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International Union of Crystallography Commission on Crystallographic Apparatus Single-Crystal Radiation Damage Survey

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The integrated intensities of up to 21 different reflections were measured, as a function of increasing X-radiation exposure, from single crystals of each of nine materials of widely different chemical composition. Eight investigators from three countries took part in the Survey. The materials reported included an inorganic mixed oxide, three aromatic molecules, four metal–organic complexes, and an antibiotic. Changes in intensity were detected in each case, some large, others of marginal significance. In no case did all reflections studied change uniformly: in one crystal, some reflections decreased by as much as an order of magnitude after radiation exposure. In five crystals, some reflections increased as others decreased in intensity. Recommendations are made for including a diagnostic check of possible radiation damage produced in the course of measuring integrated intensities for crystal-structure determinations.

Survey objectives

The integrated intensities of some single-crystal X-ray reflections are known to vary as a function of increasing exposure to X-rays. Reference to such changes are scattered througout the literature. Many crystallographers have observed the intensity of one or more reference reflections to exhibit X-ray exposure time-dependence, and various techniques have been adopted to take the effect into account in deriving structure-factor magnitudes. Several mechanisms leading to radiation-induced intensity change are possible (*cf.* Abrahams, 1969). Degradation in quality of crystalline perfection can lead to large increases in integrated intensity. Reduction in long-range or short-range order by radiation damage causes a corresponding loss in integrated intensity. Chemical change may result either in increase or decrease of intensity for particular reflections. Combinations of these different mechanisms may take place, resulting in complex intensity variation with exposure.

The interest of the Commission on Crystallographic Apparatus in accurate single-crystal intensity measurements, *cf.* Conference Report (1969) led to a study of representative measurement procedures and the possibility of variation between crystals (Abrahams, Hamilton & Mathieson, 1970; Hamilton & Abrahams, 1970). At the Eighth IUCr Congress, concern with the condition of the specimen crystal was extended to a survey of the effects of radiation damage on single-crystal intensity measurement. Accordingly, all interested crystallographers were invited (International Union of Crystallography, 1969, 1970) to take part in a preliminary survey. The experimental requirements were designed to be relatively easily accommodated within normal crystal-structure data-collection procedures.

The objectives of the preliminary survey were to determine the magnitudes of the effects of radiation damage on integrated intensities for those crystals chosen by the participants and, if a sufficient range of materials were represented, to detect trends in the sensitivity of various categories of chemical composition or other class characteristic to radiation damage.

Participation in survey

In addition to the general invitations to participate in the survey (International Union of Crystallography, 1969, 1970), personal invitations were extended by Commission members, and sign-up sheets were made available for those interested at the American Crystallographic Association meetings in New Orleans (February, 1970) and Ottawa (August, 1970) and at the J. M. Robert-

Table 1. *Participants in the Survey*

Crystallographer	Laboratory
Calleri, M.	Istituto di Mineralogia e Geochimica dell'Università, Via San Massimo 24, 10123 Torino, Italy.
Duchamp, D. J.	Upjohn Company, Kalamazoo, Michigan 49001, U.S.A.
Eisenberg, R.	Department of Chemistry, Brown University, Providence, Rhode Island 02912, U.S.A.
Graeber, E. J.	Sandia Laboratories, Albuquerque, New Mexico 87115, U.S.A.
Hope, H.	Department of Chemistry, University of California, Davis, California 95616, U.S.A.
Lenhert, P. G.	Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37203, U.S.A.
Skelton, E. F.	Naval Research Laboratory, Washington, D.C. 20390, U.S.A.
Truter, M. R.	Agricultural Research Council, Inveresk House, 346 Strand, London WC 2, England.

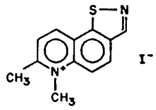
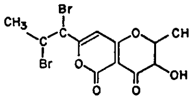
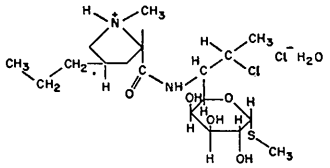
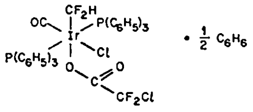
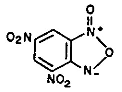
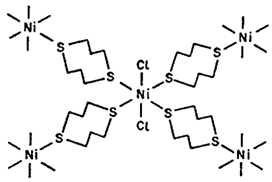
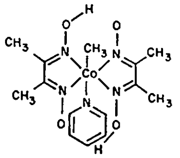
son Symposium on Chemical Crystallography (Glasgow, September 1970). A total of 48 crystallographers indicated a preliminary interest in taking part in the survey, 31 from the U.S.A., 8 from the U.K., 3 from Canada, 2 from Australia, 2 from Germany, 1 from Italy and 1 from South Africa.

Results were finally submitted by the eight crystallographers named in Table 1.

Experimental requirements

No restriction was placed on the choice of crystal, radiation, or type of diffractometer used by the participant. Three reflections were to be selected by each experimenter from the stronger, medium, and weaker intensity classes. For orthorhombic or higher symmetry, the selection was confined to the first octant (+*h*,

Table 2. *Survey crystal data**

Crystal	Structural or chemical formula	Space group	Lattice constants	Radiation†	Absorption coefficient	Investigator
1		$Pca2_1$	$a=18·14$ Å $b=11·28$ $c=7·12$	Cu	188·0 cm^{-1}	Calleri
2		$P2_12_12_1$	$a=10·247$ Å $b=24·959$ $c=5·504$	Cu	82·6	Calleri
3		$P2_1$	$a=9·50$ Å $b=9·91$ $c=13·48$ $\beta=104·4°$	Cu	34·5	Duchamp
4		$P\bar{1}$	$a=18·31$ Å $b=12·15$ $c=10·92$ $\alpha=106·98°$ $\beta=94·75$ $\gamma=108·97$	Mo	36·8	Eisenberg
5		*Pbcm*	$a=18·641$ Å $b=9·160$ $c=9·911$	Mo	1·8	Graeber
6		$P2_1/n$	$a=9·46$ Å $b=11·70$ $c=7·93$ $\beta=99·20°$	Mo	18·5	Hope
7		$P\bar{1}$	$a=9·151$ Å $b=11·445$ $c=9·270$ $\alpha=87·02°$ $\beta=114·40$ $\gamma=87·19$	Mo	10·4	Lenhert
8	β-$Gd_2(MoO_4)_3$	*Pba*2	$a=10·390$ Å $b=10·415$ $c=10·699$	Mo	148·1	Skelton
9	$[Cu(CF_3COCHCOCF_3)_2]$ $[N(CH_2CH_2)_3N]$	*Pnnm*	$a=16·148$ Å $b=8·427$ $c=7·743$	Mo	11·9	Truter

* All intensity measurements were made on 4-circle type diffractometers.

† Estimates of X-ray flux at each crystal suggest a variation among the ten experiments no larger than an order of magnitude.

$+k$, $+l$). For monoclinic or triclinic symmetry, the first two octants ($\pm h$, $+k$, $+l$) were used. The resulting nine reflections were to be distributed throughout the selected region of reciprocal space as uniformly as possible. A second set of nine reflections was then to be chosen, related to the first set by any symmetry operation of the lattice.

The integrated intensity of each reflection in this group of 18 was then to be measured, at least 10 times, throughout the series of intensity measurements made on the participant's crystal in course of normal structure determination. As uniform an interval as possible was to be maintained between repeated measurements of each reflection, with the total crystal-exposure time noted at the beginning of each measurement. The standard deviation of each integrated intensity measurement was also required, based only on counting stat-

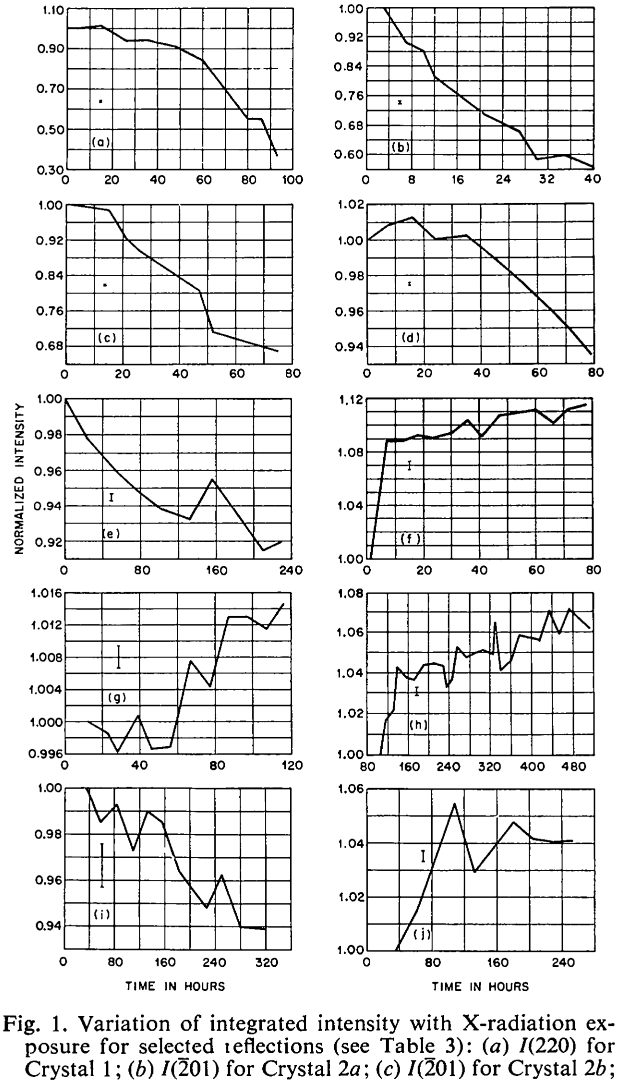
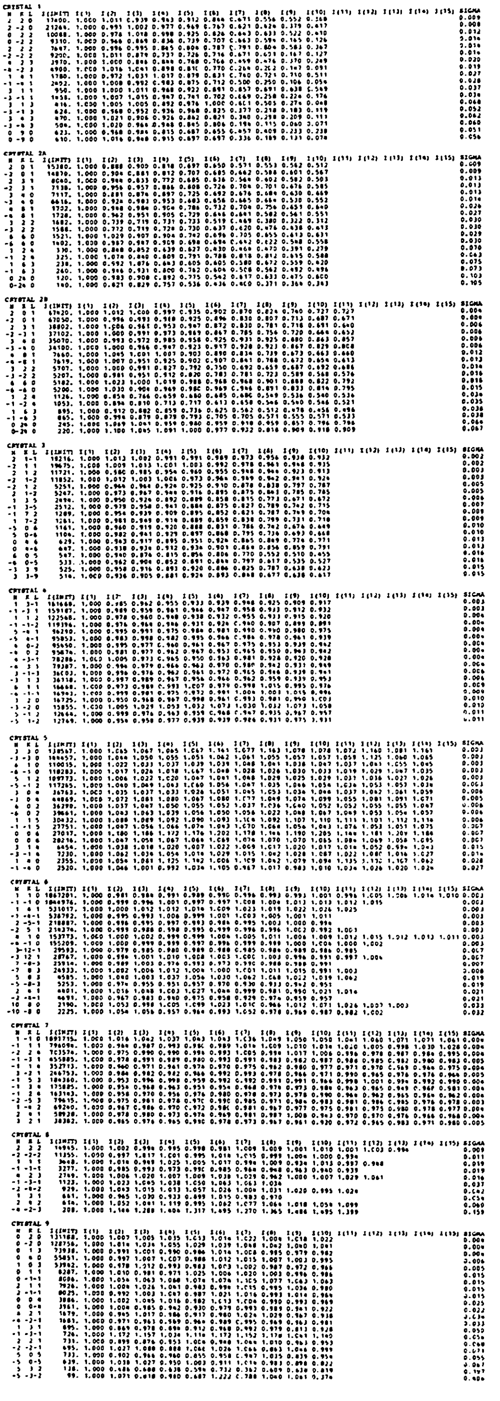


Fig. 1. Variation of integrated intensity with X-radiation exposure for selected reflections (see Table 3): (*a*) $I(220)$ for Crystal 1; (*b*) $I(\bar{2}01)$ for Crystal 2*a*; (*c*) $I(\bar{2}01)$ for Crystal 2*b*; (*d*) $I(\bar{2}11)$ for Crystal 3; (*e*) $I(112)$ for Crystal 4; (*f*) $I(115)$ for Crystal 5; (*g*) $I(\bar{1}\bar{1}0)$ for Crystal 6; (*h*) $I(1\bar{1}0)$ for Crystal 7; (*i*) $I(\bar{1}\bar{1}\bar{1})$ for Crystal 8; and (*j*) $I(0\bar{2}0)$ for Crystal 9. The error bar shown on each graph represents one sigma (see Table 3).

Table 3. *Intensity change as function of radiation exposure*

The values of $I(1)$, $I(2)$ ... $I(N)$ are obtained from $I(N)=I'(N)/I(\mathrm{INIT})$. SIGMA is given by $\sqrt{2}[\sigma^2 I(1)+\sigma^2 I(N)]^{1/2}/[I(1)+I(N)]$. N in hours is given in Fig. 1. $I(\mathrm{INIT})$ for Crystal 3 is given in dekacounts. Every other normalized intensity value is given for Crystal 7, which was reported with $N=29$.



istics. Additional information sought included the space group, lattice constants, density, linear absorption coefficient, crystal dimensions and experimental measurement conditions, a selection of which are given in Table 2.

Experimental results

The set of integrated intensity measurements reported for the group of reflections studied on each crystal is presented in Table 3, with magnitudes in each set normalized to the initial value. These normalized measurements were also plotted as a function of radiation exposure: the plotting subroutine *BE TPLOT* (Kaiser & Sitar, 1967) automatically chooses both abscissa and ordinate scales, thereby facilitating the detection of trends in the data. A selected plot of one reflection for each crystal is shown in Fig. 1, which also indicates the exposure times. It should not be assumed that the intensity changes recorded in Table 3 are necessarily characteristic of the behavior of each crystal to radiation exposure.

Crystal 1

The final normalized intensity $I(N)$ (see footnote to Table 3) of $\overline{22}0$ agrees within about 10 % of that of 220: a larger spread is observed in twofold symmetry related pairs of all other reflections. Fig. 1(*a*) illustrates the variation of $I(220)$ with increasing exposure. After 60 h exposure the polar crystal was observed to change color from light to dark orange, and then to pale green by 93 h. Crystal dimensions were $0{\cdot}027\times0{\cdot}162\times0{\cdot}70$ mm.

Crystal 2

Two different crystals of this acentric material were used. Crystal 2(*a*) had dimensions $0{\cdot}099\times0{\cdot}009\times0{\cdot}198$ mm, Crystal 2(*b*) was $0{\cdot}092\times0{\cdot}066\times0{\cdot}317$ mm. Crystal 2(*b*) was coated with a thin protective layer of plastic and, as can be seen by comparing Fig. 1(*b*) and (*c*), the decrease in $I(\bar{2}01)$ was much less for a given radiation exposure than for Crystal 2(*a*). The final normalized intensities of reflections related by a mirror in Crystal 2(*a*) generally agreed within 20 %, except for one medium and two weak reflections. In Crystal 2(*b*), reflections related by a two-fold axis agreed within 10%, except for one weak and one medium reflection (see Table 3). It is likely that chemical damage, associated with loss of bromine, results from the exposure.

Crystal 3

Considerable variation is found in the magnitudes of the final normalized intensity values among strong and weak groups in this polar crystal. Thus, in the strong class, $I(\bar{2}11)$ became 0·935 and in the weak class, $I(605)$ became 0·455: note that $I(\mathrm{INIT})$ in Table 3 is given in dekacounts. The variation of I with exposure is generally more complex in the weak class than for $I(\bar{2}11)$, see Fig. 1(*d*). Agreement among the final normalized intensities of reflections related by a twofold axis is generally better than 6%. Crystal dimensions were $0{\cdot}15\times0{\cdot}031\times0{\cdot}29$ mm.

Crystal 4

Variations in intensity with radiation exposure are relatively small in Crystal 4, but are generally highly significant (Table 3). The overall trend in eight of the nine independent reflections decreases in intensity, as illustrated in Fig. 1(*e*), but increases in $I(\bar{3}20)$. The final normalized intensities of all but one Friedel pair agree within 4%; the $I(320)$ pair agrees within 5·5%. Crystal 4 had dimensions $0{\cdot}435\times0{\cdot}218\times0{\cdot}145$ mm.

Crystal 5

Each reflection measured, without exception, tends to increase as a function of increasing radiation exposure. The intensity–exposure function is typically illustrated by Fig. 1(*f*) (see also Table 3). The initial rise in all intensities within the first few hours of radiation exposure, ranging from about 1 to 18%, is probably not attributable to a change in the very stable X-ray flux. The final intensities of all reflections related by two-fold symmetry agree within 10%. Crystal 5 dimensions were $0{\cdot}17\times0{\cdot}26\times0{\cdot}41$ mm.

Crystal 6

The intensity changes in Crystal 6 are generally small, with the exception of $I(583)$ which oscillates by 2–3σ (see Table 3) with an increasing trend on exposure. By contrast, $I(\overline{583})$ also oscillates but with a decreasing intensity trend. The variation in one of the strongest reflections reported is shown in Fig. 1(*g*). Apart from $I(583)$ and $I(\overline{583})$, all other Friedel pairs agree within 6·5%, and many within 1·5%. Crystal 6 was a sphere of radius 0·175 mm.

Crystal 7

A range of final normalized intensity values, with two significantly greater and the remainder less than unity, was found in Crystal 7 on exposure to Mo K X-rays. The clearest trend is shown by $I(1\bar{1}0)$, the strongest reflection, and is illustrated in Fig. 1(*h*). The measurements were begun after the crystal had been exposed for 104 h. The intensities of symmetry-related pairs of reflections, as a function of X-ray exposure, were not reported: structure factors were given (but not included in Table 3) for 13 Friedel pairs, with one member of each pair typically exposed for about 120 h, the other for about 260 h. No differences greater than 1·8% were found. The crystal was a polyhedron with dimensions about $0{\cdot}2\times0{\cdot}4\times0{\cdot}7$ mm and volume 0·057 mm^3.

Crystal 8

Data for Crystal 8 were measured with the sample immersed in kerosene within a Be/diamond-anvil pressure cell (Weir, Piermarini & Block, 1969), at normal pressure. The essentially monotonic decrease of $I(\overline{111})$ is shown in Fig. 1(*i*). The variation of other reflections

(Table 3) for this polar and metastable crystal includes an increase in $I(\bar{4}\bar{2}\bar{3})$ and random fluctuations in others. Apart from $I(423)$ and $I(\bar{4}\bar{2}\bar{3})$, the other four Friedel pairs of reflections reported differ in final intensity by less than 8%. Crystal 8 dimensions are $0{\cdot}13\times0{\cdot}15\times0{\cdot}20$ mm.

Crystal 9

$I(0\bar{2}0)$, one of the strongest reflections, exhibits complex behavior as a function of radiation exposure [Fig. 1(*j*)]: $I(020)$ also exhibits complex variation (Table 3), with a final intensity of $1{\cdot}022\pm0{\cdot}004$. The final intensities of six Friedel-related pairs of reflections agree within 8%, three others (all weak) disagreeing more widely.

Survey conclusions and recommendations

The number and range of materials reported in this Survey are clearly too small to allow more than the most tentative conclusions to be drawn. However, examination of the extensive data in Table 3 or the selected presentations in Fig. 1 demonstrates that exposure to X-radiation in the course of normal crystal-structure intensity measurements may result in significant changes in intensity. The standard deviations reported in this Survey, estimated from counting statistics alone, are most probably too small. The variance associated with each measurement of integrated intensity is correctly given by a sum of variances that includes contributions from all independent sources of error, such as variations in X-ray beam flux, in detector sensivity and in mechanical alignment, in addition to the variance given by the counting statistics. The significance of the trends in intensity with radiation, as illustrated in Fig. 1, although necessarily diminished by any increase in the standard deviations is likely to remain high for most, if not all, of the materials studied in this Survey.

The dependence of these intensity changes on such factors as chemical composition, absorption cross section and radiation energy cannot be determined without ambiguity from the present Survey. It may, however, be noted that the halogen-containing organic compounds studied with Cu *K* radiation (Crystals 1, 2 and 3) appear to suffer the greatest radiation damage. Further study is needed to identify the factors associated with sensitivity to radiation damage. Determination of the physical and chemical nature of the damage processes requires additional major study. The most important conclusion of the Survey is that radiation-induced intensity changes may occur in crystals of widely different chemical composition and need be neither monotonic nor uniform over all reflections. Indeed, uniform behavior in all reflections was not reported for any crystal exhibiting a significant intensity change.

It is recommended that the possibility of radiation damage be investigated in all X-ray crystal-structure determinations. This may be accomplished by extending the normal procedures used in measuring integrated intensities diffractometrically. Instead of the customary small number of arbitrarily chosen 'reference reflections', at least three strong, three medium and three weak reflections distributed throughout reciprocal space should be measured periodically in the course of data collection. The variation, if any, of these multiple reference reflections should be presented in the report of the structure determination. A normalized intensity format similar to Table 3, based on initial intensity values measured with the crystal exposed to the least possible X-radiation exposure should be used. The elapsed exposure time corresponding to each intensity measurement should also be included.

The structural information sought in any X-ray diffraction experiment is generally intended to be related to the properties of the crystal in a state undisturbed by radiation damage. In the presence of substantial damage, as indicated by a large spread among the magnitudes of the nine normalized sets of intensities, it may be advisable to use an alternative radiation for the investigation, such as thermal neutrons (with energy on the order of 0·1 eV). In the case of minor radiation damage, allowance for the effect may be made by an appropriate increase in the standard deviation assigned to individual reflections. Quantitative measures of acceptable radiation-damage limits are not presently available.

It is a pleasure to thank each participant for his generous cooperation in this international survey, the participants, the members of the 1969-1972 Commission on Crystallographic Apparatus and in particular the past Chairman, A. McL. Mathieson, for numerous constructive comments on this report, and J. L. Bernstein for performing the *BETPLOT* computations.

Discussion at an open meeting of the Commission on Crystallographic Apparatus

A report based on the Single-Crystal Radiation Damage Survey was presented at an Open Meeting of the Commission on Crystallographic Apparatus during the Ninth IUCr Congress in Kyoto. In the ensuing discussion, a consensus was reached that interpretation of the results of crystal-structure studies on materials that undergo radiation damage would be improved by always reporting visually observable changes in crystal color or appearance resulting from X-ray exposure: by always giving the total elapsed time from initial X-radiation exposure of the crystal to the time at which the reference intensity was measured in reporting normalized intensities tabulated as a function of exposure time, in addition to the total number of hours irradiated, if these times are not identical, *e. g.*, if the X-ray beam is shuttered during part of the measurement procedure: and by remeasuring and reporting the lattice constants of the irradiated crystal if appreciable radiation damage is detected.

There was also general agreement on the need for study of the physical and chemical processes leading to radiation damage in single crystals, and of methods for adequate correction of radiation effects.

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Mechanism of Photodimerization in Single Crystals of Anthracene

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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 $a = 8·562$, $b = 6·038$, $c = 11·184$ Å, and $\beta = 124°42'$ (Mason, 1964); di-*p*-anthracene crystals are orthorhombic (*Pbca*) with unit-cell dimensions of $a = 8·127$, $b = 12·08$, and $c = 18·85$ 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]