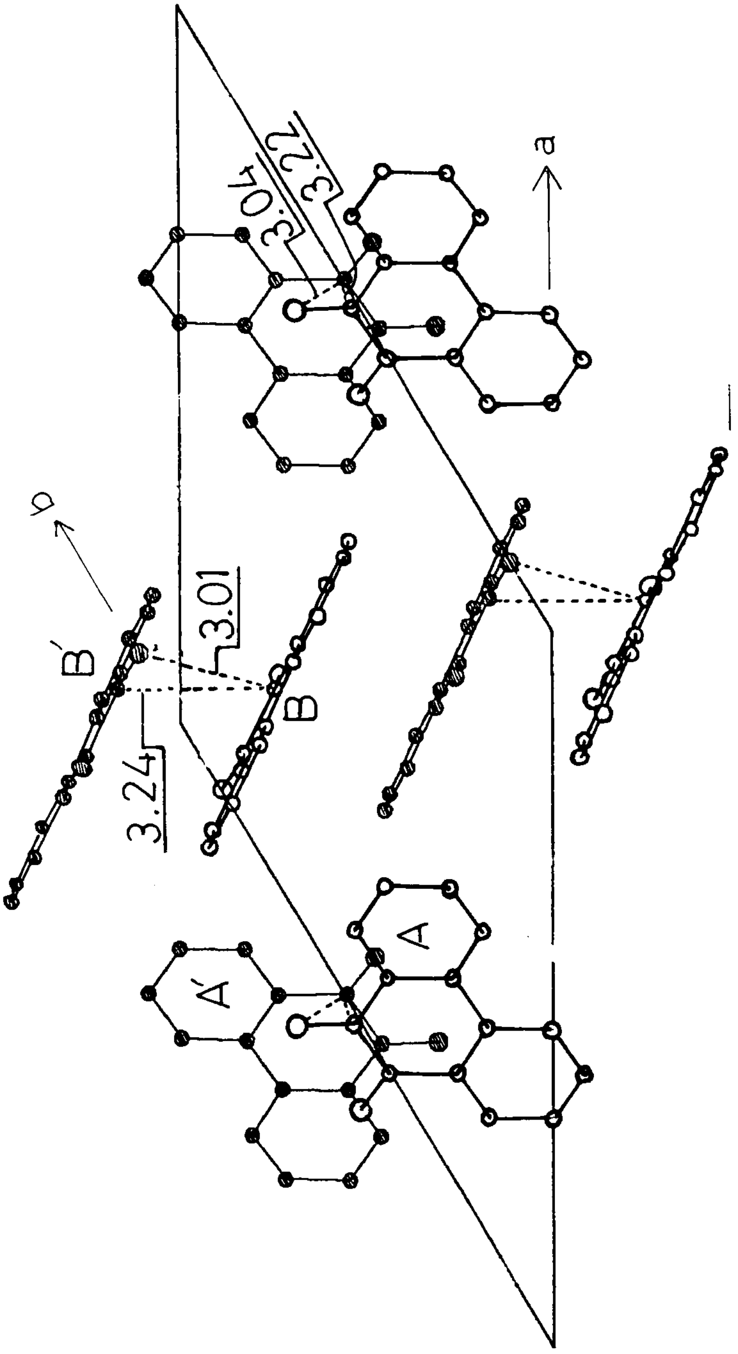

FIGURE 4 The projection along the *c* axis of the β form of the PHQ crystal.

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TABLE VII

Somes of the shortest interatomic distances between neighboring molecules (Å).

| α-form<br>atom—atom | | distance (σ) | β-form<br>atom—atom | | distance (σ) | SVWR* |
|---|---|---|---|---|---|---|
| $OA_1$ | $OB_1$ | >3.80 | O2A | O2A′ | 3.32(1) | 2.8 |
| $OA_1$ | $OA_2$ | >3.80 | O2A | O1A′ | 3.37(1) | |
| $OA_1$ | $C4B_1$ | 3.68(2) | O2A | C1A′ | 3.04(1) | 3.1 |
| | | | O2A | C14A′ | 3.05(1) | |
| | | | O1B | C14B′ | 3.01(1) | |
| | | | O1B | C1B′ | 3.12(2) | |
| $C2A_1$ | $C5A_2$ | 3.50(2) | C1B | C1B′ | 3.22(2) | 3.4 |
| $C3A_1$ | $C6A_2$ | 3.52(3) | C14A | C14A′ | 3.24(2) | |
| $C7A_1$ | $C7A_2$ | 3.50(2) | C13B | C13B′ | 3.24(1) | |
| $C2B_1$ | $C5B_2'$ | 3.45(2) | C2A | C2A′ | 3.40(1) | |
| $C3B_1$ | $C6B_2'$ | 3.57(2) | | | | |
| $C7B_1$ | $C7B_2'$ | 3.47(2) | | | | |
| $H(C4B_1)$ | $H(C5A_1)$ | 2.41(13) | | | | 2.4 |
| $H(C5B_1)$ | $H(C4A_1)$ | 2.42(11) | all(H—H) | | >2.50 | |
| $H(C3A_1)$ | $H(C3B_1)$ | 2.47(11) | | | | |

*The sum of the van der Waals radii.

ways of piling; in one way, the molecular planes are normal to the plane (110) and in the other, they are almost in the plane (110). The angle between the planes of these two pairs is 80.9(2)°. Some of the shortest interatomic distances between neighboring molecules in (β) are also listed in Table VII. It should be noted that the phenanthrene frames in a pair do not overlap in spite of the fact that their planes are parallel. Instead, one carbonyl group of one molecule in a pair is closer to that of the other than the expected position from their SVWR. The extraordinary short oxygen-carbon and carbon-carbon distances are shown in Figure 4. Similar results have not been reported in other *o*-quinones.[1b,2]

Short O...O═C contacts have been reported by several authors,[11] but in their reports the molecules in crystals don't make a pair and the planes of two interacting molecules are nearly normal to each other. Such a short O...O═C contact as is observed in (β), therefore, is unique.

## OTHER CRYSTAL FORMS

There may exist two other forms, (5) and (6), in addition to (α), (β), and the quasistable phase. The crystal (6), had an endothermic transition peak at 159°C in DTA, besides the before-mentioned unique

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lines in its powder pattern. We call it the γ form here. Single crystals of (γ) can not be obtained, because if the melt is cooled so slowly as to grow a single crystal, it must become (α).

Crystallines obtained from the benzene solutions were rectangular tablets, needles, or thoroughly cracked pieces, according to the observation by light microscopy, and showed endothermic peaks at 168, 173, or 193°, depending on crystals. They were not mixed up under a certain experimental condition, but the reproducibility in shape was very poor. The crystal (5) of rectangular tablets is one of them and may differ from (β), although its powder pattern and its transition point are similar to those of (β). However, crystals suitable for structure determination could not be found.

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