study of the physical and chemical processes leading to radiation damage in single crystals, and of methods for adequate correction of radiation effects.

References

ABRAHAMS, S. C. (1969). *Phys. Today*, **22**, No. 8, 30–37.

ABRAHAMS, S. C., HAMILTON, W. C. & MATHIESON, A. McL. (1970). *Acta Cryst.* A**26**, 1–18.

CONFERENCE REPORT (1969). *International Meeting on Accurate Determination of X-ray Intensities and Structure Factors, Acta Cryst.* A**25**, 1–276.

HAMILTON, W. C. & ABRAHAMS, S. C. (1970). *Acta Cryst.* A**26**, 18–24.

INTERNATIONAL UNION OF CRYSTALLOGRAPHY (1969). *Acta Cryst.* B**25**, 2668.

INTERNATIONAL UNION OF CRYSTALLOGRAPHY (1970). *Acta Cryst.* A**26**, 165.

KAISER, J. F. & SITAR, E. J. (1967). Unpublished Bell Telephone Laboratories Report *A versatile subroutine for automatically generating complete graphs on the* 4020 *Microfilm printer*.

WEIR, C. E., PIERMARINI, G. J. & BLOCK, S. (1969). *Trans. Amer. Cryst. Assoc.* **5**, 105–111.

Acta Cryst. (1973). A**29**, 116

Mechanism of Photodimerization in Single Crystals of Anthracene

BY MAUREEN M. JULIAN

3863 *Red Fox Drive, Roanoke, Virginia* 24017, *U.S.A.*

(*Received* 2 *December* 1971; *accepted* 14 *September* 1972)

The anthracene photodimer, di-*p*-anthracene, crystallizes in at least six orientations within the anthracene single crystal. The orientations are classified, according to mosaic spread, into two sets of three orientations each. The relative spatial arrangements of the three orientations in each set are identical and each form a simulated repeated twin. The photodimerization begins as a surface reaction. The particular mechanism depends upon the geometry of the surface where the dimerization begins. Two mechanisms are described in this paper. One, associated with the (001) face of anthracene and low mosaic spread reflections, is the uniting of symmetry-related monomer units and the other, associated with the $(20\bar{1})$ face and the high mosaic spread reflections, is the uniting of translation-related monomer units. More molecular movement is needed for the uniting of the translation-related monomer units as inferred from the greater mosaic spread of their reflections.

When single crystals of anthracene photodimerize, the photodimer, di-*p*-anthracene, crystallizes inside the anthracene crystal in the ordinary crystal structure of the dimer (O'Donnell, 1968). The crystals of dimer are related to the anthracene crystal in several different geometric ways or orientations. At least six distinct orientations of dimer, denoted as *A*, *B*, *C*, *D*, *E* and *F*, are found inside the anthracene crystal (Julian, 1972). The relative spatial relationships among *A*, *B*, and *C* are identical to those among *D*, *E* and *F*. It will be shown that orientations *A*, *B* and *C* (or analogously *D*, *E* and *F*) appear to simulate a common type of repeated twinning, consisting of three individuals, known as trilling. The usage of the word twin (or trill), in the case of a single crystal which undergoes a syntactic topotactic reaction, is in the spirit of Lonsdale (1966). J. D. H. Donnay (private communication) suggests twins of this sort should be referred to as 'simulated'. The present work demonstrates that the particular reaction mechanism depends upon the geometry of the surface where the dimerization begins. Once initiated, the specific nucleating mechanism continues as long as the dimer is formed. Two mechanisms, one associated with the (001) face of anthracene and one with the $(20\bar{1})$ face, are described.

Anthracene crystals are monoclinic ($P2_1/a$) with unit-cell dimensions of $a = 8{\cdot}562$, $b = 6{\cdot}038$, $c = 11{\cdot}184$ Å, and $\beta = 124°42'$ (Mason, 1964); di-*p*-anthracene crystals are orthorhombic (*Pbca*) with unit-cell dimensions of $a = 8{\cdot}127$, $b = 12{\cdot}08$, and $c = 18{\cdot}85$ Å (Ehrenberg, 1966). The dimer looks like two anthracene butterflies facing each other (Fig. 1). Reflections from dimer orientations *A*, *B* and *C* have low mosaic spread (less than 4°) and reflections from orientations *D*, *E* and *F* have high mosaic spread (greater than 16°). All six orientations have a good epitaxic fit to the monomer (Julian, 1972; Table 1).

Table 1. *Corresponding repeat directions between parent anthracene crystal and the six orientations of dimer formed within the parent crystal*

Anthracene	Dimer orientation		
	A	*B*	*C*
[100]	[100]	$[0\bar{1}0]$	$[2\bar{1}0]$
[010]	[010]	$[\bar{1}00]$	[110]
[304]	[001]	$[00\bar{1}]$	[001]

Anthracene	Dimer orientation		
	D	*E*	*F*
[902]	[100]	$[0\bar{1}0]$	$[2\bar{1}0]$
[010]	$[0\bar{1}0]$	[100]	$[\bar{1}\bar{1}0]$
[102]	[001]	$[00\bar{1}]$	[001]

The average volume occupied by two molecules of anthracene, as calculated from lattice dimensions, is 476·3 Å^3. The average volume occupied by one molecule of dimer, also calculated from lattice dimenisons is 462·6 Å^3. Hence there is a net decrease in volume of 12·7 Å^3 per dimer or 2·7%. The dimerized crystals are more fragile than pure anthracene crystals. No change in the anthracene lattice dimensions was observed during dimerization. The dimer reflections could not be observed at sufficiently great angle to detect a change of lattice constant.

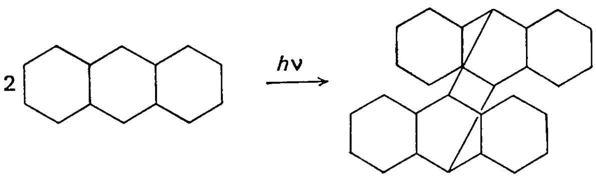

Fig. 1. Photodimerization of anthracene reaction.

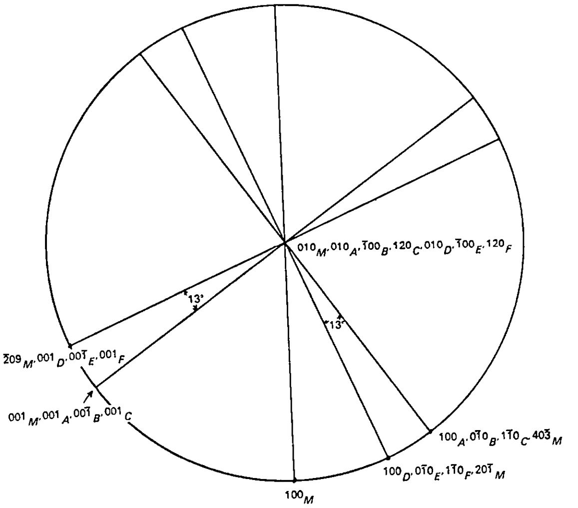

Fig. 2. Stereographic projection of the main reciprocal lattice rows of anthracene monomer (subscript *M*) and di-*p*-anthracene orientations *A* through *F* (subscripts *A* through *F*).

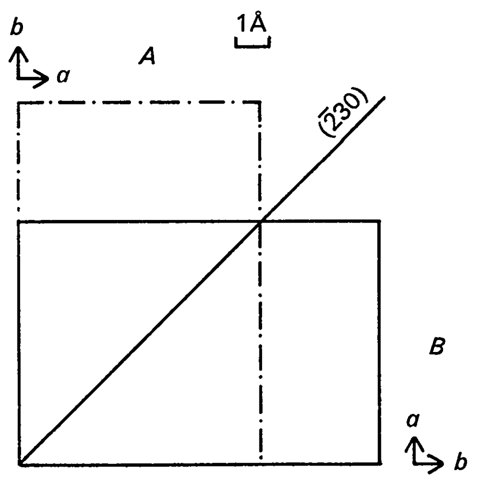

Fig. 3. Relation of orientations *A* and *B*.

The anthracene crystals were about 10^6 Å or about 10^5 layers thick. (The monomer layers are 9·1 Å apart down c^*.) Bree & Lyons (1956) have measured the molar extinction coefficients of crystalline anthracene as a function of wavelength. The 3930 Å absorption peak is the strongest absorption peak, in the ultraviolet, with a wavelength greater than 3000 Å. (The dimerization reaction proceeds when wavelengths less than 3000 Å are excluded.) A beam of 3930 Å radiation polarized parallel to the *b* crystallographic axis is 50% absorbed by anthracene in about 20 layers. A beam of 3360 Å radiation is 50% absorbed in about 100 layers. All the ultraviolet is 50% absorbed in about 300 layers. To test for dimer within the interior, anthracene crystals, which had undergone dimerization, were mostly dissolved in solvent. X-ray diffraction photographs were taken of the remaining lump. A weakened dimer pattern persisted showing that some dimer had formed beneath the surface. The presence of mixed-indices reflections of the dimer indicates that enough of the dimer is present to give a three-dimensional diffraction pattern.

Fig. 2 is a stereographic projection of the principal reciprocal-lattice rows of anthracene and of the six orientations of dimer. Orientations *A*, *B* and *C* coincide with dimer orientations *D*, *E* and *F* respectively when rotated approximately 13° about [010] of anthracene. The complement of the angle between the normals to the (001) and $(20\bar{1})$ faces of anthracene is 12°44′. Morphologically these faces are the best developed faces of the anthracene crystal. Table 2 gives important parallel planes relating orientations *A*, *B* and *C* and by implication relating orientations *D*, *E* and *F*. The monomer environment surrounding orientations *A*, *B* and *C* is different from the monomer environment surrounding orientations *D*, *E* and *F*.

Table 2. *Parallel planes of di-p-anthracene configurations*

A	*B*	*C*
(100)	$(0\bar{1}0)$	$(1\bar{1}0)$
(010)	$(\bar{1}00)$	(120)
(001)	$(00\bar{1})$	(001)

Fig. 3 shows the relative positions of orientations *A* and *B*. Orientation *A* could be considered twinned to orientation *B* across the $(\bar{2}30)$ plane (Table 3). Observe that $3a = 2b$. Now consider, in Fig. 4, the molecular projection along the *c* axis of anthracene. There is nearly a mirror plane along $(\bar{2}30)$. The angle between [100] and [320] is 44°45′. Since the dimer is formed from crystallized monomer units, the newly formed dimer crystal might, with equal probability, form in orientations *A* or *B* (or analogously *D* or *E*). Orientations *A* and *B* (and *D* and *E*) do form in equal amounts. The twinned orientations could conceivably be isolated or in contact. No twinning is observed among single crystals of pure di-*p*-anthracene. If the projection of the whole unit cell is constructed, the $(\bar{2}30)$ plane is not, even crudely, a mirror plane. Thus the twinning between orientations *A* and *B* is supported primarily by similarity of repeat distances and secondarily by molecular orientation of the individual dimer.

Table 3. *Matching repeat distances between each pair of dimer orientations of di-p-anthracene formed within the anthracene crystal*

All distances in ångstroms.

Orientation *A*	Orientation *B*
3[100] = 24·39	2[010] = 24·16
2[010] = 24·16	3[100] = 24·39
[001] = 18·85	[001] = 18·85
Orientation *B*	Orientation *C*
7[100] = 56·91	4[110] = 58·24
5[010] = 60·40	$3[2\bar{1}0]$ = 60·75
[001] = 18·85	[001] = 18·85
Orientation *A*	Orientation *C*
5[100] = 40·65	$2[2\bar{1}0]$ = 40·50
5[010] = 60·40	4[110] = 58·24
[001] = 18·85	[001] = 18·85

In Fig. 5, m_1 represents the $(\bar{2}30)$ plane. The normal to m_1 is 58°39′ from (in the notation of orientation *A*) the normal to the (160) plane; m_2 represents the (160) plane. The dimer configuration of m_1 is not similar to that of m_2. [Aragonite twins on (110) to form a trilling. The angle between the normals to (110) and $(1\bar{1}0)$ is 62°46′ (Dana, 1932, p. 521).] Orientation *C* is produced by reflecting orientation *A* across m_2. Note however that if m_2 is rotated about [001] by 120°, a third mirror plane is not produced; *i.e.* orientation *C* is *not* related by a mirror plane to orientation *B*. Orientation *C* may be made to coincide with orientation *B* by a counterclockwise rotation of approximately 120° about [001] (perpendicular to the plane of the paper). Table 3 gives the matching repeat distances between *A* and *C* and also between *B* and *C*. This trilling of the photodimer appears to be an example of trilling *without* hexagonal symmetry. Buerger (1960) has discussed a hypothetical example of trilling without hexagonal symmetry. The dimer crystallizes in orientation *C* less often than in orientations *A* or *B*, likewise in orientation *F* less often than in *D* or *E*. This is supported by Table 3 where the matching repeat distances are smaller for orientations *A* to *B* than either for *A* or *B* to *C* (or similarily substitute *D*, *E* and *F* respectively for *A*, *B* and *C*). The amount of dimer produced in orientations *A*, *B* and *C* is of the same order of magnitude as the amount produced in orientations *D*, *E* and *F* with the latter amount favored slightly.

Hypothetically other orientations can be proposed with excellent repeat distance fits of dimer to monomer. The particular observed triplet occurs twice in the same host. In addition the three components complement each other in a remarkable way simulating a trill. There is apparently no twinning relation between triplets (experimentally a great difference in mosaic spread is observed). Since the photodimerization reaction begins on a surface and since the most prominent anthracene surfaces are about 13° apart, it is not too surprising that the triplets are related by that angle.

Only monomer units in the exposed anthracene sheets will be considered as candidates for participation in the initial steps of the dimerization. As the dimer is produced, the ultraviolet light can penetrate deeper and deeper into the interior of the anthracene crystal. The early layers of dimer formed then act as a template for new dimer layers.

The relative orientations of the unit-cell vectors of the dimer crystals with respect to the monomer lattice are obtained from the X-ray diffraction photographs. The structures of anthracene and di-*p*-anthracene are known. The mechanism is inferred from superpositions of appropriate anthracene and di-*p*-anthracene projections in conjunction with the chemical evidence that the dimerization begins as a surface reaction and that the monomer surfaces and the dimer triplets are both related by a 13° angle. A similar analysis, also aided by a study of various superpositions of projections, was made by Lonsdale, Nave & Stephens (1966) in their X-ray studies of the mechanism of the single crystal chemical reaction of the photo-oxide of anthracene decomposing into mixed crystals of anthraquinone and anthrone.

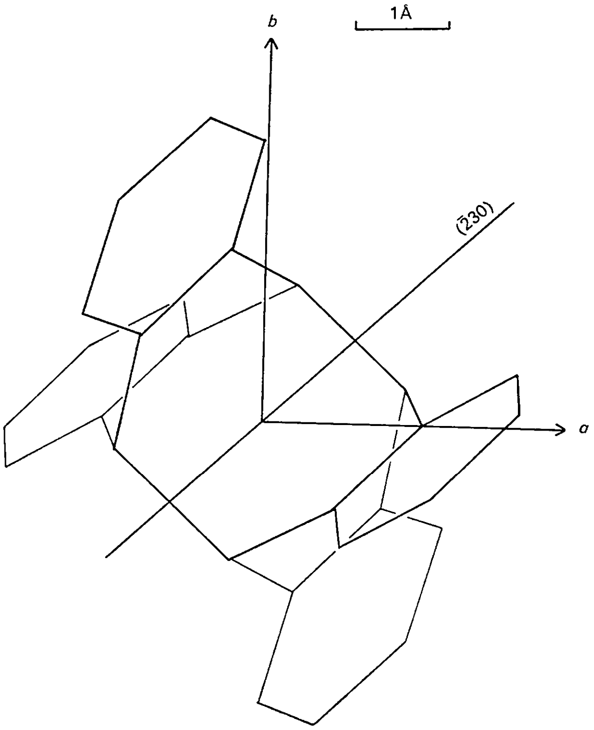

Fig. 4. Projection along the *c* axis of di-*p*-anthracene showing approximate mirror plane along $(\bar{2}30)$.

Fig. 6 is a superposition of the (001) face of anthracene and a single layer of the (001) face of di-*p*-anthracene orientation *A*. The X-ray diffraction photographs show that the *a* axis of anthracene is parallel to the *a* axis of di-*p*-anthracene and that the respective *b* axes are also parallel. This particular superposition indicates that the symmetry-related monomer units unite to form the dimer. The next monomer layer is 9·2 Å below and is displaced 6·4 Å or $\frac{3}{4}$ along the *a* axis (due to the monoclinic angle). This displacement of $\frac{3}{4}$ along **a** would cause shifting of the newly formed dimer of $\frac{1}{4}$ along the *a* axis of anthracene. The dimer layers are separated by 9·4 Å. Dimer orientations *B* and *C* are associated with this anthracene face. Molecularly they do not align as beautifully with the monomer as orientation *A*. I consider orientations *B* and *C* as twinned to the main dimer crystal, orientation *A*. Lonsdale, Nave & Stephens (1966) have a similar situation in their work on the photo-oxide of anthracene.

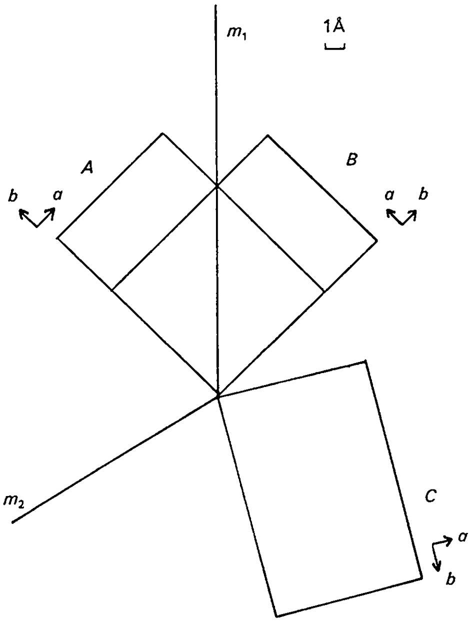

Fig. 5. Trilling of di-*p*-anthracene. Orientation *A* is related by mirror m_1 to orientation *B*, orientation *A* is related by mirror m_2 to orientation *C*, orientation *C* is related to orientation *B* by a rotation axis normal to the plane of the paper.

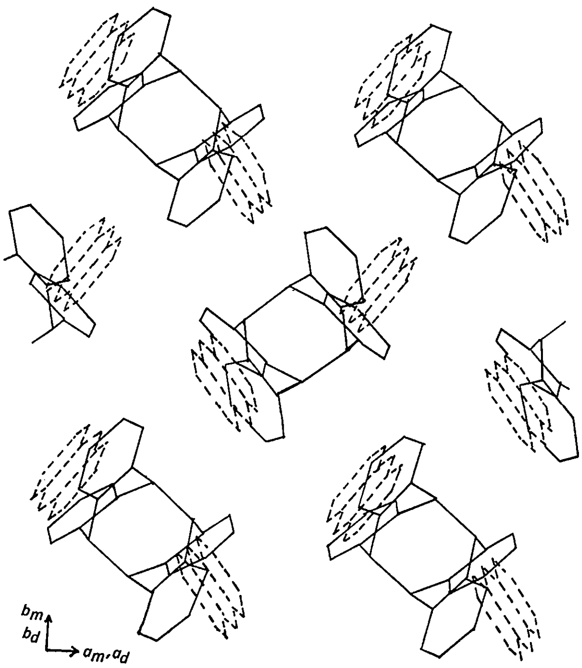

Fig. 6. Superposition of the (001) anthracene face and a single layer of the (001) di-*p*-anthracene face of a low mosaic spread orientation.

Fig. 7 is a superposition of the (20$\bar{1}$) face of anthracene and a single layer of the (100) face of di-*p*-anthracene orientation *D*. Again the information for the alignment of the respective parallel axes is from the X-ray diffraction films. Both *b* axes are parallel and the [102] of the monomer is parallel to the *c* axis of the dimer. The reacting monomer units are related by a translation along the *b* axis. Note that considerable shifting has to be done in alternate rows to accommodate the observed structure. This shifting possibly accounts for the great mosaic spread observed to be associated with this face. The next anthracene layer is 4·2 Å below and the next di-*p*-anthracene layer is 4·1 Å below. Because of the non-orthogonality of the anthracene axes, the next anthracene is displaced by about one ångstrom along [102] axis and because of the symmetry elements of space group *Pbca* of di-*p*-anthracene, the next dimer layer below has molecules centered midway between the molecules of the first layer. The readjustment of the dimer molecules again contributes to the great mosaic spread associated with this anthracene face. Dimer orientations *E* and *F* are present which are associated with this anthracene face and these dimer orientations are considered twinned to the original dimer orientation *D*.

The results indicate that on the (001) anthracene face, the symmetry-related anthracene molecules unite and on the (20$\bar{1}$) anthracene face monomers related by a translation along **b** unite. Thus the mechanism appears to be strongly influenced by the regularity of the surrounding unreacted anthracene molecules. The crystals formed from the symmetry-related anthracene monomers are far superior in quality (mosaic spread less than 4°) to crystals formed from the translation-related monomers (mosaic spread greater than 16°). More molecular displacement is needed for the uniting of the translation-related monomer units and their greater mosaic spread supports this interpretation.

I am greatful to the late Dame Kathleen Lonsdale for laboratory facilities in the Department of Crystallography, University College, London, England, and for helpful discussions. I thank Professor J. D. H. Donnay and Professor Gabrielle Donnay, both of

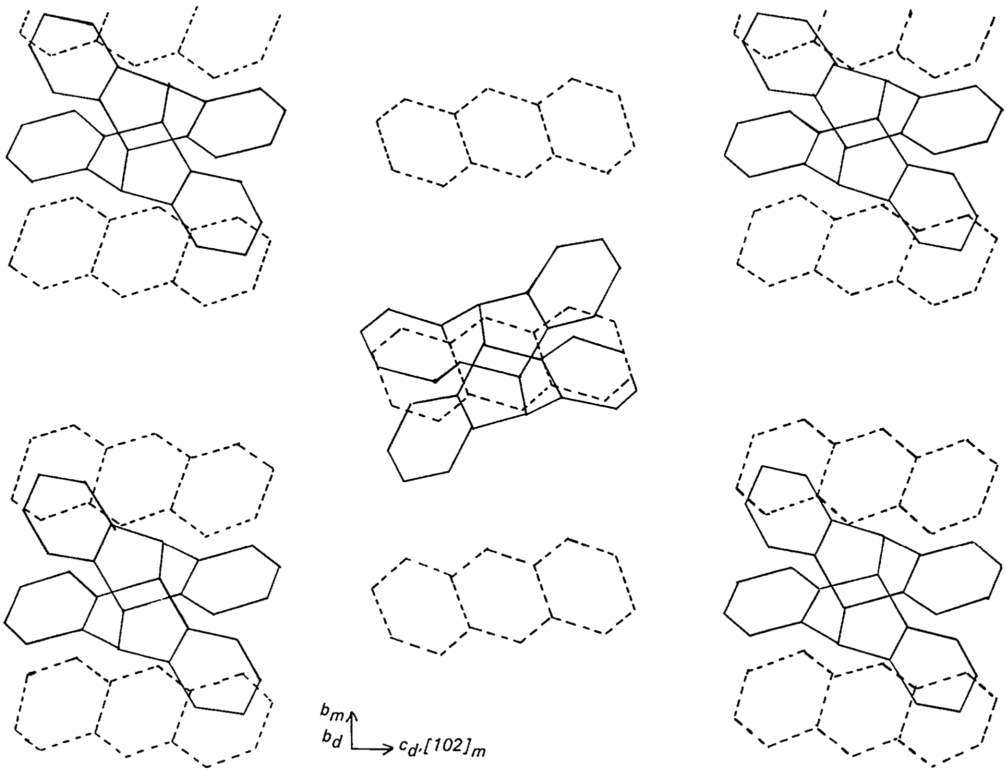

Fig. 7. Superposition of the (20$\bar{1}$) anthracene face and a single layer of the (100) di-*p*-anthracene face of a high mosaic spread orientation.

Montreal, Canada, for their useful conversations and Dr Carl L. Julian of the Norfolk and Western Railway, Roanoke, Virginia for reading the manuscript.

References

Bree, A. V. & Lyons, L. E. (1956). *J. Chem. Soc.* pp. 2662–2670.

Buerger, M. J. (1960). *Crystal Structure Analysis*, p. 62. New York: John Wiley.

Dana, E. S. (1932). *Textbook of Mineralogy*. New York: John Wiley.

Ehrenberg, M. (1966). *Acta Cryst.* **20**, 177–182.

Julian, M. M. (1972). *J. Chem. Soc. Dalton Trans.* pp. 558–560.

Lonsdale, K. (1966). *Acta Cryst.* **21**, 5–7.

Lonsdale, K., Nave, E. & Stephens, J. F. (1966). *Phil. Trans.* A**261**, 1–31.

Mason, R. (1964). *Acta Cryst.* **17**, 547–555.

O'Donnell, M. (1968). *Nature, Lond.* **218**, 460–461.