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Radiation Damage of an Organic Crystal

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A study has been made of the kinetics of radiation damage of copper hexadecachlorophthalocyanine with an electron microscope. It is considered that cross-linking between neighbouring molecules along [100] or [110] is an initial process for radiation damage. Optical diffraction from the high-resolution micrograph revealed a dynamical deformation of the crystal structure.

1. Introduction

The instrumental resolving power of a conventional electron microscope is 2–3 Å. Thus the structure determination of organic or biological materials by electron microscopy would be straightforward but for radiation damage (Unwin & Henderson, 1975). Many authors have reported the kinetics of radiation damage, employing various methods for measurement of the degradation of specimens, *e.g.* light absorption, mass loss, contrast fading, electrical properties and the fading of the diffraction intensity. However, these results give only general information about radiation damage and little about the details. It would be of interest if the kinetics of radiation damage could be investigated down to molecular order at least.

For this purpose, we chose copper hexadecachlorophthalocyanine, which has considerable resistance to electron irradiation (Harada, Taoka, Watanabe, Ohara, Kobayashi & Uyeda, 1972; Kobayashi & Reimer, 1975). The direct observation of its molecular image was achieved by Uyeda, Kobayashi, Suito, Harada & Watanabe (1972). Uyeda & Ishizuka (1974) explained the image formation, taking into account both the spherical aberration and defocus condition of the objective lens. Its crystal structure was determined by Uyeda *et al.* (1972). The c axis of a crystallite grown epitaxically on a KCl substrate makes an angle of about 26° with the normal of the substrate, and planar molecules are stacked parallel along **c**. In order to observe the molecular image, the c axis of the crystallite must be made parallel to the electron beam with a tilting stage.

We give here, as a first step, the kinetics of radiation damage observed in successive steps and also some details of the damaged structure, obtained by optical diffraction.

2. Experimental

The substrate single crystal of KCl was cleaved in air and immediately placed in an evaporation chamber which was evacuated to about 10^{-6} torr. The substrate was baked out at 450°C for 1 h. Copper hexadecachlorophthalocyanine was evaporated from a Mo boat on to the substrate which was held at $350 \sim 400$ °C. The film thickness was kept at less than 150 Å, which is considered suitable for high-resolution work without interference from dynamical scattering. The specimen film was then mounted on a dimpled Cu grid on which a porous carbon film had been deposited. The grid was used instead of a goniometer stage because it was more stable and also provided various orientations of the crystallite. Electron-microscope observation was carried out with a JEM 100C. In most cases, the magnification was 150 000. An X-ray film (Ilford, Industrial G) was used for recording the image with an exposure time <2 s. To examine the damaged structure, an optical diffractometer was used.

3. Results

Fig. 1 shows a series of electron micrographs taken under nearly the same focus condition (800–900 Å). Correction for focus and astigmatism needed 10–15 s at least. Therefore, Fig. 1(*a*) shows a crystallite that has already suffered from electron irradiation at the local areas marked by letters $A-E$, which are much whiter than the surroundings. These areas spread out gradually with increasing exposure and finally join. When exposed for a long time, the specimen film shows a uniformly faded contrast which suggests severe degradation (Fig. 1*d*).

From general features, it can be inferred that the crystal was damaged preferentially along [100], [110] and [1$\bar{1}$0]. The boundaries running along those directions distinguish the surviving from the damaged areas (see *f*, *g*, *h* in Fig. 1). The fact that we can observe the molecular image clearly even in the vicinity of boundaries, suggests that a crystallite was not damaged gradually and uniformly over a wide area but preferentially, probably related to the crystal structure. Thus a molecule near the boundary, but in the surviving area, has a narrow escape from radiation damage.

The molecular image (Fig. 1) is in good agreement with the simulated image at 900 Å underfocus (Uyeda & Ishizuka, 1974), and Fig. 2 is in good agreement with the image at an overfocus of about -200 Å. It can also be seen that the molecular image changes

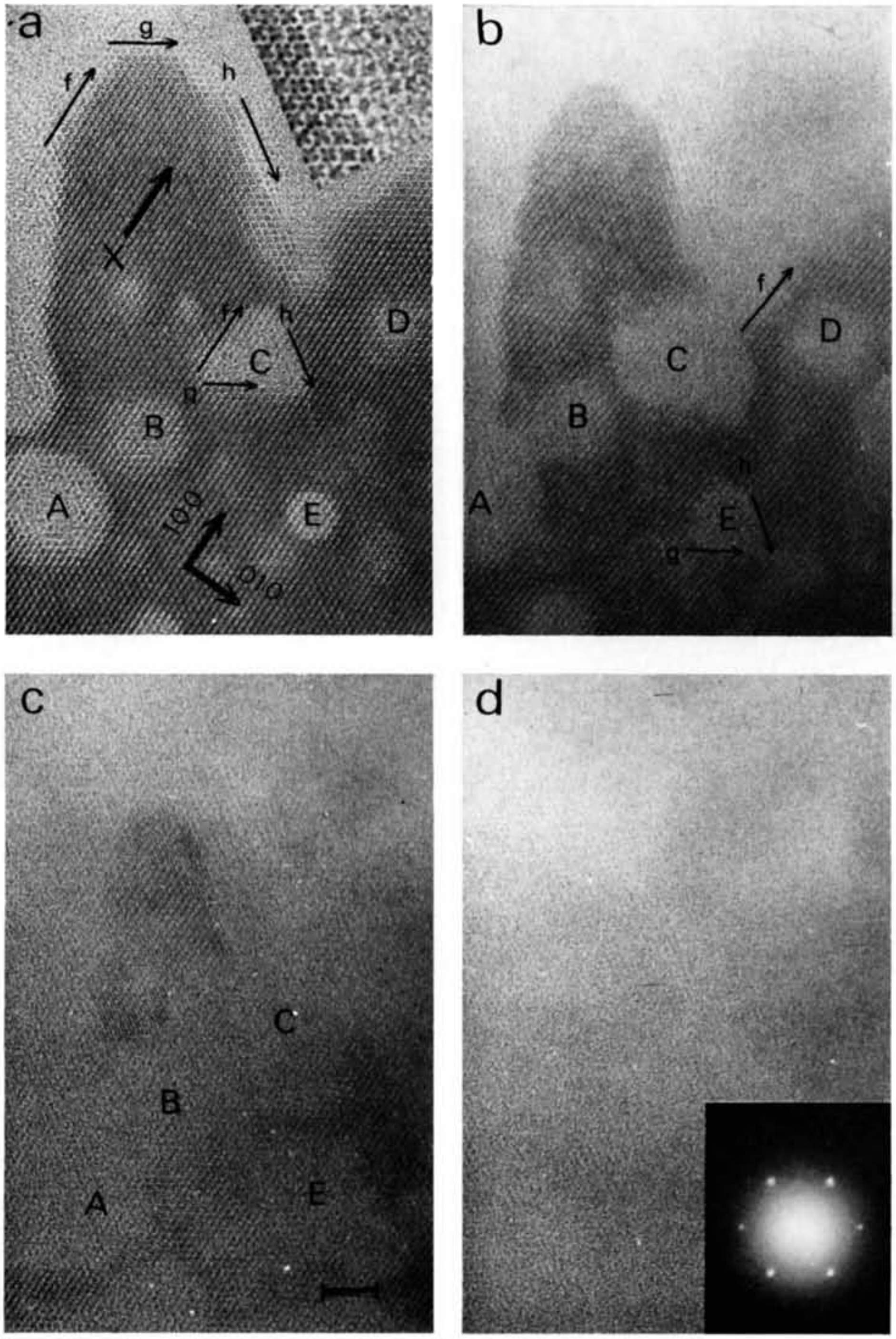

Fig. 1. Electron micrographs of copper hexadecachlorophthalocyanine, taken at approximately the same focus condition (800 – 900 Å underfocus). (*a*) after 10 s, (*b*) 30 s, (*c*) 60 s, (*d*) 120 s. Arrows *f*, *g*, *h* represent the [100], [110], $[\bar{1}10]$ directions, respectively. The insets show an enlarged micrograph (× 2) and a selected-area electron diffraction pattern. Scale bar corresponds to 100 Å.

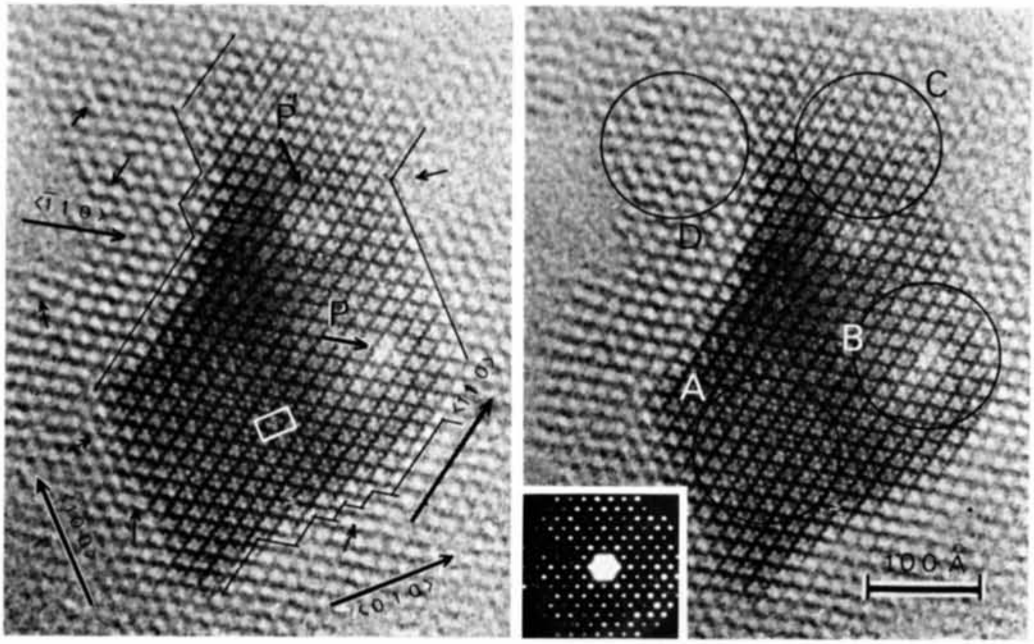

Fig. 2. Molecular image at -200 Å overfocus, showing the reverse image contrast, Letters *A*–*D* show the selected areas for optical diffraction. Inset: a selected-area electron diffraction pattern showing the (*hk*0) reciprocal section.

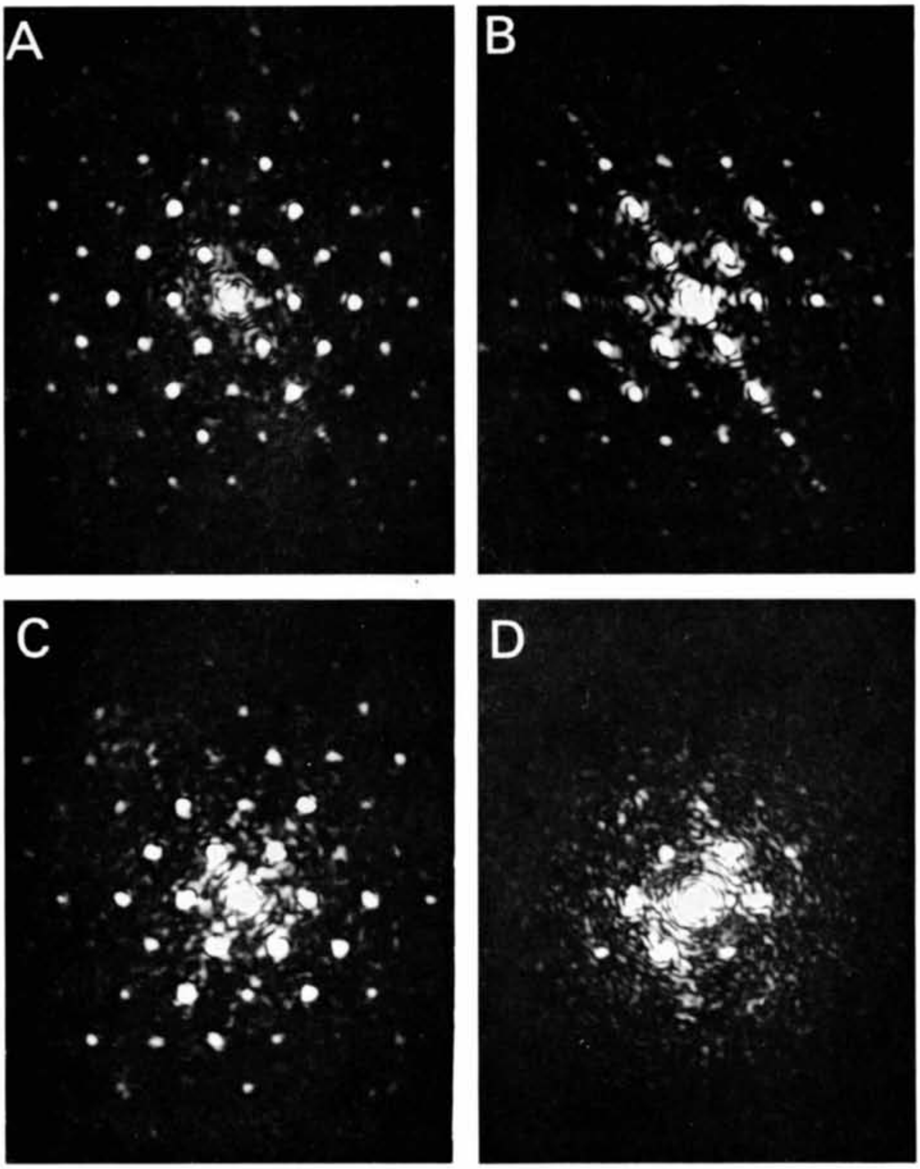

Fig. 3. Optical diffraction patterns from the selected areas, $A-D$, in Fig. 2. (A) is used for a standard for other optical diffraction patterns, (B)$-$(D).

continuously, depending on the focus condition, across a micrograph as shown by *X* in Fig. 1.

Fig. 2 shows an example, in which the damaged structure was resolved with the reverse image contrast due to overfocus as described above. We can see straight boundaries as in Fig. 1. In general, the crystallite was damaged gradually from its periphery by electron irradiation. However, at the same time, a small area containing a few molecules was damaged as shown by *P*, *P'*. When viewed along the arrow at *P*, it appears that two molecules join together by cross-linking along $[\bar{1}10]$. Similar features can be found elsewhere as marked by the short arrows, although they are not resolved in detail.

Furthermore, zigzag boundaries are also observed in Fig. 2. These are ascribed to the result of competitive reaction along the above directions. However, no straight boundary parallel to [010] was observed in this specimen. These facts suggest that the radiation damage has a close relation to the crystal structure.

Before discussing this point, it is worth examining the local structure in a micrograph (Fig. 2) by use of an optical diffractometer.

Fig. 3 represents the optical diffraction patterns, (*A*)–(*D*), obtained from the corresponding areas, *A* – *D*, in Fig. 2. The broadening of the spots in optical diffraction patterns is due to the diffraction from a small area (size effect). (*A*) shows a uniform intensity distribution similar to the electron diffraction pattern in Fig. 2, which suggests that area *A* did not suffer extensive irradiation damage. (*B*) and (*C*) show some disappearance of structural details, and more diffuse background than (*A*). Finally (*D*) exhibits only a few diffraction spots and a much more diffuse background, which means that area *D* was seriously damaged by electron irradiation, though some regularities still remained. The interplanar spacings in (*D*) were measured, with (*A*) as a standard (Table 1). A slight expansion of interplanar spacing was found in (020), $(\bar{1}10)$ and (130) whereas (110) and (200) showed a contraction. These optical diffraction patterns from local areas reveal the slight changes of the crystal structure. On the other hand, the electron diffraction pattern obtained from the severely damaged area did not reveal structural changes.

Table 1. *Comparison of interplanar spacings* (Å)

*hk*0	*A*	*D*
200	8·8 (8·8)*	8·10
020	13·0 (13·02)	13·74
110	14·44 (14·58)	13·56
$\bar{1}10$	14·56 (14·58)	15·02
130	7·94 (7·78)	8·14

* Calculated values from crystal data.

4. Discussion

Fig. 4 represents schematically the arrangement of copper hexadecachlorophthalocyanine projected along **c**. The plane of the molecule makes an angle of about 25° with the projected plane. Solid circles indicate Cl atoms. The crystal data are $a = 19{\cdot}62$, $b = 26{\cdot}04$, $c = 3{\cdot}76$ Å, $\beta = 116{\cdot}5^\circ$, monoclinic, space group $C2/c$ or $C2/m$. Unsubstituted copper phthalocyanine has two modifications (α and β) which differ in their molecular packing (Fig. 5*a*) (Brown, 1968; Kobayashi, 1970). In both forms, Cu is coordinated by four N atoms which correspond to the inner N atoms of phthalocyanine, resulting in a square planar configuration. In the β form, two additional N atoms (corresponding to the outer N atoms) of adjacent molecules are situated above and below Cu to form a distorted octahedral configuration. On the other hand, in the chlorinated phthalocyanine (Fig. 5*b*), two atoms which correspond to the inner N atoms are situated above and below Cu, which is somewhat different from either form of copper phthalocyanine. We may conclude that the Cl atoms control the intermolecular forces both within and between columns. This interaction presumably plays a part in the radiation damage.

We have seen that the contrast of the crystallite faded preferentially along a few particular directions and that the area with the faded contrast showed only a poor optical diffraction pattern. It may be that the fading could be caused by another mechanism, such as loss of Cl atoms. However the transparency to the electron beam increases with loss of substance so that we shall have the same overall effect. Therefore, a C–Cl bond is broken by electron bombardment in the initial stage; an activated molecule then reacts with its nearest neighbour as shown in Fig. 2. The fading of contrast can be ascribed to both effects; degradation of crystallinity due to cross-linking, and loss of Cl atoms. While the regularity of the crystal structure is largely conserved at the initial stage, as shown by the optical diffraction patterns, the damaged area reveals dynamical deformation: expansion and contraction of interplanar spacings. If investigated by means of selected-area electron diffraction, the slight local changes may be obscured by the intense beam diffracted from another area, in which the crystallinity is

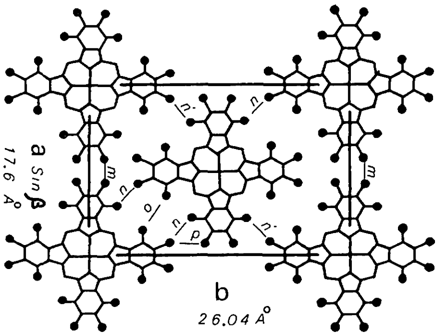

Fig. 4. Projection of copper hexadecachlorophthalocyanine along **c**. Solid circles represent Cl atoms.

retained. We believe that, in a study of radiation damage, optical diffraction is a useful method for demonstrating structural deformation.

Letters $m-p$ in Fig. 4 indicate the distances between Cl atoms of neighbouring molecules. They are $m=3{\cdot}4$, $n=n'=3{\cdot}8$, $o=4{\cdot}3$, $p=4{\cdot}9$ Å. m is the smallest and is parallel to [100]. n is next smallest and is approximately parallel to [120]. These were calculated by taking into account the molecular inclination. If molecules link with each other along [100], the molecular inclination becomes less so that the corresponding distance (m') becomes shorter than the original m, which induces further reaction between molecules: similarly for the [110] and [$\bar{1}$10] directions. On the other hand, cross-linking along a direction such as [010] is hardly possible from the molecular packing. It is plausible that cross-linking along particular directions acts as a trigger for the consequential reaction and results in the expansion or contraction of some interplanar spacings. If the probability that cross-linking propagates along [100] or [110] is almost equal, a competitive reaction can occur along the two directions, and a zigzag line will result.

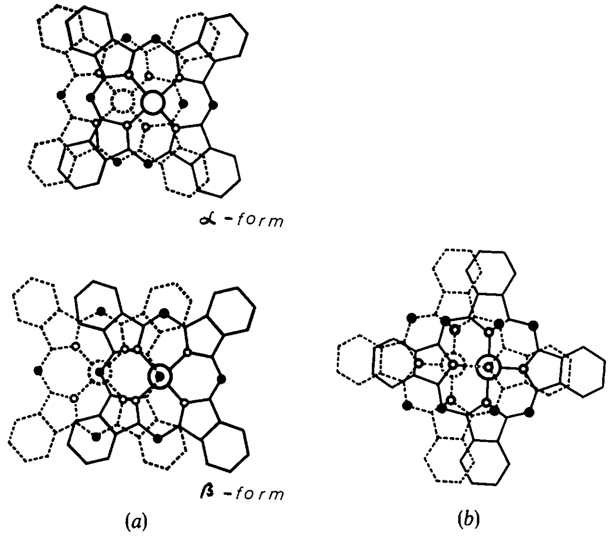

Fig. 5. Molecular packing. (a) α and β forms of copper phthalocyanine, (b) copper hexadecachlorophthalocyanine. Open and solid circles correspond to the inner and outer N atoms respectively.

We have been concerned mainly with the interaction between molecular columns. However, we should consider also the interaction within a column. The interplanar distance is ~3·4 Å, but information obtained along other directions will be required before an interpretation can be made.

Finally, it has been thought that the use of X-ray film is unprofitable for high-resolution electron microscopy. However, the molecular image was clearly resolved (Figs. 1 and 2). With X-ray film, we have also succeeded in resolving the molecular image of copper phthalocyanine, which is less resistant to the electron beam than the present specimen (Murata, Fryer & Baird, 1976). The usefulness of X-ray film is thus beyond question.

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