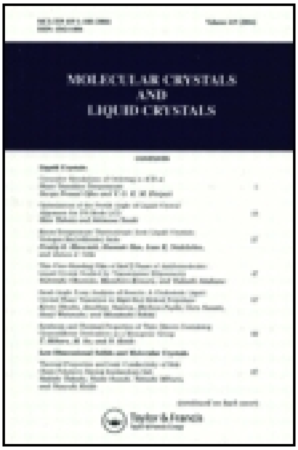

Molecular Crystals and Liquid Crystals

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ELECTRON MICROSCOPY OF MOLECULES

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Abstract Modern electron microscopes are capable of resolving individual molecules in organic crystals but the achievement of this resolution is determined by the contrast and radiation stability of the molecular crystal. This paper discusses the parameters of the molecule that affect the resolution and shows how the technique of high resolution electron microscopy has been applied to phthalocyanines and planar aromatic hydrocarbons.

INTRODUCTION

The resolution of molecules in the electron microscope has been limited by their radiation sensitivity, difficulty of specimen preparation and contrast. These limitations are now understood and in some cases capable of circumvention and it is the purpose of this paper to examine the extent to which the electron microscope can provide information at the molecular level of organic molecular crystals.

To obtain the image of a molecule in the transmission electron microscope it is necessary for the microscope to be capable of discriminating the molecule from the noise engendered by the supporting film and imperfect electron optics. A modern electron microscope has a resolution of 2-3Å for a weak phase object and at the appropriate defocus will faithfully reproduce object structure of greater size than this.[1,2] The molecules under consideration are all of greater size than this and therefore for all subsequent discussion the microscope will be considered as a perfect optical device and limitations that may exist inherent to contemporary microscopes will be disregarded.

The resolution of a molecule can be expressed by the inequality:

$$d \geqslant \frac{{}^{S}/_{N}}{C\sqrt{f\ Ncr}}$$

where d is the resolution

${}^{S}/_{N}$ the signal:noise ratio

C contrast

f the electron utilisation efficiency factor

Ncr the critical electron dose to cause distruction of the crystal or molecule.

The electron utilisation efficiency concerns the proportion of electrons providing information in the image compared to the number impigent on the specimen. Since a perfect microscope is being assumed with a coherent electron beam this factor (~25%) will not be considered further.

The resolution d is the minimum separation between two points. For the shape of a molecule to be resolved then the resolution is much lower and is expressed by:^{2}

$$d_n = 2d(1+\cos\frac{\pi}{n})(\sqrt{n/\pi \cot{}^{\pi}/n})$$

to resolve a polygon of n sides.

Provided the other difficulties can be overcome it is this resolution that makes the availability of very high resolution microscopes important.

The contrast of a single molecule is small and will increase with the square root of the number of superimposed atoms. Thus a planar molecule viewed in the plane of the molecules will have n atoms superimposed and the contrast will be improved by a factor of $n^{\frac{1}{2}}$ compared to a molecule viewed normal to the plane. To improve the contrast of a molecule it is useful to form thin crystals in which the electron beam is parallel to a column of superimposed molecules. This effect is shown in Fig.1 for a crystal of α-phase copper phthalocyanine. This crystal is in an agglomerate of randomly arranged crystals produced by mechanical grinding.[3] Only one crystal is in the correct orientation for molecular superimposition and the enhanced contrast is clear.

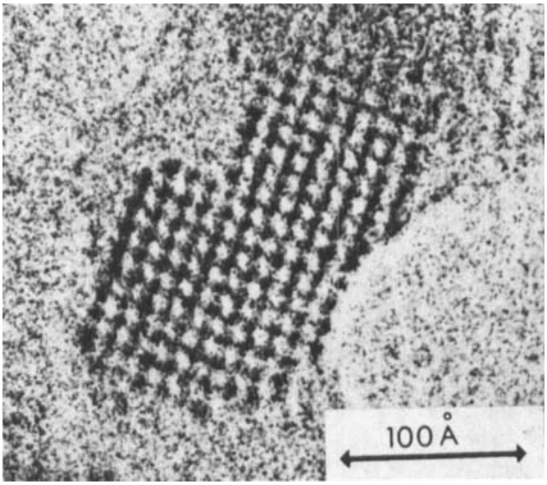


Fig.1 α-phase copper phthalocyanine crystal with b axis parallel to incident beam.

Apart from fortuitous orientation crystals can be aligned correctly by tilting the specimen but the time and prolonged exposure to the electron beam during this prevents its general application. A more successful technique is to prepare the crystal as an epitaxial film in a controlled orientation. The method is to cleave a substrate crystal such as KCl on the (100) face and mount it on a heater above an evaporation boat containing the organic material. After cleaning the substrate surface by preheating under vacuum (10^{-5}-10^{-6} torr) the substrate is heated to the requisite temperature for thin film formation. As a general rule this temperature is 1/3 of the boiling point of the material (°K)$^{\oplus}$ but where this is not known a rough guide is 2/3 of the melting point but optimum conditions can only be obtained by experimental investigation.

When the appropriate substrate temperature has been attained the organic material is evaporated from the boat normally by resistance heating of the boat. The organic film is strengthened by evaporating on a thin layer of carbon, floated off on water and picked up on an electron microscope grid. To reduce radiation damage - as will be discussed later - a further thin film of carbon can be evaporated onto the top surface of the specimen.

Molecules can orient themselves in various ways on a substrate. This is a function of the temperature, conditions of crystal growth and the nature of the substrate. Fig.2 shows the variations of orientation possible with planar molecules.

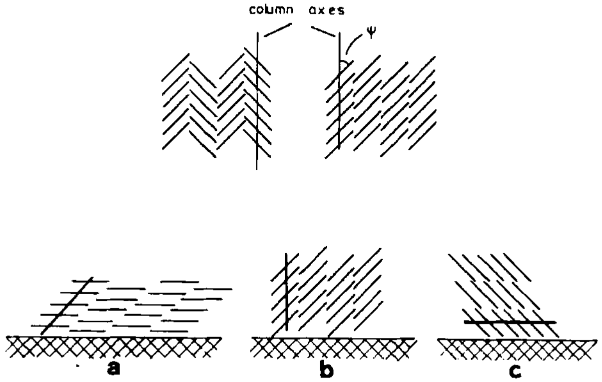
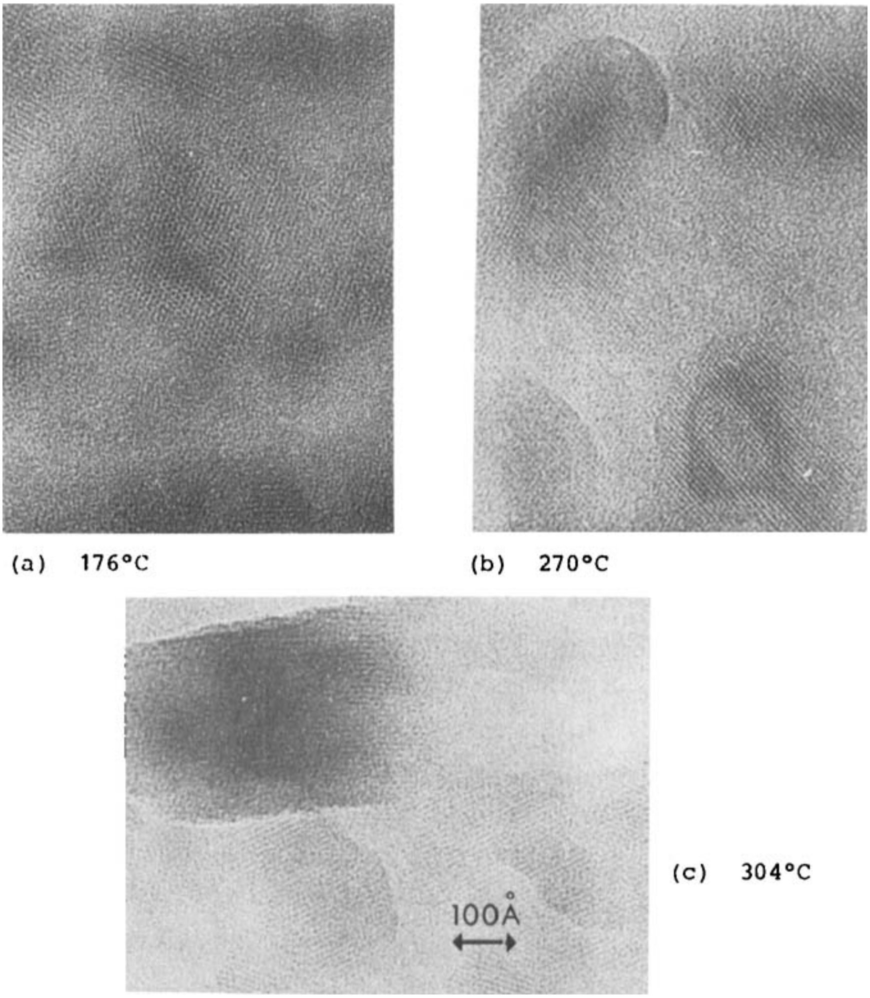


Fig.2 Planar molecules showing two types of stacking and how the molecules in a crystal may relate to a substrate. For molecular imaging the electron beam direction must be that of molecular superimposition e.g. (b). For situation (a) the substrate must be tilted to bring the elec- beam parallel to the column axis.

Where atomic matching can take place between the molecule and the substrate then case (a) can occur and it is necessary to tilt the resultant film. Organic molecules are normally much larger than the lattice parameters of the substrate and coincidence at intervals will give an orientation as in case (b) which is ideal. Case (c) normally occurs when there is very little interaction with the substrate and also on crystallisation from solution.

Heating the substrate after evaporation produces similar results to heating during evaporation but the growth of organic crystals is not similar to metals in that simple island annealing or isotropic growth are dominated by the shape of the molecule. Fig.3a,b,c shows a chlorinated copper phthalocyanine film heated to three temperatures. Evaporation onto a room temperature substrate results in an amorphous film. Crystal growth commences at ~150°C as shown by the very small crystals at 176°C. It continues at higher temperatures with the crystals becoming wedge-shaped permitting easy diffusion of the planar molecules onto the growing face of the crystal. In this experiment the chlorinated copper phthalocyanine was growing on KCl and the orientation of the molecules with respect to the crystal surface was maintained.

Another phenomena common to organic crystal films is that the crystals have a fixed orientation to the substrate but the crystals align with principal planes or steps associated with emergent dislocations in the substrate. Fig.4 shows coronene grown on KCl(100) with crystals aligning themselves with curved steps on the substrate surface as well as in a square array corresponding to the cubic symmetry of the substrate. This alignment with the symmetry of the substrate is vividly shown by quaterrylene ($C_{40}H_{20}$)



(a) 176°C

(b) 270°C

(c) 304°C

Fig.3 Chlorinated copper phthalocyanine annealed on KCl. Where molecular columns are parallel to electron beam the lattice images become discrete spots representing individual columns of molecules.

that always has a (110) orientation with the substrate irrespective of its nature.[5] Fig.5a shows arrangement of molecules in the unit cell, 5b the random lateral arrangement of small crystals grown on carbon at room temperature, 5c the square arrangement of crystals on KCl at room temperature and 5d the hexagonal arrangement of crystals on

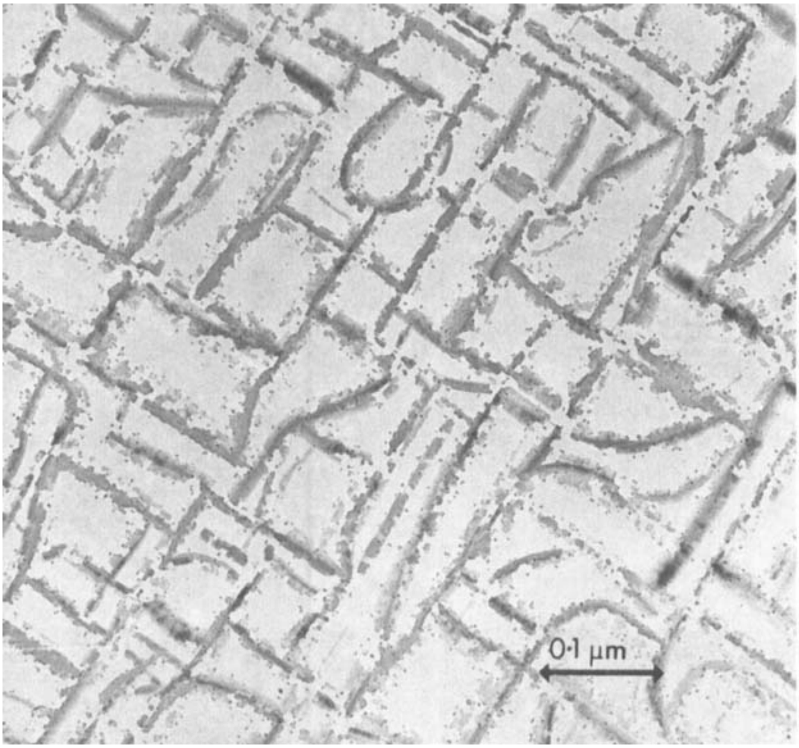


Fig.4 Coronene grown on KCl(100) at 210°C.

graphite at 200°C. At 200°C on KCl large crystals similar to those on graphite are formed but in a square array.

Quaterrylene is well suited for microscopy in terms of radiation resistance but does not form crystalline films in the ideal orientation for molecular superimposition. Thus although fine detail down to 3Å can be resolved molecular detail only becomes clearer through image averaging.[6,7] Superimposition of images either via a computer or photographically enhances the signal to noise ratio. Fig.6a shows the photographically averaged image of quaterrylene in the (110) projection and Fig.6b the computed image[8] that confirms this interpretation.

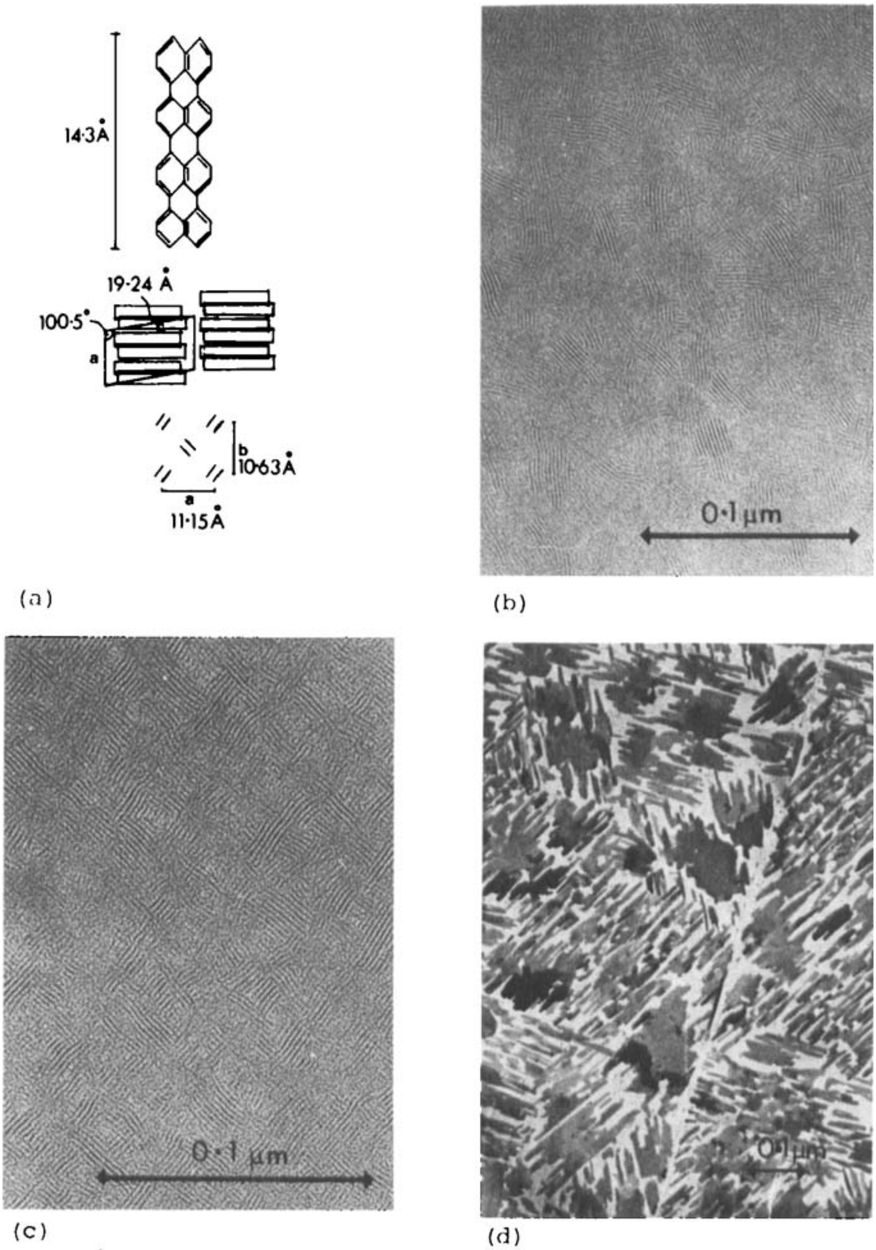


Fig.5 Quaterrylene epitaxial films formed by vacuum evaporation.

a) Quaterrylene $C_{40}H_{20}$ crystal structure. Molecule represented by rectangles in unit cell diagram.

b) Grown on amorphous carbon at room temperature.

c) Grown on KCl(100) at room temperature.

d) Grown on Graphite(002) at 200°C.

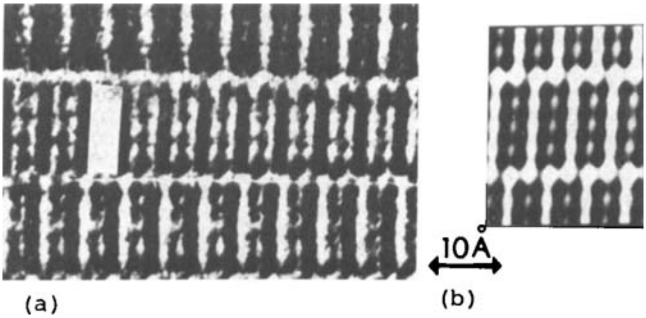


Fig.6 a) High resolution image of quaterrylene photographically averaged over 10 molecules.
b) Computed image of quaterrylene in (110) projection assuming a microscope resolution of 3.6Å and the specimen to be a weak phase object.

Chlorinated copper phthalocyanine is another molecule of high radiation resistance that forms epitaxial crystals on KCl(100) with the molecular plane parallel to the substrate so that the molecular column is inclined at an angle of 26.5°. A constant tilt of this angle can be put on the specimen so that superimposition with respect to the electron beam can be achieved. Fig.7a shows the image of chlorinated copper phthalocyanine taken at 500kV. Fig.7b shows the computer averaged image[9] and Fig.7c the contour map of a single molecule. In the latter two images the chlorine atoms are clearly resolved.

A further use of image averaging arises with the lattice image of a crystal where a lattice plane of high structure factor is oriented correctly for imaging. A lattice image of a particular separation is an averaged point image of the appropriate separation continued over a lateral extent. The improvement in apparent resolution is shown in Fig.8 of naphthacene whereas the calculated maximum point resolution is ~10Å. The lattice image provides information about the extent, orientation and perfection of crystals but information is restricted to the lattice periodicity in that achievement of a 5Å lattice image does not imply that point

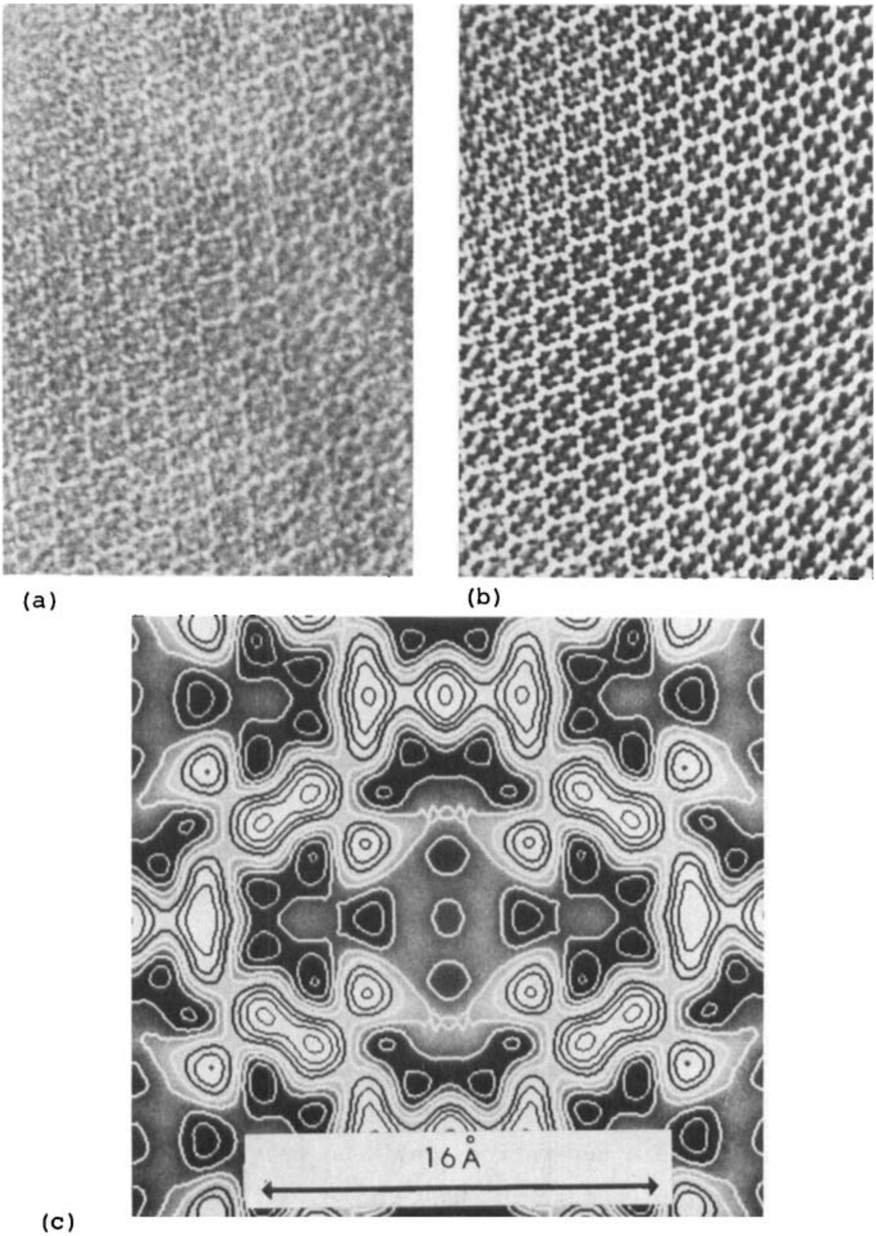


Fig.7 a) High resolution image of chlorinated copper phthalocyanine
b) Computer averaged images of a)
c) Contour map of a single molecule computed from the averaged image. High scattering points - e.g. Cl atoms - are dark with white contour lines.

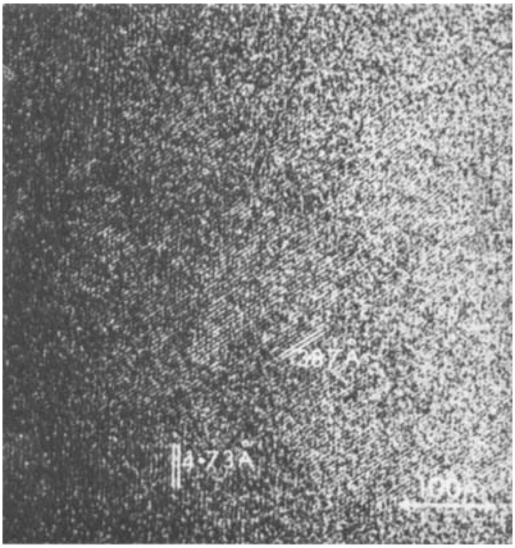


Fig.8 Multiple lattice image of naphthacene.

information of 5Å is available because this will be obscured in the background noise. For non-perfect electron optical systems spherical aberration also limits the information obtainable from lattice images. Lattice images of relatively fragile molecular crystals such as paraffins have been obtained[10] although molecular imaging would not be possible at room temperature.

The most critical feature of imaging molecules in molecular crystals is the sensitivity of molecular crystals to radiation damage. The damage process has the form of excitation of all the atoms in the molecule by inelastic collisions of the electron beam. Atoms which are displaced will either diffuse away from the parent moiety through the lattice or recombine with the parent. Thus backbone carbon atoms in a ring or chain will tend to recombine whilst peripheral hydrogen atoms will diffuse away. Thus the lifetime of a molecular species under the electron beam will be a function of the number of atoms lost compared to those that recombine and the stability of the residual radical or ion remaining in the lattice. The stability of a molecule can be increased by substituting peripheral hydrogen atoms by larger atoms such as a halogen. This decreases the diffusion rate and hence aids recombination. Also the stability of the remaining radical and ion can be increased by reduction of temperature.[11,12,13] Recombination can also be improved by coating the specimen with a carbon layer thus encapsulating the released atoms. For hydrogenated molecules the protection factor is ~3 and for chlorinated molecules a factor of 6-9 depending upon the specimen thickness.

Comparative radiation stabilities at room temperature for various molecules are shown in Fig.9. For aromatic molecules the stability is sufficient for resolution. For more fragile molecules a reduction in specimen temperature is necessary. This table lists typical molecules but some new polymers for example are much more stable than those listed.

To illustrate the extent of information that can be obtained Fig.10 shows a grain boundary arising from mismatch between two growing crystals in chlorinated copper phthalocyanine. The following features can be recognised.

1. Radiation damaged areas A and B. Once a molecule degrades through radiation damage then it creates space and assists diffusion of other peripheral atoms away from

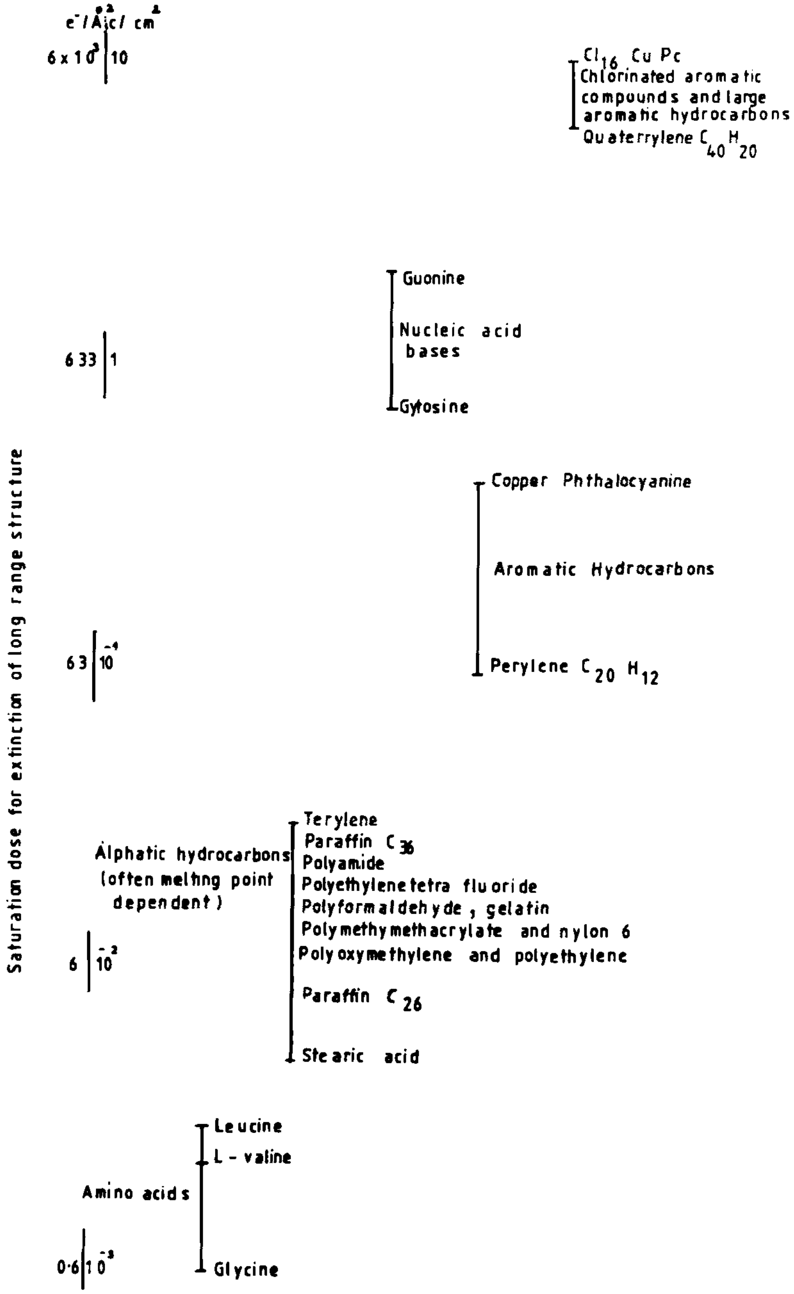


Fig. 9 Susceptibility of compounds to radiation damage by 100 KeV electrons.

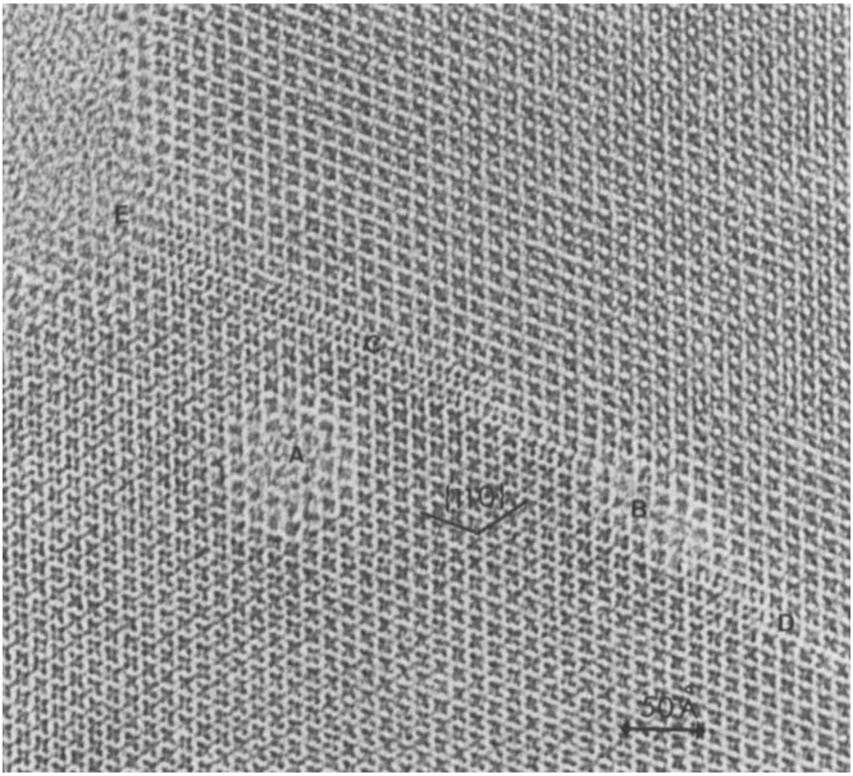


Fig.10 Grain boundary in chlorinated copper phthalocyanine showing molecular positions.

their parent molecule. Therefore radiation damage is self-propogating. The void caused by the damage also releases strain in the lattice and at A and B there is a slight bending of the {110} planes towards the void. It is of interest that radiation damage does not occur preferentially at the boundary indicating that any strain energy located there does not contribute to radiation degradation.

There is also radiation damage at the edges of the crystal.

2. The structure of the grain boundary varies across the crystal, at C the two crystals are exactly d(110) out of register whereas at D the mismatch is less symmetrical.

However the two rows of molecules along the boundary at C exhibit a different contrast to those in the rest of the crystal indicating that the molecular tilt angle is slightly different. Thus the strain of the grain boundary in this region is accommodated by the molecules in the two crystals being in a symmetrical relationship - i.e. displaced ½ unit cell in <110> and also by adjustment of the molecular stacking angle to create a new phase two molecules wide.

At D there is a less symmetrical displacement and there is no evidence of a new phase but the molecule columns are staggered with respect to each other so that there is curvature in the rows of molecules that dissipates the mismatch energy over a greater number of molecules.

3. The exit of the boundary on the crystal surface at E is not well defined. The localised new phase continues to the surface and the line of the boundary spreads like a delta adjacent to the surface.

4. The radiation damage area at B is at the junction of the two structures of the boundary. This presumably created considerable mismatch with greater distances between the molecules leading to enhanced diffusion and molecular degradation.

The extent to which information can be quantified from such a discontinuity as discussed above depends upon the resolution achieved and the nature of the crystal. Optical diffraction can provide more accurate measurements but the orientation of the dislocation with respect to the orientation of the specimen film is crucial. Molecular imaging, and in some cases dislocation analysis, has been performed for chlorinated copper phthalocyanine,[14,15] copper and zinc phthalocyanines,[16] metal free phthalocyanine,[17] quaterrylene[5], silver TCNQ,[18] anthanthrene[19] and hexabenzocoronene.[20]

Many other aromatic molecules could be studied by this technique together with the more stable polymers, organometallic compounds and crystal junctions. Studies carried out at reduced temperatures extend this further and high resolution images of aliphatic molecules have already been obtained at 77K and 4K.

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