X-RAY STUDIES OF A SINGLE CRYSTAL CHEMICAL REACTION: PHOTO-OXIDE OF ANTHRACENE TO (ANTHRAQUINONE, ANTHRONE)

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[Plates 1 to 16]

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When a single crystal of the photo-oxide of anthracene is subjected to X-irradiation (CuK or MoK) at room temperatures, it changes gradually into a mixed 'single' crystal of anthraquinone + anthrone, which is in fact a mosaic with *ca.* 15° randomness in all directions. The external shape of the crystal is not changed but the unit cell changes

from $a = 15{\cdot}94$ Å, $b = 5{\cdot}86$ Å, $c = 11{\cdot}43$ Å, $\beta = 108{\cdot}2°$, $Z = 4$
to $a = 15{\cdot}8$ Å, $b = 4{\cdot}0$ Å, $c = 7{\cdot}9$ Å, $\beta = 102°$, $Z = 2$.

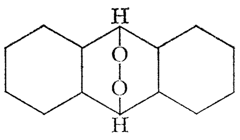
The space group remains $P2_1/a$ but the final product is always twinned about $(\bar{2}01)$ and (001), not necessarily equally. The twinning about (001) is not related to the structure or unit cell dimensions of anthraquinone or anthrone, which are closely isomorphous, but is a consequence of a geometrical relation between the unit cell of this twin and that of the original anthracene photo-oxide.

The chemical reaction proceeds via intermediate stages of disorder, decomposition and recrystallization which can be followed in detail by means of X-ray diffraction at room temperatures, since the reaction is then slow, taking upwards of 200 h for completion or near completion. As the temperature is raised the rate of reaction increases and X-irradiation becomes unnecessary except for the diffraction studies. At 80 °C the reaction takes 7 to 20 h but a 'single' crystal still results. The geometrical mechanism of the reaction seems to be the same whether it is caused by X-irradiation or by heat. Above 110 °C the original crystal is liable to fall to a powder in a few minutes, and at or near to the m.p. 166 °C, it explodes. The 'single crystal' reaction generates some 5% 'free space' in the original crystal, thus allowing room for the gaseous products of the reaction to remain within the structure. The natures of the final product and of some probable breakdown and intermediate molecules or radicals were determined by mass spectrometry. Some related reactions are discussed.

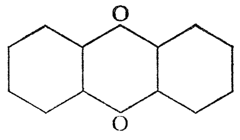
1. INTRODUCTION

Dufraisse & Gérard (1935) reported that when a weak solution of anthracene in carbon disulphide is exposed to bright sunshine it rapidly forms a photo-oxide (I). Bender & Farber (1952) made the same peroxide by irradiating a solution of anthracene in carbon disulphide by ultraviolet light while oxygen was bubbled through it. The same method can be used (P. Gaston, this laboratory) with a chloroform solution, although the yields are smaller. Bender & Farber reported that (after three recrystallizations from carbon disulphide) their crystals exploded when heated to 160 °C and they gave the density as 1·28 g/ml. Dufraisse & Badoche (1935) had given 120 °C as the temperature of explosive decomposition. Good single crystals given to us by Professor Dufraisse appeared to be stable at room temperatures and were found to be monoclinic ($P2_1/a$) with a measured density $D_m = 1{\cdot}356$ g/ml. as compared with calculated $D_x = 1{\cdot}374$ g/ml. for four (asymmetric) molecules per unit cell, the dimensions at 20 °C being

$$a = 15{\cdot}94\ \text{Å},\quad b = 5{\cdot}863\ \text{Å},\quad c = 11{\cdot}43\ \text{Å},\quad \beta = 108{\cdot}2^\circ.$$



(I)



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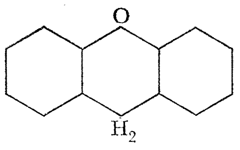

(III)

An early X-ray analysis of the crystal structure showed that although the single crystals retained their outward shape, they were slowly affected, even at low temperatures, by X-irradiation. At room temperatures a complete conversion to a somewhat mosaic single crystal apparently of anthraquinone (II) had occurred within 6 months on intermittent exposure to the radiation from a copper target, during which time the crystal may have had some 200 h total CuK irradiation.

Later experiments showed:

(1) That the conversion took place in a very variable time even at room temperatures, sometimes being apparently complete after 60 h irradiation, sometimes not quite complete after 485 h irradiation, presumably depending upon the size, purity and history of the sample.

(2) That radiations from copper and molybdenum targets were equally effective.

(3) That the conversion also took place when the sample was heated with or without irradiation, the speed being strongly dependent upon the temperature.

(4) That the final product was not pure anthraquinone, but a mixture or mixed crystal, in varying amounts, of anthraquinone + anthrone (III), probably with other impurity molecules present in a disorganized state.

The early X-ray experiments will first be described, as these, which were carried out by J.F.S. in 1957–58, showed much of the essential geometrical mechanism of the reaction although not all of it was then understood.

2. Early X-ray experiments (J.F.S.)

2·1. [010] *rotation photographs*

The research had begun as a straight single-crystal structure determination of the photo-oxide of anthracene (p.o.a.), with no expectation that any change would take place at room temperatures. The first hint of a change (after a few weeks) was the appearance of spots on new layer lines on the [010] rotation photographs of p.o.a., corresponding to a change of identity distance from 5·86 Å to about 4 Å. Gradually the b = 5·86 Å layer-line reflexions weakened and then disappeared, while the b' = 4 Å reflexions increased in intensity. The alinement of b, b' axes was exact, but the new rotation photograph was more limited at large θ values than the original. The transformation is shown in figures 1 (*a* to *e*; *f* to *j*), 2 (*a* to *c*), 3 (*a* to *c*), plates 1 and 2. (Compare figure 4 (*a* to *c*), plate 3.)

2·2 [100] *and* [001] *rotation and oscillation photographs*

A similar transformation was found to occur on [100] and [001] rotation photographs (figures 5 (*a* to *e*), plate 4) from an original a = 15·9 Å to an *apparent* c' = 7·9 Å and from c = 11·4 Å to an *apparent* a' = 15·8 Å respectively, although in these cases the transformed patterns were much more limited in extent, indicating a less exact alinement of the rotation axes of the final product of the transformation with those of the original. The slowness of the reaction at room temperatures was indicated by the fact that it was possible to get complete sets of 15° oscillation photographs about [100] and [001] before any changes were observed at all.

2·3. [010] *Weissenberg photographs*

However, intensity measurements on $h0l$ Weissenberg photographs made at room temperatures and at or near the temperature of liquid nitrogen did seem to show that even at the low temperature small changes of intensity were occurring on successive, apparently identically repeated $h0l$ photographs. These, however, were very near to the limits of errors of observation. Irradiation was not continued at low temperatures to the point where new spots appeared on the Weissenberg photographs. There were very marked intensity differences between the room-temperature and low-temperature $h0l$ patterns. A preliminary structure determination was carried out for the [010] projection; and $h0l$ Fourier maps were made on the Eller photosommateur. The map obtained from the room-temperature data was very much blurred, implying large thermal vibration amplitudes and perhaps disorder, there being no resolution of the oxygen atoms along the bridge. The low-temperature map showed well-resolved oxygen and carbon atoms, implying little thermal vibration or disorder (figures 6(*a*, *b*), plates 5 and 6).

2·4. *Laue photographs and* [100], [001] *Weissenberg photographs*

An attempt to study the diffuse reflexions due to thermal vibrations on Laue photographs of fresh p.o.a. crystals then revealed structural changes which *preceded* the appearance of the new layer-line spots on rotation photographs. A Laue photograph with the incident X-rays from a copper target along [010], taken on a plane film (figure 7(*a*), plate 7) showed, in addition to the normal Laue pattern of spots, strong Cu$K\alpha$ and Cu$K\beta$ nearly continuous circles, centred on the incident beam trace. A faint concentric circle of larger diameter could also be seen on the negative. When the crystal was tilted a new small and very intense circle appeared (figure 7(*b*)), passing through the origin and increasing in diameter as the tilt increased. After 72 h X-irradiation a corresponding oscillation photograph with the X-rays along [010] (mean position) and with the original [001] vertical, had changed to the pattern shown in figure 5(*f*). This had near to the centre a little pattern of six spots, which turned out to be very characteristic of the Laue photograph of anthraquinone with X-rays along b and with c vertical (figure 5(*d*)). It was recognized, at about this time, that the rotation photographs of the transformed p.o.a. were very similar to those of a rather fibrous single crystal of anthraquinone, for which (Murty 1957, 1960; Lonsdale, Milledge & El Sayed 1966) $P2_1/a$, $Z = 2$,

$$a = 15{\cdot}83\ \text{Å}, \quad b = 3{\cdot}97\ \text{Å}, \quad c = 7{\cdot}89\ \text{Å}, \quad \beta = 102{\cdot}5^\circ, \quad D_x = 1{\cdot}43\ \text{g/ml}.$$

The rings on Laue photographs of p.o.a. taken with the X-rays along [010] correspond with the pattern expected for one dimensional periodicity along [010] but with no sideways regularity. This was confirmed by Laue photographs taken with the incident beam normal

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Description of plate 1

FIGURE 1 (*a* to *e*). Rotation photographs about [010], 1 h exposure time, taken with unfiltered CuK radiation (30 kV, 15 mA), showing gradual decomposition of photo-oxide of anthracene (p.o.a.) and formation of anthraquinone–anthrone (A:A) crystal. These are selected from a continuous series of alternate 'rotations' (1 h exposure) and 'stills' (30 min exposure) taken over a period of about 150 h (conversion not complete), with the crystal on a goniometer head.

(*a*) Nearly fresh p.o.a., after a total 6¾ h irradiation, CuK unfiltered, spent in testing and setting the crystal.

(*b*) The same after 16¼ h total (not continuous).

(*c*) After 41¼ h.

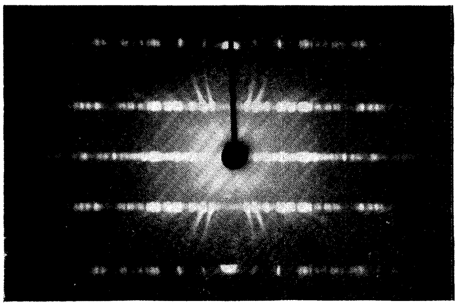
(*d*) After 77¼ h.

(*e*) After 141¾ h.

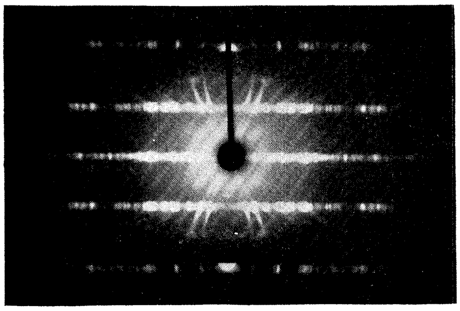
(*f* to *j*) 'Still' photographs taken of the same specimen with the same radiation from a Cu target (white + Cu$K\alpha$, β) 30 kV, 15 mA, 30 min exposure time; [010] vertical.

(*f*) Corresponding to 1(*a*), showing strong continuous layer-line streaks.

(*g* to *j*) Corresponding with 1(*b* to *e*), showing gradual appearance of an A:A fibre pattern, and the break-up of the continuous p.o.a. streaks into a p.o.a. fibre pattern. Note also the low-angle diffuse scattering and broad diffuse rings.



1 (*a*)



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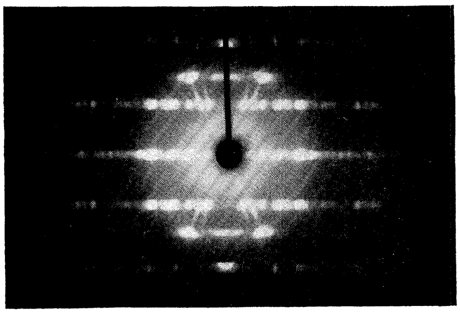

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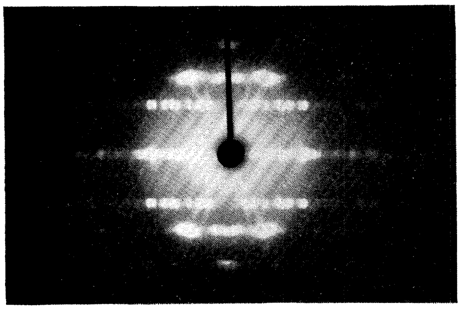

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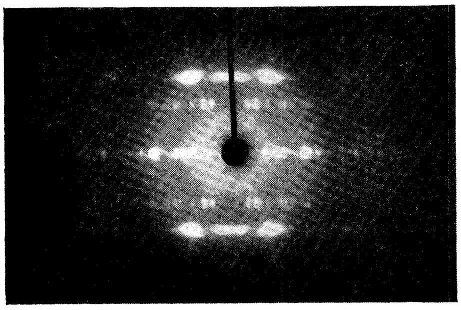

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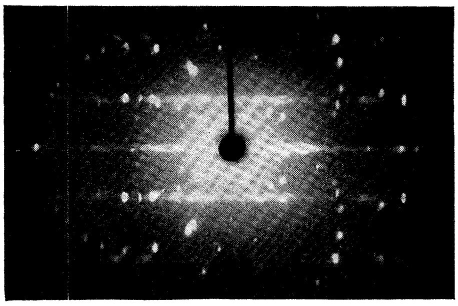

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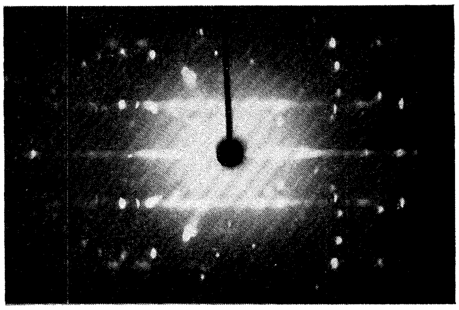

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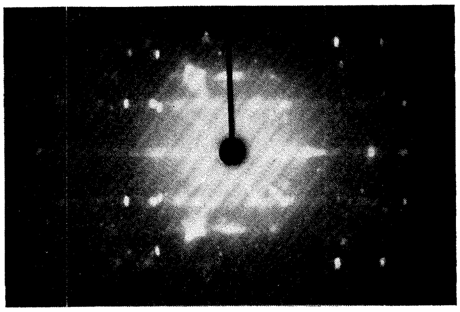

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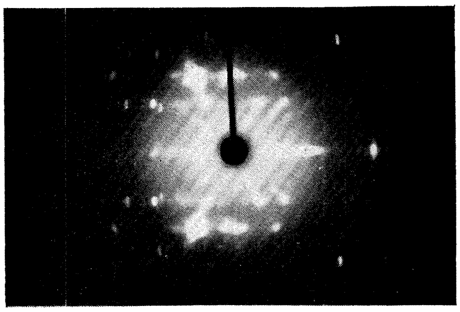

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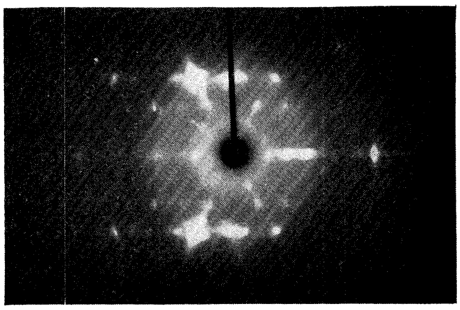

1 (*j*)

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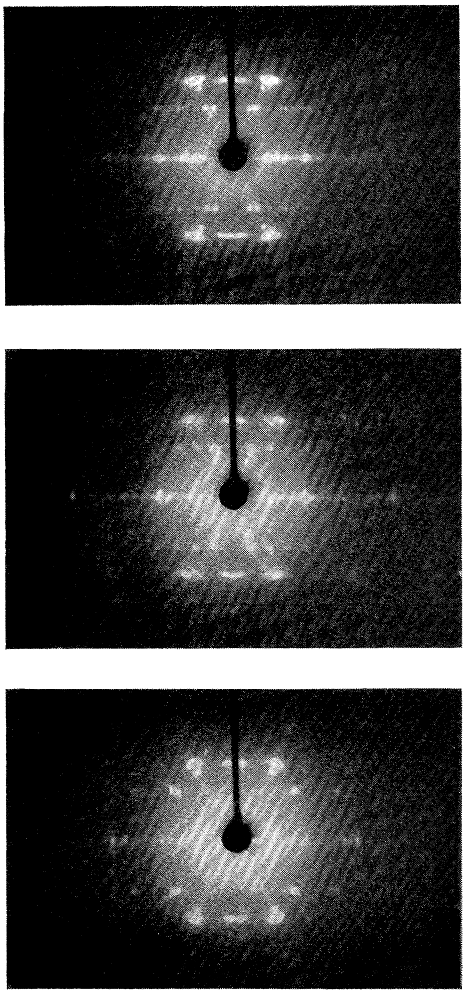
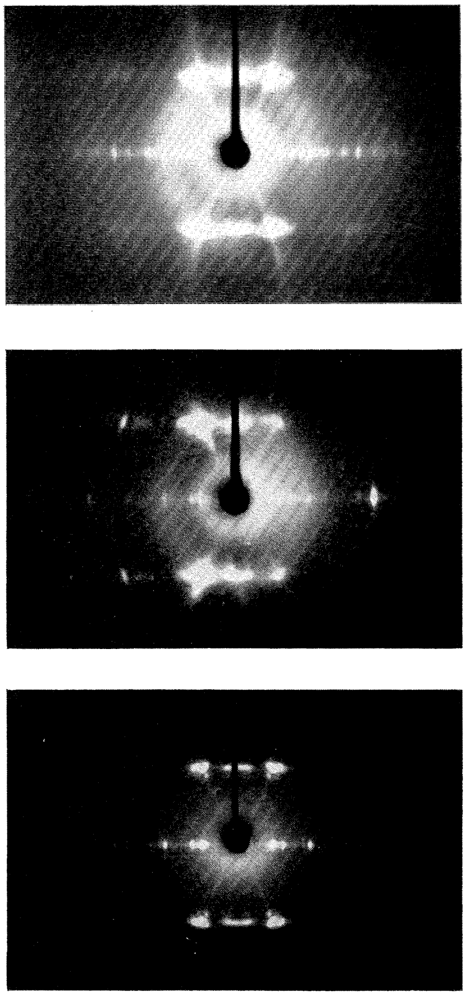


2 (*a*)

2 (*b*)

2 (*c*)



3 (*a*)

3 (*b*)

3 (*c*)

FIGURE 2. (*a*) Rotation about [010] of another crystal, after a total 55·7 h Cu*K* irradiation (specimen randomly selected from a sample placed inside a lead cap over an X-ray tube window).

(*b*, *c*) Two corresponding 'stills', mutually orthogonal, [010] vertical (56·2 and 56·7 h total irradiation respectively) which show clearly (since there should be no planes of symmetry intersecting in monoclinic [010] that the original p.o.a. was or has become twinned, and that the final *A*:*A* is also twinned or consists of crystallites which bear to one another the relationship of twinned individuals (compare figure 20).

FIGURE 3. (*a*) Completely converted crystal. Rotation about [010], Cu*K*, 30 min exposure, after total 125·3 h Cu*K* irradiation, inside lead cap; showing considerable disorder, and also diffuse rings due to very small (colloidal sized) crystallites and near amorphous groups.

(*b*) 'Still' photograph corresponding to 3(*a*). The crystal position is identical with that for figure 1(*f* to *j*) and a similar fibrous character is evident.

(*c*) Cu*K* [010] rotation of another crystal nearly completely converted after 60 h Mo*K* irradiation inside lead cap to X-ray tube window. 30 min exposure. The differences between 3(*a*) and 3(*c*) are not associated with the radiation used but with the perfection of the original crystal. Many similar photographs have been obtained under all conditions.

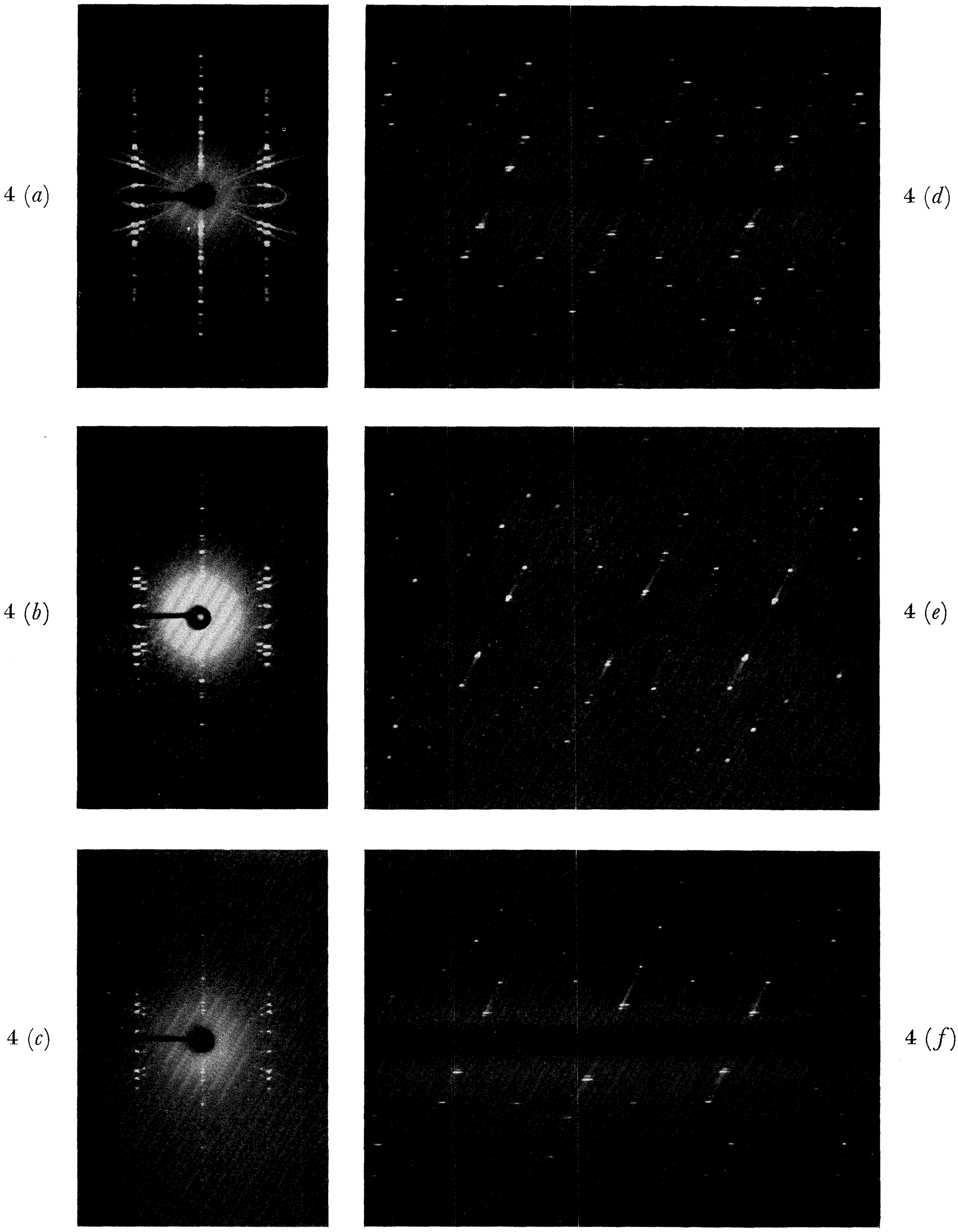
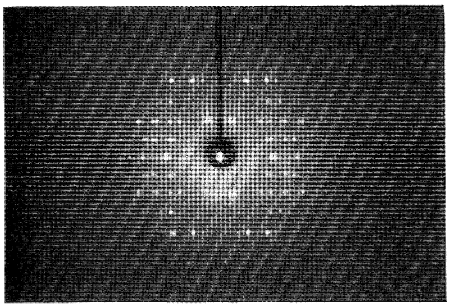


FIGURE 4. (*a*) CuK [010] rotation of anthraquinone, recrystallized from benzene.

(*b*) The same of anthrone, recrystallized from hot ethyl alcohol.

(*c*) The same of 50:50 anthraquinone:anthrone, recrystallized from the melt in a capillary tube (J. W. Harris 1965).

(*d, e, f*) Weissenberg $h0l$ photographs corresponding to (*a, b, c*).



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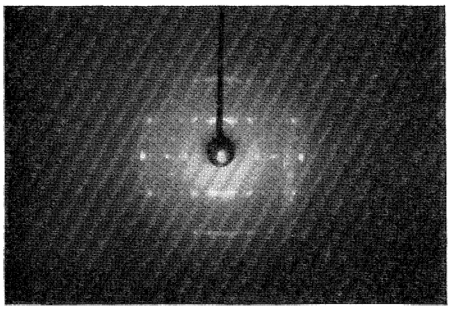

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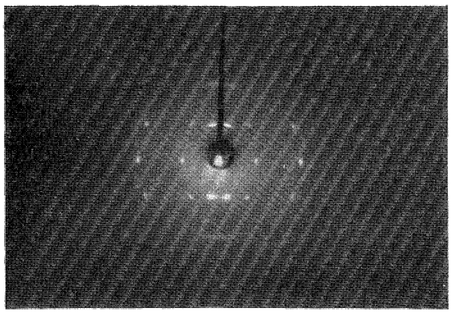

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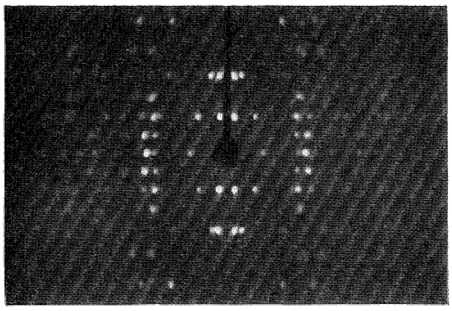

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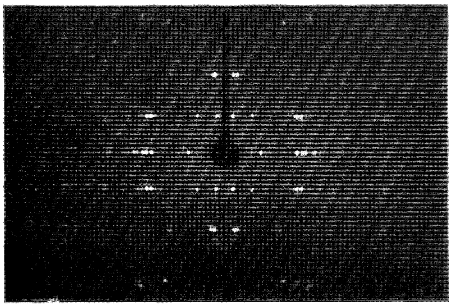

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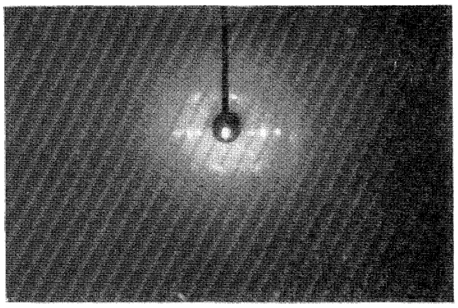

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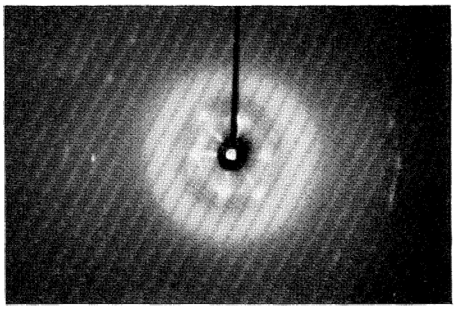

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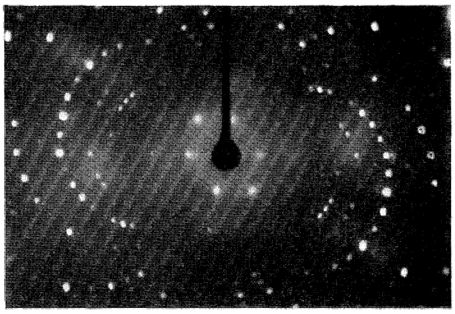

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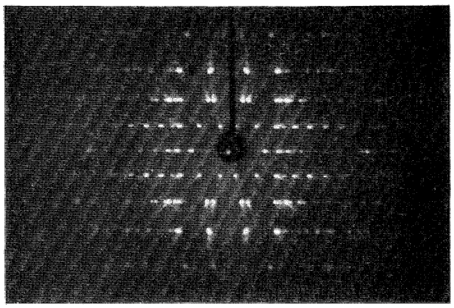

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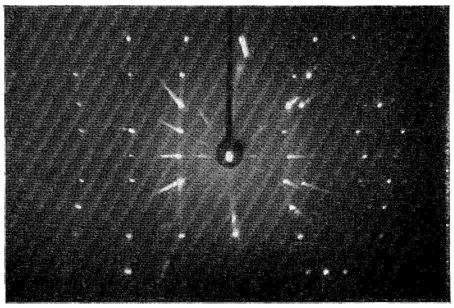

5 (*j*)

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to [010], which showed layer-line streaks (figure 1 (*f*)) and by a Weissenberg *hk*0 photograph (figure 22 (*a*), plate 15), which showed beautifully fine $k = 1 \cdots 5$ continuous festoons from a small, good, nearly fresh crystal. This, however, showed a few even smaller and unidentified satellite spots, which may have been due to intruding first layer-line reflexions, but which were more probably due to small p.o.a. crystallites which had become disorientated relative to the main crystal. The $k = 1$ festoons tend to become less well defined at their extremities where these satellites occur. This Weissenberg photograph also showed the presence of some weak 'anthraquinone' reflexions, easily distinguished because they are so much less sharp than the p.o.a. spots, and because they appear on new $k' = 1,2$ festoons, which become stronger on successive exposures.

It was found that as the 'anthraquinone' spots increased in intensity, so the p.o.a. [010] continuous layer-line streaks tended to break up into a fibre pattern (figure 1 (*g* to *j*)); and that Laue patterns of the final 'anthraquinone' crystal, which was strictly pseudomorphous on the original p.o.a. (figure 16, plate 11) also showed only a fibre oscillation pattern of 'anthraquinone', whatever the crystal orientation (figure 2 (*b*, *c*)). The oscillation pattern indicated a randomness of orientation within the 'single crystal' residue which approached, but was generally less than, 15°.

Description of plate 4

Figure 5. (*a*, *b*, *c*) Cu*K* [100] rotation of p.o.a. showing conversion to *A*:*A*. (The Cu target was slightly contaminated with Ni, giving long-wavelength satellites to all intense spots.) The odd-numbered layer lines weaken as if the identity distance were being halved, but even after more than 450 h irradiation they do not disappear. This effect is due to twinning. The superposition of rotation photographs about [100] and twin [001] of *A*:*A*, for which $a = 2c$, will cause enhancement of the even, relative to the odd layer lines.

(*d*) Cu*K* [100] rotation of anthraquinone, for comparison.

(*e*) Cu*K* [001] rotation of anthraquinone, for comparison.

(*f*) Oscillation about [100] of converted crystal. Incident Cu*K* beam along [010] at centre of oscillation range. The odd layer-line reflexions (especially those for $h = \pm 7$) show up more strongly. The pattern of six reflexions near to the central spot is very similar to that seen in figure 5(*h*). Note that there is *unequal* twinning of this little group about the vertical (001) plane.

(*g*) Similar, but 'still' photograph of another converted crystal. Strong impurity ring.

(*h*) Laue photograph of anthraquinone, Cu*K* + white, incident beam along [010]. Compare 5(*f*).

(*i*) Cu*K* [001] rotation of p.o.a. (radiation contaminated with Ni, as for 5(*a*)). Very faint $\bar{2}01$ *A*:*A* reflexions are just beginning to appear. These correspond to the intense, innermost, second-layer spots on 5(*c*). The final photograph of the converted product, which is not shown, is almost exactly like that from the [100] rotation, owing to the combination of pseudo-symmetry and twinning.

(*j*) Oscillation about [001], p.o.a. The incident Cu*K* beam is at a small angle to [100], and strong *b* axis layer-line streaking is here seen as row-line streaking, including the $k = 0$ streak (here curved). The presence of this streak implies the loss of *sideways periodicity* (normal to [010]) in the mesomorphic phase, as well as the loss of phase relations.

3. Later X-ray diffraction studies

Repeat sets of experiments and various new ones were carried out from 1961 to 1965 on crystals of p.o.a. which had been kept in a refrigerator and had not been previously irradiated or heated; and on freshly-prepared crystals; and on others which had been subjected to heat or to various kinds of irradiation for various periods. The early studies of the structure of p.o.a. had only given the projection on (010). Later intensity measurements (by Dr H. J. Milledge and Dr M. Ehrenberg) led to satisfactory agreement for the [100] and [001] projections also and hence to the trial structure which was afterwards refined by Dr C. J. Brown from fresh data using the Pegasus computer. The three-dimensional refinement, details of which will be published elsewhere, gave a discrepancy factor $R = 0{\cdot}12$, from 456 independent reflexions.

3·1. *Rotation and Laue photographs*

Figures 1 and 2 show some of the results of successive X-irradiation, at room temperatures, of a fresh p.o.a. crystal. After $7\frac{1}{2}$ h of exposure to the whole radiation from a Machlett tube with a copper target, run at 30 kV and 15 mA, half-wave rectification, the new layer-line spots on an [010] rotation photograph could hardly be seen, but the Laue photograph showed strong continuous layer lines superimposed on the normal pattern. These also form a continuous background to the layer lines of reflexions on the rotation photograph, but they were at first overlooked because, until observed on Laue photographs, they were not expected. Rotation and Laue photographs were taken alternately (1 h and $\frac{1}{2}$ h exposure times respectively); and after 40 h the new layer-line spots were strong on the rotation photographs, while some had also appeared on the Laue photographs (thus proving the fibrous or coarsely mosaic nature of the decomposition product). At the same time the continuous layer lines became much less well defined and spotty (rather diffuse spots, not sharp like the original p.o.a. spots), indicating some break-up of the original p.o.a. structure into partially disorientated crystallites. After 145 h there was still a considerable amount of the original p.o.a. left, but it was becoming less well orientated as a whole. During the course of these successive exposures, the X-irradiation was deliberately halted for 2 months. When photographed again, the specimen was found not to have changed noticeably during that period. Repeat experiments on other crystals showed variations of the time taken to reach the different stages of decomposition, but no variation of the essential geometrical mechanism of the reaction. Figures 3 (*a*, *b*, *c*) show the final stage when the p.o.a. spots have disappeared, or practically disappeared from the rotation and 'Laue' photographs, the latter showing only the pseudo-oscillation pattern of the decomposition product, although occasionally traces of a Laue photograph of the final 'anthraquinone' were also obtained. The final product, in fact, was still a single crystal, although of a very coarsely mosaic type; and it retained the exact shape of the original p.o.a. crystal (figure 16 (*a*, *b*), plate 11). Although opaque and somewhat fragile, it could be handled for setting purposes. The reaction, therefore, was quite literally a solid state reaction, although the mechanism involved various kinds of structural disorder. Presumably the *surface* remained unchanged.

3·2. *Mesomorphic phase*

In order to study the early stage of continuous layer lines more carefully, an 'inclined-beam' Laue photograph (Milledge 1963) was taken of a large and nearly fresh p.o.a. crystal, with the [010] axis vertical (figure 7 (*c*)). This showed continuous layer lines corresponding to $k = 0, 1, 2, 3, 4, 5$ of Cu$K\alpha, \beta$ superimposed on the normal Laue pattern. Such continuous lines on Laue photographs correspond to parallel and equally-spaced continuous k-constant *planes* in reciprocal space, including one through the origin, the spacing corresponding to that of the original p.o.a. crystal, $b = 5{\cdot}86$ Å. The rings originally observed on Laue photographs taken with the incident beam parallel or nearly parallel to [010] are sections of these planes by the Cu$K\alpha, \beta$ spheres of reflexion. Two films (figure 8, plate 8) showing eight 'inclined beam' oscillation photographs, four on each film, taken for overlapping 29° ranges such that the eighth repeats the first, show the same continuous layer-lines. These, and the festoons observed on $hk0$, $hk1$, $hk2$, $0kl$, $1kl$, $2kl$ Weissenberg photographs (figures 22 (*a*, *b*); 24 (*a*), plates 15, 16) confirm the effects found on the Laue photographs, although the rotating crystal methods alone could not have decided between continuous *rows* and *planes* in reciprocal space.

These planes of scattering power in reciprocal space correspond to Cu$K\alpha$ diffraction from *isolated* [010] *chains* of p.o.a. molecules still having the original 5·86 Å identity distance. This is an example of the mesomorphic phase of one-dimensional regularity in a three-dimensional system designated by C. Hermann (1931) as translation type no. 3, and called *SSD* in the notation of Mabis (1962). In the description of this mesomorphic structure given by Mabis:

> 'Molecular centres are spaced at equal intervals along straight parallel lines. The side packing of the lines is random, and the parallel displacement of lines is random. The reciprocal lattice consists of one set of parallel equally-spaced planes.'

It should be emphasized, however, that in p.o.a. the [010] chains of molecules *coexist* with the unchanged structure. It may be that single chains become disconnected and displaced (sideways and lengthways) though still parallel with respect to their neighbours, or that pockets of many such chains lose their sideways periodicity, while still remaining parallel with the main structure. The fact that the *exact* periodicity is retained along these isolated [010] chains (for the rings on the Laue photographs and the original festoons are very sharp) proves that *the molecules in them are still the photo-oxide molecules, linked along the chain as they are in the main structure*. Only the sideways intermolecular contacts have broken.

3·3. *Variation of conditions of X-irradiation*

In other experiments where larger samples of irradiated crystals were required for mass spectrometric tests (see later) the p.o.a. crystals were placed inside the lead cap covering one window of X-ray tubes with Cu and Mo targets respectively and were continuously irradiated for various lengths of time. Random samples were removed at intervals and X-ray photographs of various kinds were taken. No change in the general sequence of pattern changes was observed by comparison with those already described, in which the irradiation had been of a single specimen mounted on goniometer arcs in an X-ray photogoniometer. The range of times in which successive changes occurred was in any case so large that no particular speeding-up was observable when the irradiation was continuous; and no difference was found between the times or effects of Cu or Mo radiation. The Mo tube was run at 40 kV, 20 mA, the Cu tube at 30 kV, 15 mA.

3·4. *Variation of temperature of specimen*

A fresh crystal was taken, set up with [010] as rotation axis as quickly as possible and then rotation and Laue photographs were taken. Afterwards it was heated rapidly in a small furnace to 80 °C and maintained at this temperature for 1 h. The furnace was removed and the crystal allowed to cool quickly and fresh rotation and Laue photographs taken at room temperature. This procedure was repeated giving the crystal first an extra 2 h heating and then another 4 h heating. At the end of 7 h total heating at 80 °C (with three reductions to room temperature and 6 h total exposure to X-rays (figures 9 (*a* to *d*), plate 9), under the same conditions as before, the decomposition of the p.o.a. was apparently complete and, as far as could be judged, the course of the reaction was exactly similar to that produced by long X-irradiation at room temperatures.

In a later repetition of this experiment by C. J. Brown the complete conversion at 80 °C took about 20 h.

Figures 10 (*a* to *d*), plate 9, show the result of quick heating, to 138 °C, or of melting and quick recrystallization. The crystal in each case decomposed into an almost wholly disorientated powder, the lines being similar to those given by anthraquinone (figure 10 (*e*)) but with a considerable amount of small-angle scattering indicating the presence of many disorientated molecules or very small groups of molecules, not necessarily those of anthraquinone or of the original p.o.a.

Finally, fresh single p.o.a. crystals were dropped gently on to a calibrated m.p. bar and moved quickly along until they decomposed with explosive violence, sometimes before and sometimes immediately after melting at 166 °C.

Heated more slowly under their own vapour pressure, the behaviour of fresh crystals was quite different. A few crystals, enclosed in a capillary tube, were inserted on the hot stage of a microscope at 108 °C and heated. There were first some erratic movements of the single crystals, which at 120 °C began to be opaque, the edges assuming an etched appearance. At 130 °C some sublimation began and at 140 °C the crystals split in a sinuous way and the separate crystals began to merge into one another. At 192 °C wetting began and at 232 to 248 °C all traces of solidity disappeared, leaving only brown stains on the inner surface of the tube and some clearer sublimate at a distance. It was obvious that the original p.o.a. had decomposed at some lower temperature and that what was being observed here was the behaviour of the crystalline products of decomposition.

A crystal that had already been decomposed at room temperature by X-irradiation was also observed on the hot stage of the microscope, from an initial temperature of 140 °C. A small amount of sublimation began from 150 °C and continued to 200 °C, but the crystals retained their shape at this temperature. At 210 °C wetting began and this continued until complete melting occurred at 256 ± 2 °C, leaving a residue that looked like dark tar. From about 240 °C bubbles of gas appeared to be given off, but the nature of these was not ascertained. (These and the previous observations were made by Mr J. Harris.)

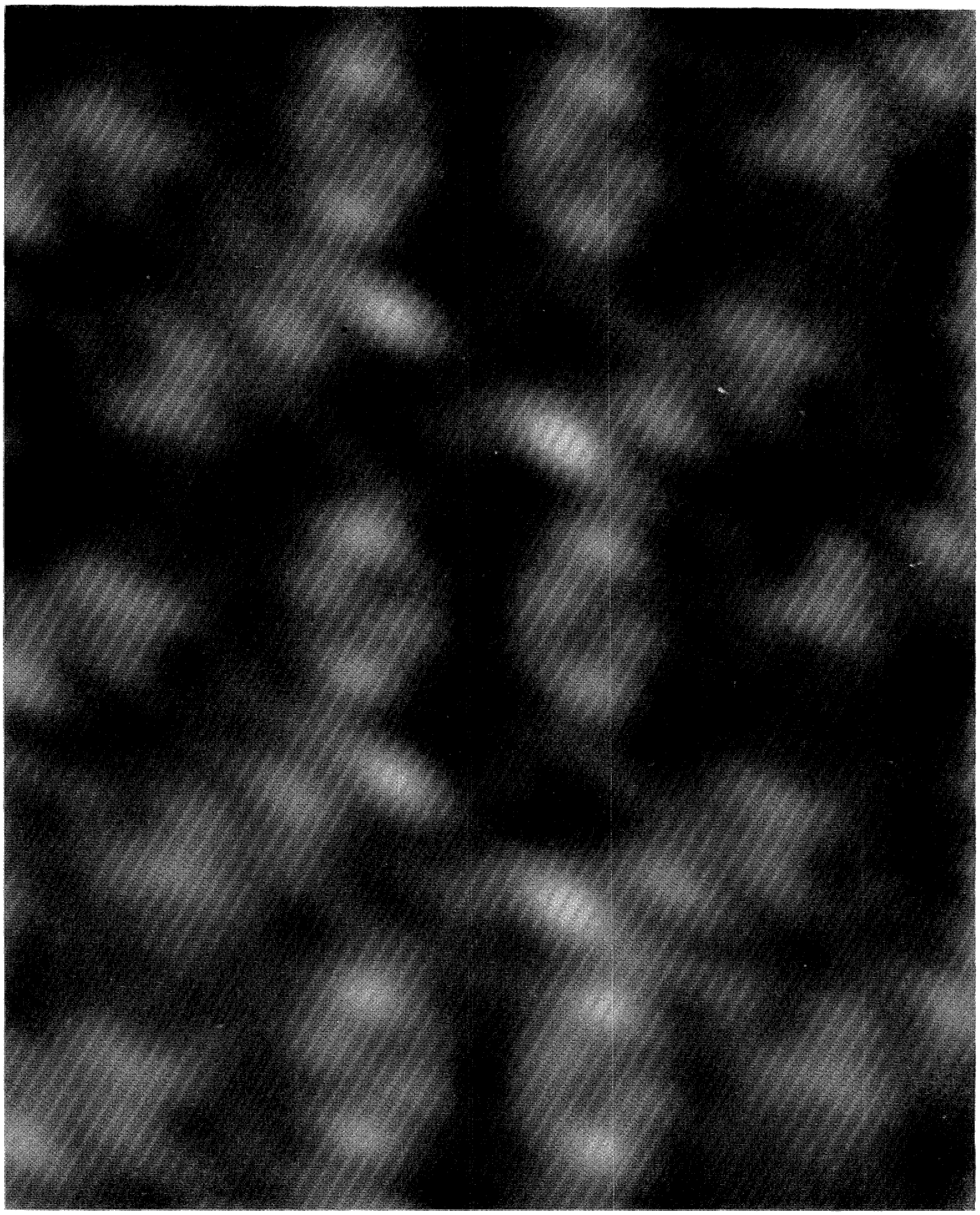


FIGURE 6(*a*). An optical synthesis, made on the von Eller photosommateur, of the p.o.a. [010] projection from room-temperature (20 °C) data. Note the lack of resolution along the O—O bridge (one oxygen is superimposed on a carbon atom of the central ring), and the general diffuseness of the side rings.

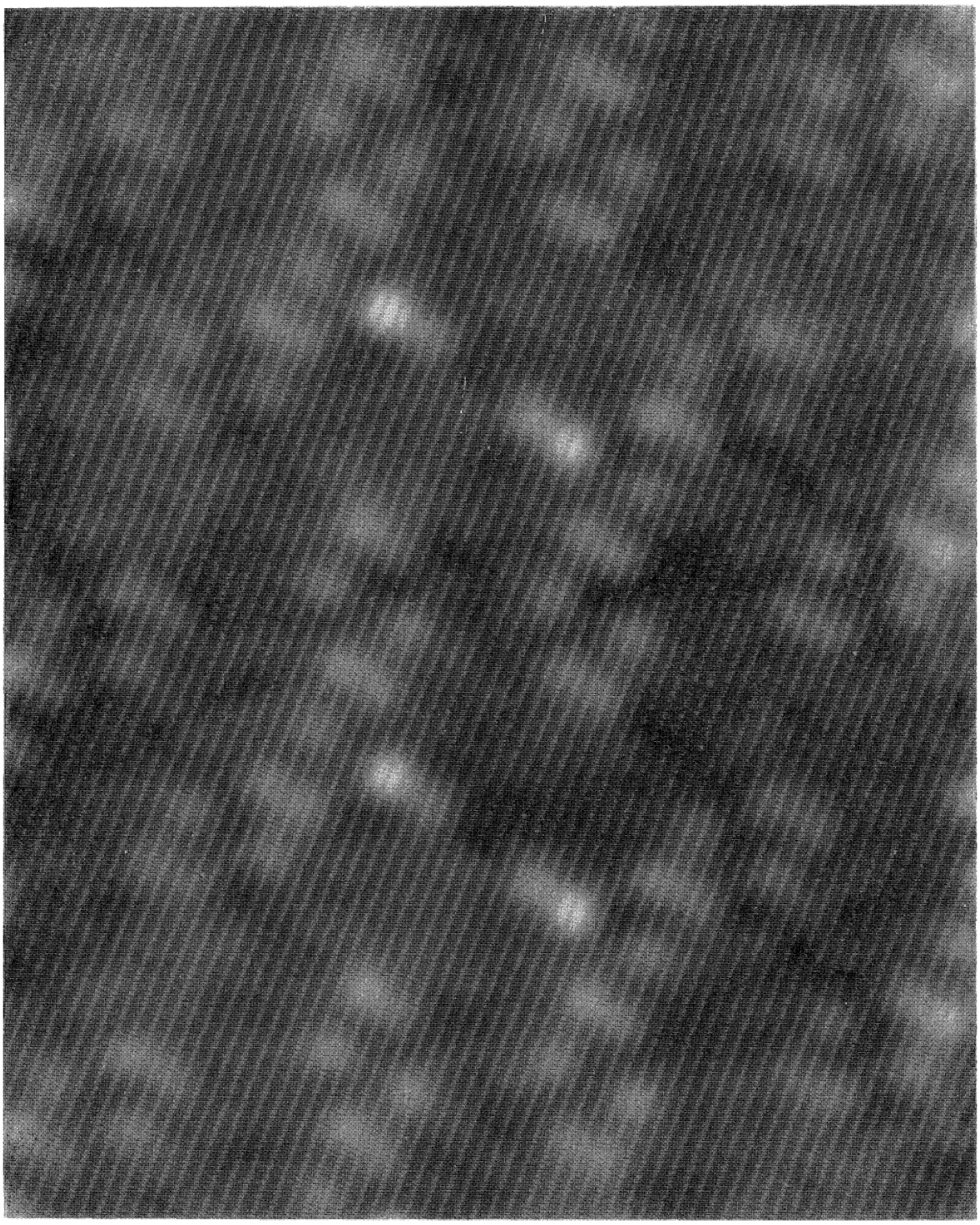
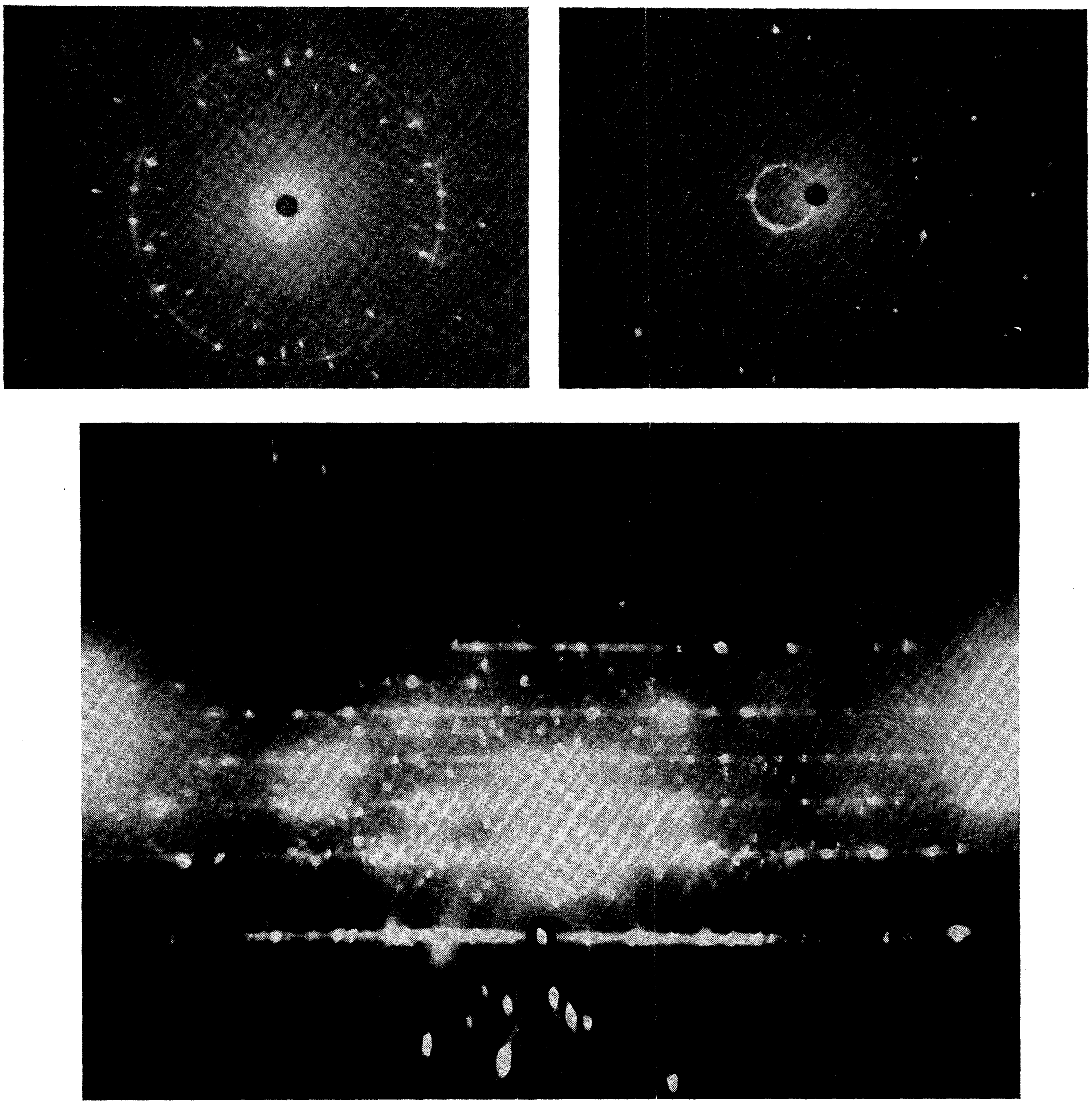


FIGURE 6(*b*). The same from low-temperature data (near to the boiling point of liquid nitrogen). The atoms are now well resolved.



7 (*a*)

7 (*b*)

7 (*c*)

Figure 7. (*a*) Laue photograph, on a flat film, of nearly fresh p.o.a., [001] vertical; incident (white + Cu*K*) radiation along [010]. A nearly continuous ring due to CuKα is seen, enhanced in the position of thermal diffuse spots and accompanied by traces of the Cu$K\beta$ ring. A second ring of larger diameter can be clearly seen on the film, but is not reproducible. These rings correspond with one-dimensional regularity along the [010] direction, first and second orders.

(*b*) The same with [010] tilted a little out of line with the incident X-ray beam. The ring of zero order now shows and is very intense. Compare the oscillation pattern figure 5(*j*), which is nearly at right angles to this ([001] vertical, [010] nearly normal to the incident beam).

(*c*) Inclined-beam Laue photograph of a large crystal of nearly fresh p.o.a., showing layer-line streaks for $k = 0 \cdots 5$.

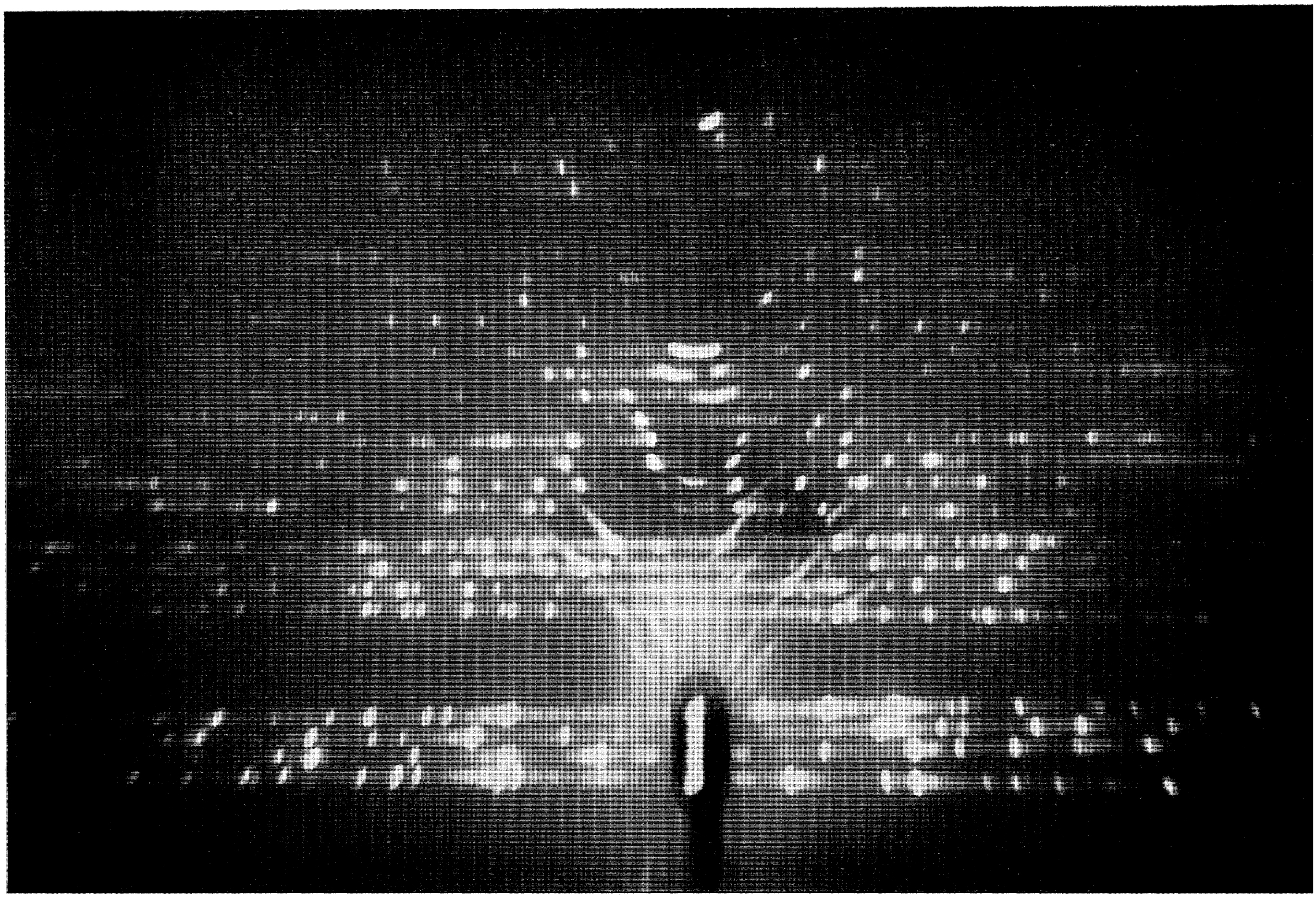


FIGURE 8. Four out of a set of eight superimposed 'inclined beam' 29° oscillation photographs (Milledge 1963), taken on two films, with the film shifted between each setting and the crystal moved by 180°/7 so that no. 8 repeats no. 1. [010] vertical, white + Cu*K* radiation.

FIGURE 9. (*a*) [010] rotation photograph on flat film of fresh p.o.a. crystal. Cu$K\alpha$ (filtered Ni) 30 kV, 15 mA, 30 min exposure time. Before heating. Faint layer-line streaking in background.

(*b*) The same after heating *in situ* for 1 h at 80 °C (+15 min heating up and 25 min cooling down). Slight mis-setting has occurred.

(*c*) The same after a further 2 h at 80 °C (+15 min to heat up and 15 min to cool down).

(*d*) The same after a further 4 h at 80 °C (total 7 h at 80° + 45 min spent in heating up from room temperature and a little more in cooling down again). Apparently, total conversion to slightly mis-set 'single crystal' with rather good spots.

(*e*) A very well exposed 'still' photograph of 9(*d*) showing that the conversion is in fact not quite complete as a fibre photograph of p.o.a. accompanies the fibre photograph of the A:A conversion product. Low-angle scattering shows that considerable amounts of impurities or of disordered material are also present.

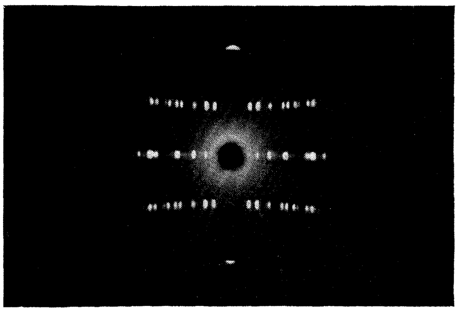
FIGURE 10. (*a*) Powder photograph (flat film) with diffuse low-angle scattering resulting from quick heating of a p.o.a. crystal to 138 °C. Compare with figures 10(*e*) and 11(*a*, *b*, *c*).

(*b*) [010] rotation (flat film), Cu$K\alpha$, of p.o.a. crystal before melting and recrystallization.

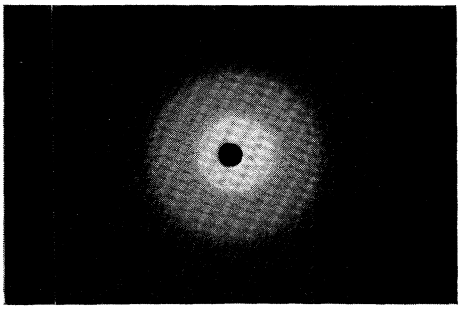
(*c*) Laue photograph of the same showing only the early stage of disorder. The crystal is single.

(*d*) The same crystal was heated slowly to its melting point (temperature not measured), when it turned yellow but remained on the fibre. It was then allowed to cool, and the photograph shows an almost disorientated powder, similar to 10(*a*, *e*) and 11.

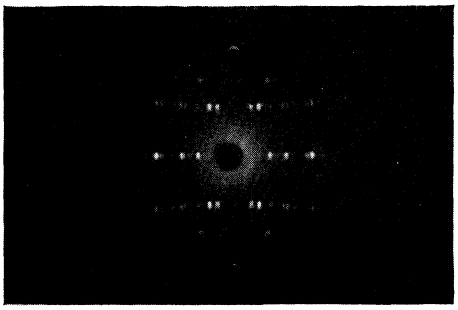
(*e*) Flat-film powder photograph of anthraquinone (in cellulose acetate tube), for comparison. Note the comparative lack of low-angle diffuse scattering; compare 10(*a*, *d*).



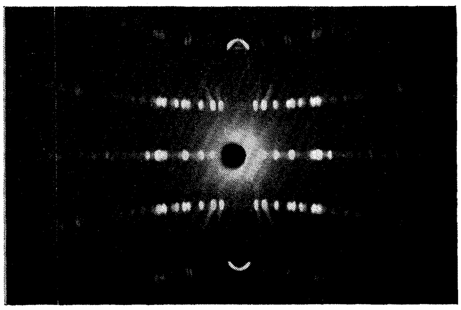
9 (*a*)



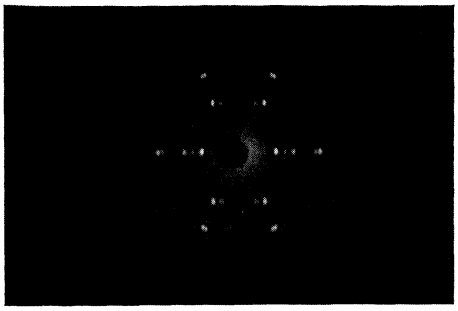
10 (*a*)



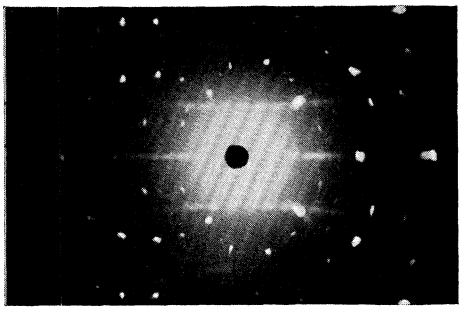
9 (*b*)



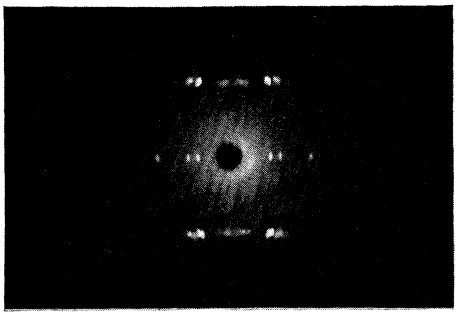
10 (*b*)



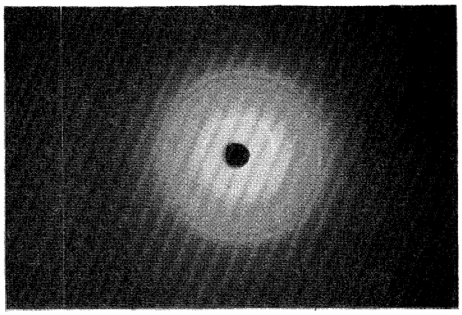
9 (*c*)



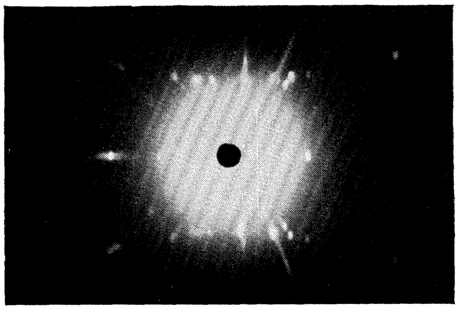
10 (*c*)



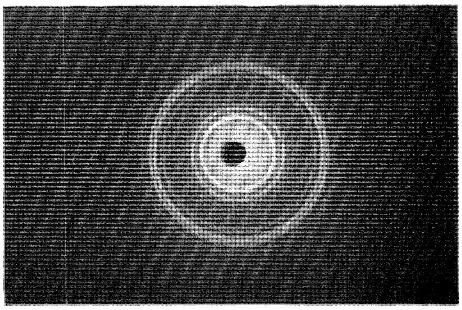
9 (*d*)



10 (*d*)



9 (*e*)



10 (*e*)

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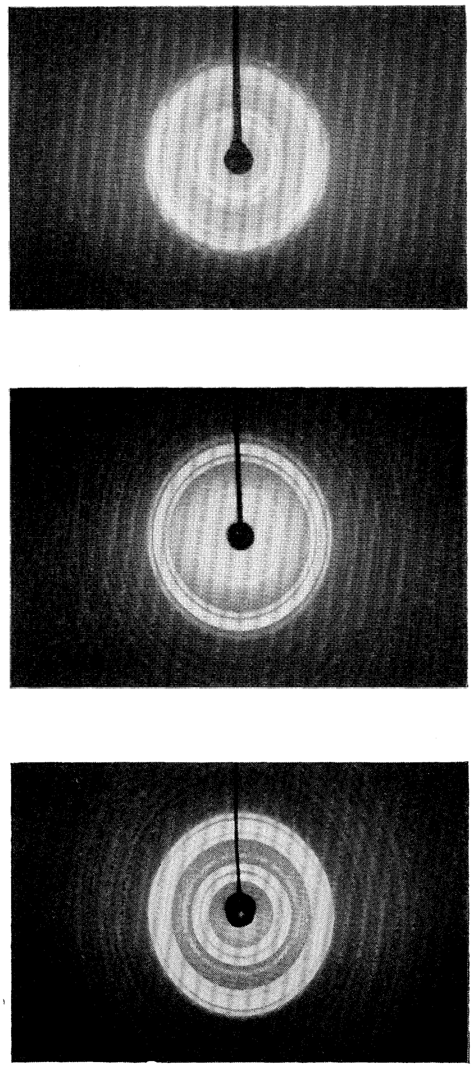
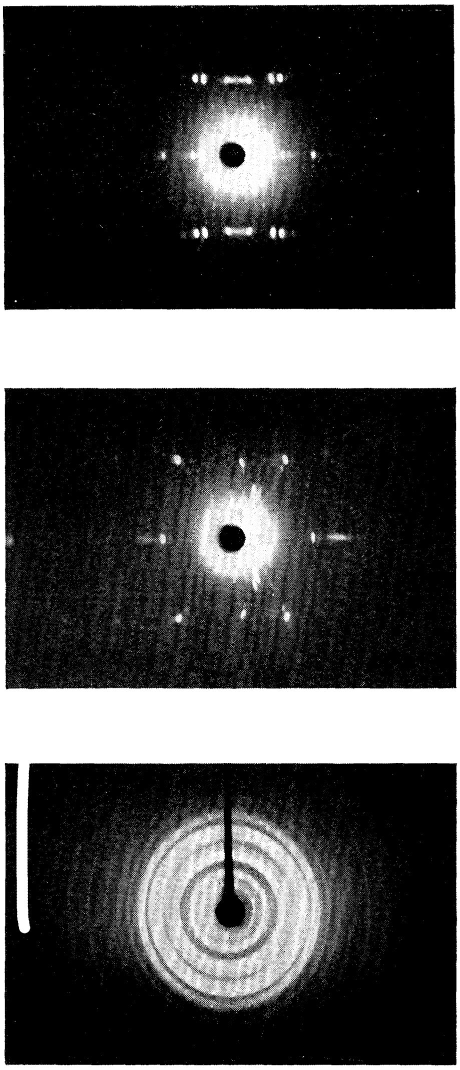


11 (*a*)

11 (*b*)

11 (*c*)



12 (*a*)

12 (*b*)

12 (*c*)

FIGURE 11. (*a*) Crystal of p.o.a. already decomposed at room temperature (~ 20 °C) by X-irradiation, then allowed to melt and recrystallized. The specimen, which was a grainy powder, contained some largish orientated crystals. It was rotated; Cu*K* radiation; 26 min exposure time. The resemblance is closer to 11(*b*) than to 11(*c*).

(*b*) Anthraquinone, for comparison.

(*c*) Anthrone, for comparison. The principal difference from 11(*b*) is in the presence of a moderately strong 201 line outside the two strong inner lines.

FIGURE 12. (*a*) Nearly converted crystal (heated for a total 3 h at 100 °C, with $1\frac{1}{2}$ h Cu*K* irradiation for setting and preliminary photographs). [010] rotation, Cu$K\alpha$, 30 min exposure, flat film. This pattern shows p.o.a. powder lines (compare 12(*c*)).

(*b*) The same; 'still' photograph in a setting similar to that of 1(*f* to *j*). This crystal shows very little twinning of A:A and none of p.o.a., but it does show much low-angle scattering and p.o.a. powder lines (compare 12(*c*)).

(*c*) P.o.a. powder pattern.

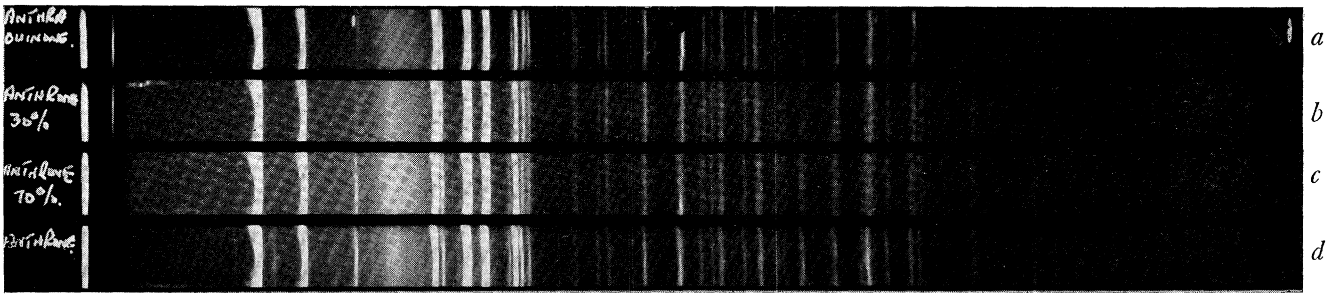


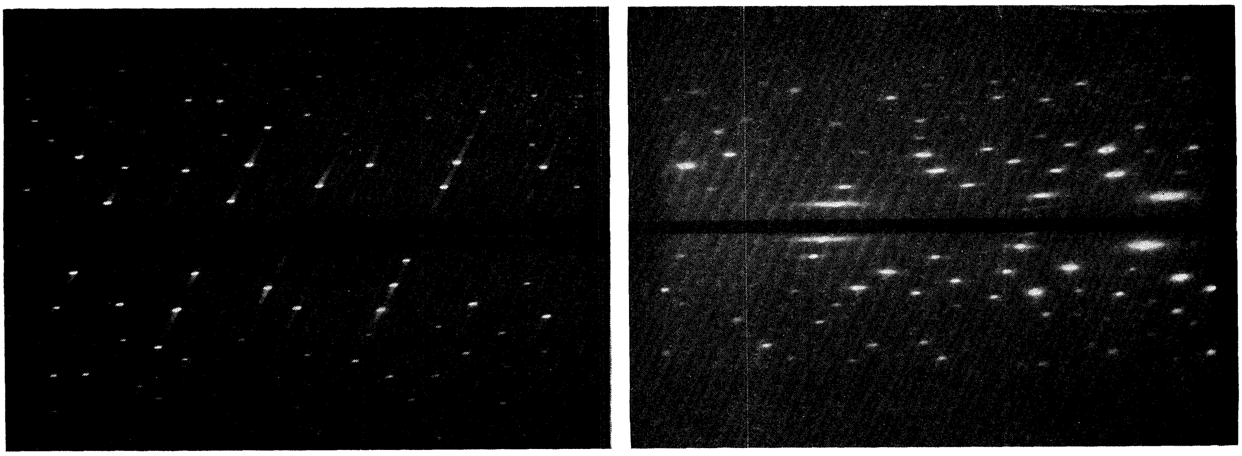
Figure 13. (*a*) Nonius powder pattern of anthraquinone, recrystallized from the melt.

(*b*) Nonius powder pattern of mixed anthraquinone: anthrone crystal (70 %, 30 %) recrystallized from melt.

(*c*) Nonius powder pattern of 30 %, 70 % mixed crystal.

(*d*) Nonius powder pattern of anthrone. Note the variation of 201, the third line. (Some weak impurity lines are present.)

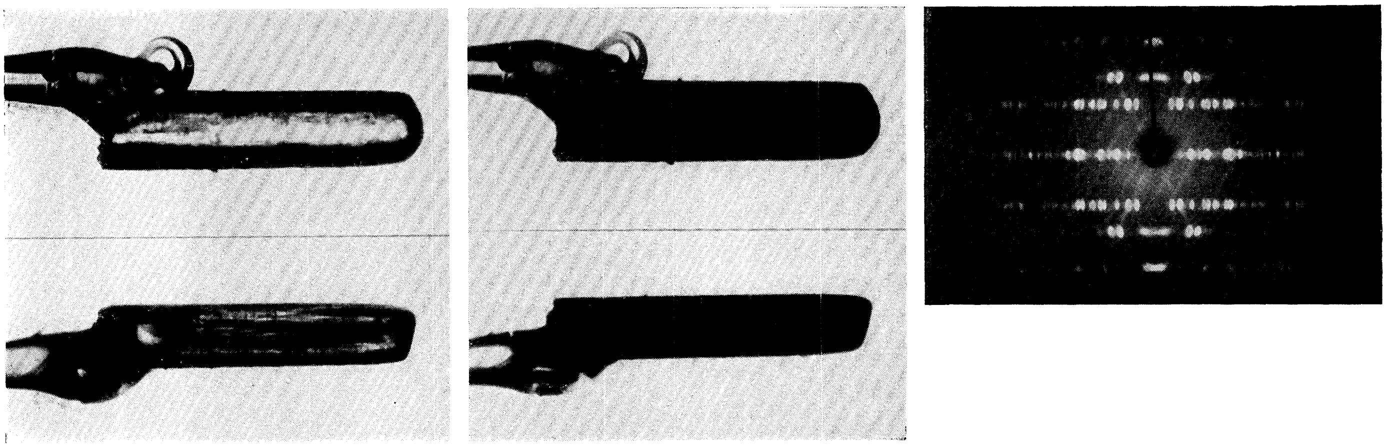
15 (*a*)



15 (*b*)

Figure 15. (*a*) Fresh p.o.a.: *h*0*l* Weissenberg photograph, Cu$K\alpha\beta$. Good crystal.

(*b*) *h*1*l* of another p.o.a. crystal, photograph strongly exposed.

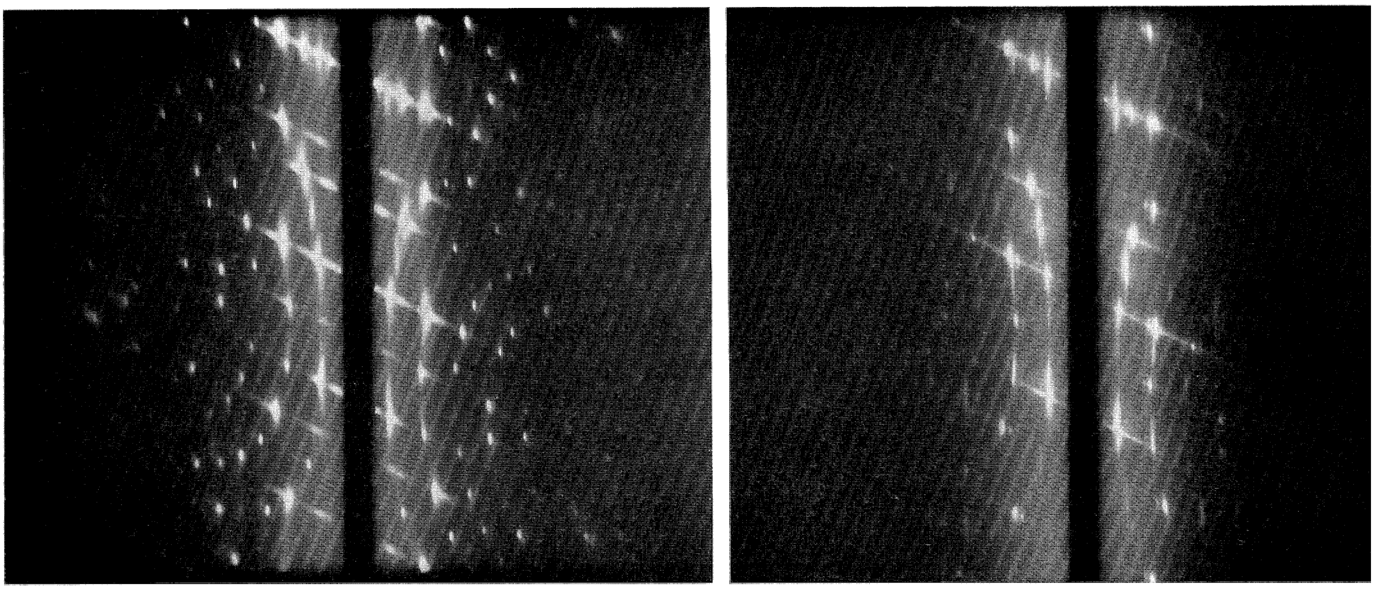


16 (*a*) 16 (*b*) 16 (*c*)

Figure 16. (*a*) P.o.a. crystal before heating (magn. × 48.)

(*b*) Same after $13\frac{1}{2}$ h at 75 to 85 °C, now opaque but with no change of shape.

(*c*) X-ray photograph showing that the crystal was about half converted at this stage.



17 (*a*) 17 (*b*)

Figure 17. (*a*) *h*0*l* Weissenberg photograph (Cu$K\alpha$, 45 h exposure time). Weak twinning across *A*:*A* (001). The p.o.a. is single.

(*b*) A similar photograph of another crystal (Cu$K\alpha\beta$, $5\frac{1}{2}$ h exposure time) at a later intermediate stage, after 84·1 h irradiation by Mo*K*, inside the lead cover of the X-ray tube window. (Compare 18(*b*), where the twinning is more nearly equal.)

(*c*) Interpretation of the main sets of reflexions on 17(*b*).

Figure 18. (*a*) h0*l* Weissenberg photograph of a doubly twinned mixed *A*:*A* crystal derived from p.o.a. The twinning across (001) is clearly duplicating the main 200 reflexion (very weakly) but the twinning across ($\bar{2}$01) is concealed by the pseudo symmetry across ($\bar{2}$01) and by the space group extinction of odd *h*00 orders. This specimen was obtained by heating p.o.a. at 80 °C. (Compare 18(*d*).)

(*b*) *h*0*l* Weissenberg photograph of a different specimen, obtained by 130 h Cu*K* irradiation at 20 °C. There can now be seen not only the nearly equal twin across (001) but a very weak twin of the twin, across ($\bar{2}$01). (Compare figure 20.)

(*c*) *h*0*l* Weissenberg photograph of another specimen after 67 h Cu*K* irradiation at 20 °C; conversion at an intermediate stage (compare 17(*a* to *c*)). The twin plane (001) is seen to correspond with (001) of the original p.o.a. (apart from the small angular shift of about 2°) and the *h*00 reflexions are twinned for both *A*:*A* and p.o.a. In this case, therefore, the original p.o.a. was twinned or became twinned in the course of the reaction. The $\bar{2}01$, $\underline{\bar{2}01}$ p.o.a. reflexions may be seen (with $\bar{4}02$, $\underline{\bar{4}02}$) on each side of $\underline{h00}$, *h*00 of *A*:*A*.

(*d*) *h*1*l* corresponding with 18(*a*). The *h*10, 011, 111 of the main individual can be determined with certainty by comparison with 19(*a*, *b*, *c*). There is strong twinning across ($\bar{2}$01), however, which causes an apparent doubling of the *c* axis. There is also a very minor twinning across (001) which duplicates the *h*10 reflexions very weakly, just as *h*00 are duplicated in 18(*a*). Note the strong [10$\bar{2}$] streaking. (Compare figure 21.)

(*e*) *h*1*l* corresponding with 18(*b*). The twinning about (001) is here almost equal, but that across ($\bar{2}$01) is still not quite equal, thus allowing the certain identification of *h*10, 011, 111.

(*f*) *h*1*l* of the same specimen as 18(*c*). Only the *A*:*A* reflexions are now seen, as the p.o.a. first layer line occurs at a different inclination angle. Again the twinning across (001) is equal, but that across ($\bar{2}$01) is unequal, so that *h*10, 011, 111 are identifiable.

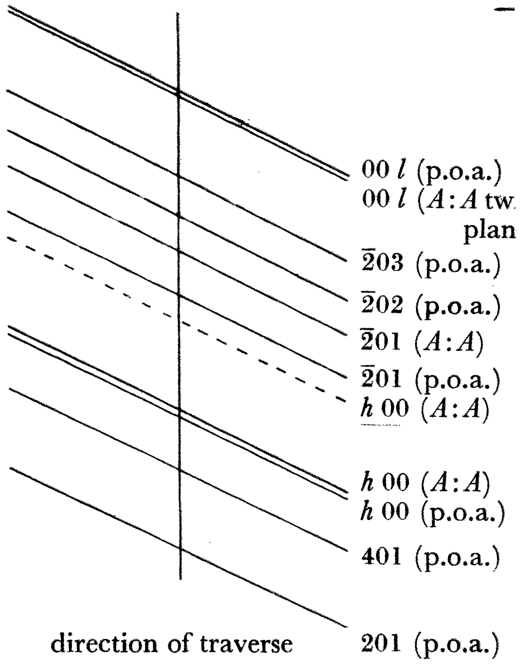
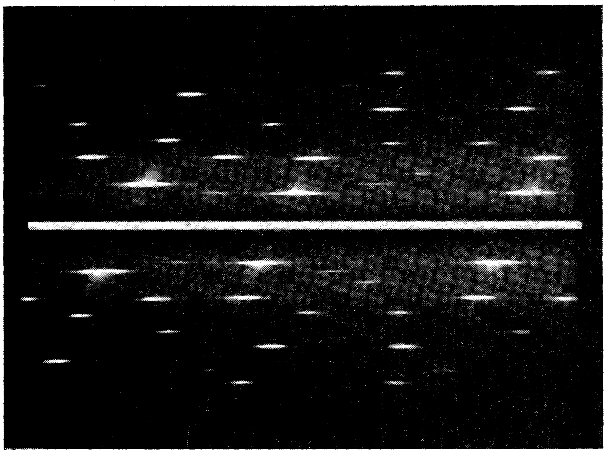
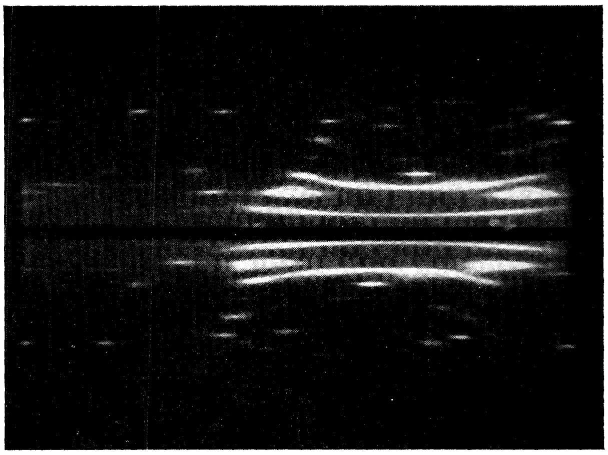
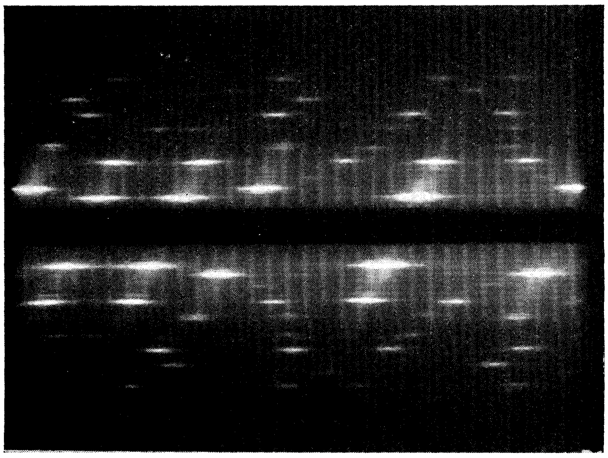
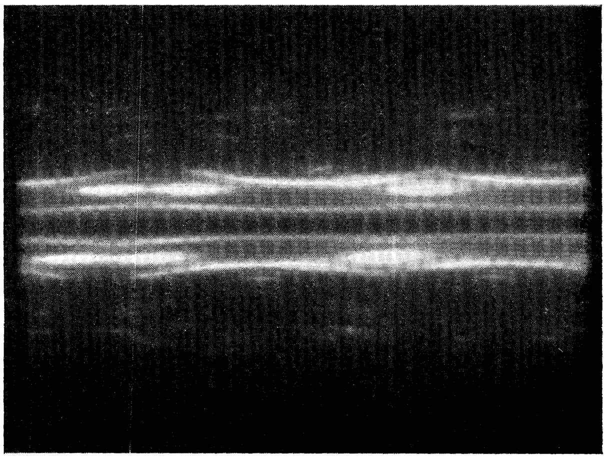

00 *l* (p.o.a.)
00 *l* (*A*:*A* tw
plan
$\bar{2}03$ (p.o.a.)
$\bar{2}02$ (p.o.a.)
$\bar{2}01$ (*A*:*A*)
$\bar{2}01$ (p.o.a.)
h 00 (*A*:*A*)
h 00 (*A*:*A*)
h 00 (p.o.a.)
401 (p.o.a.)
direction of traverse
201 (p.o.a.)

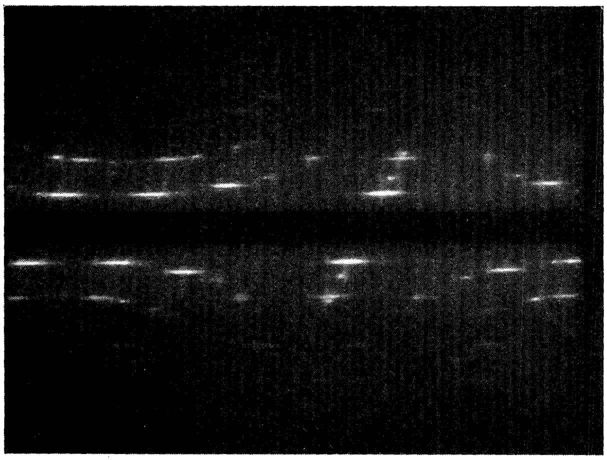
FIGURE 17 (*c*)

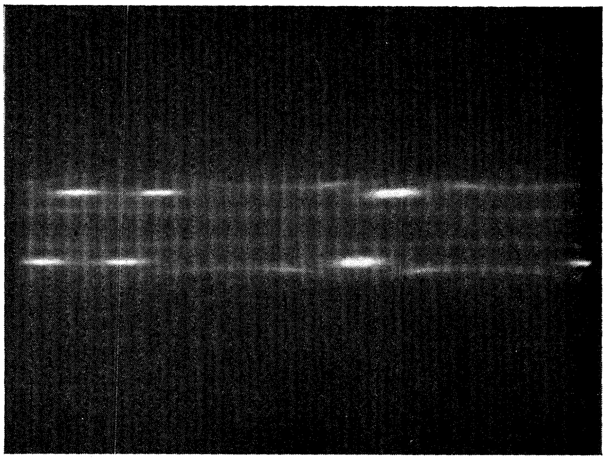

18 (*a*)


18 (*d*)

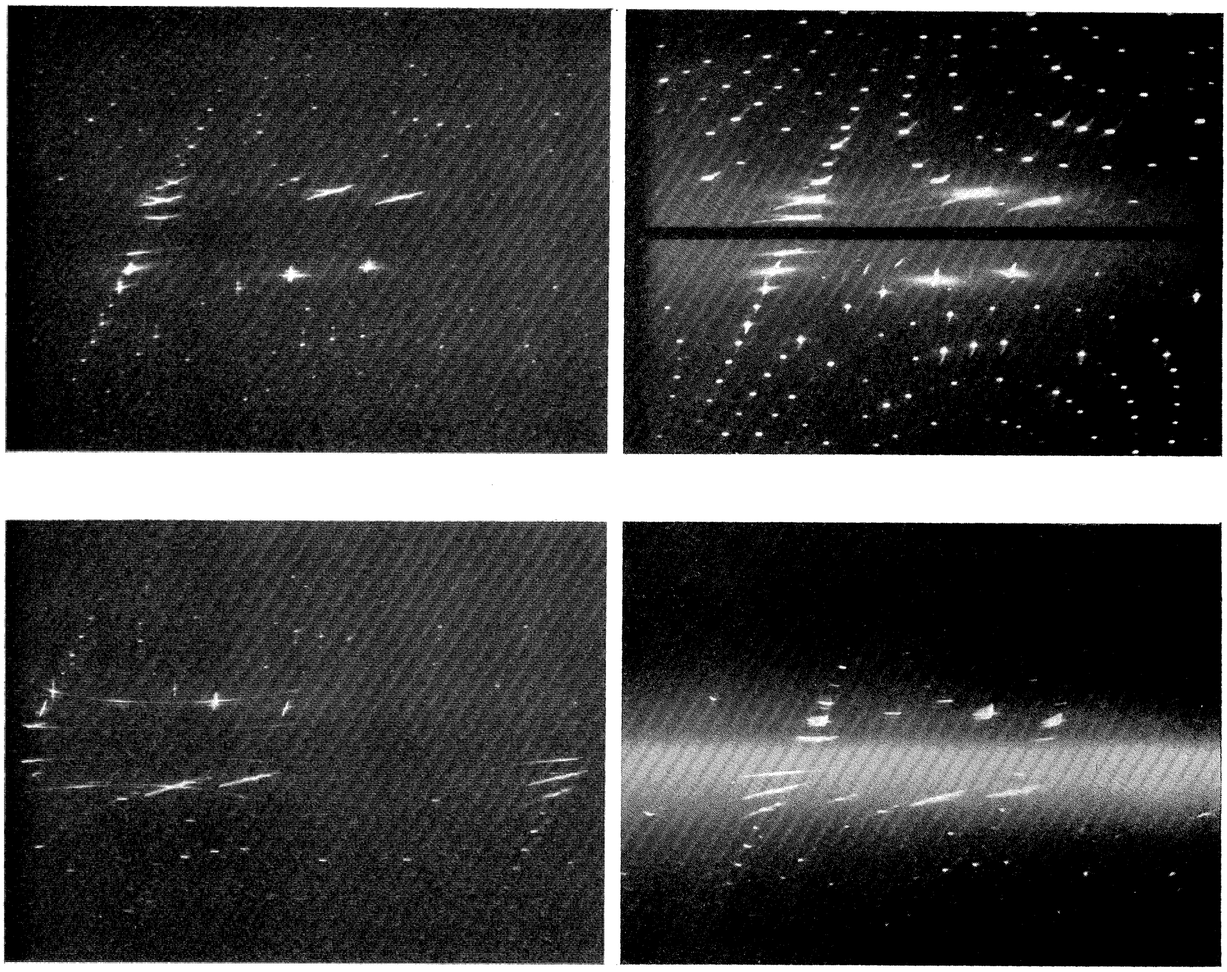

18 (*b*)


18 (*e*)


18 (*c*)


18 (*f*)

For legend see facing page.

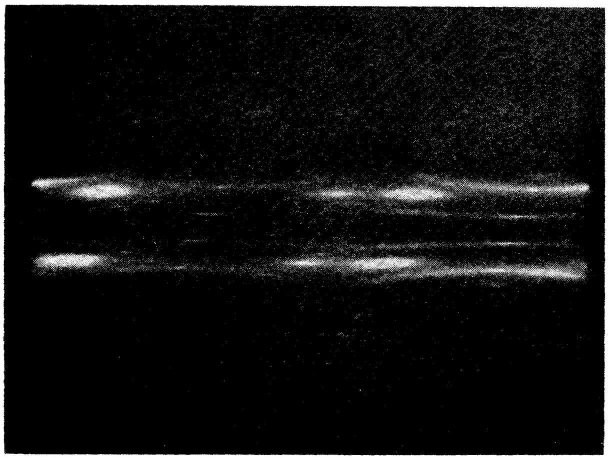


19 (*a*)

19 (*c*)

19 (*b*)

19 (*d*)



19 (*e*)

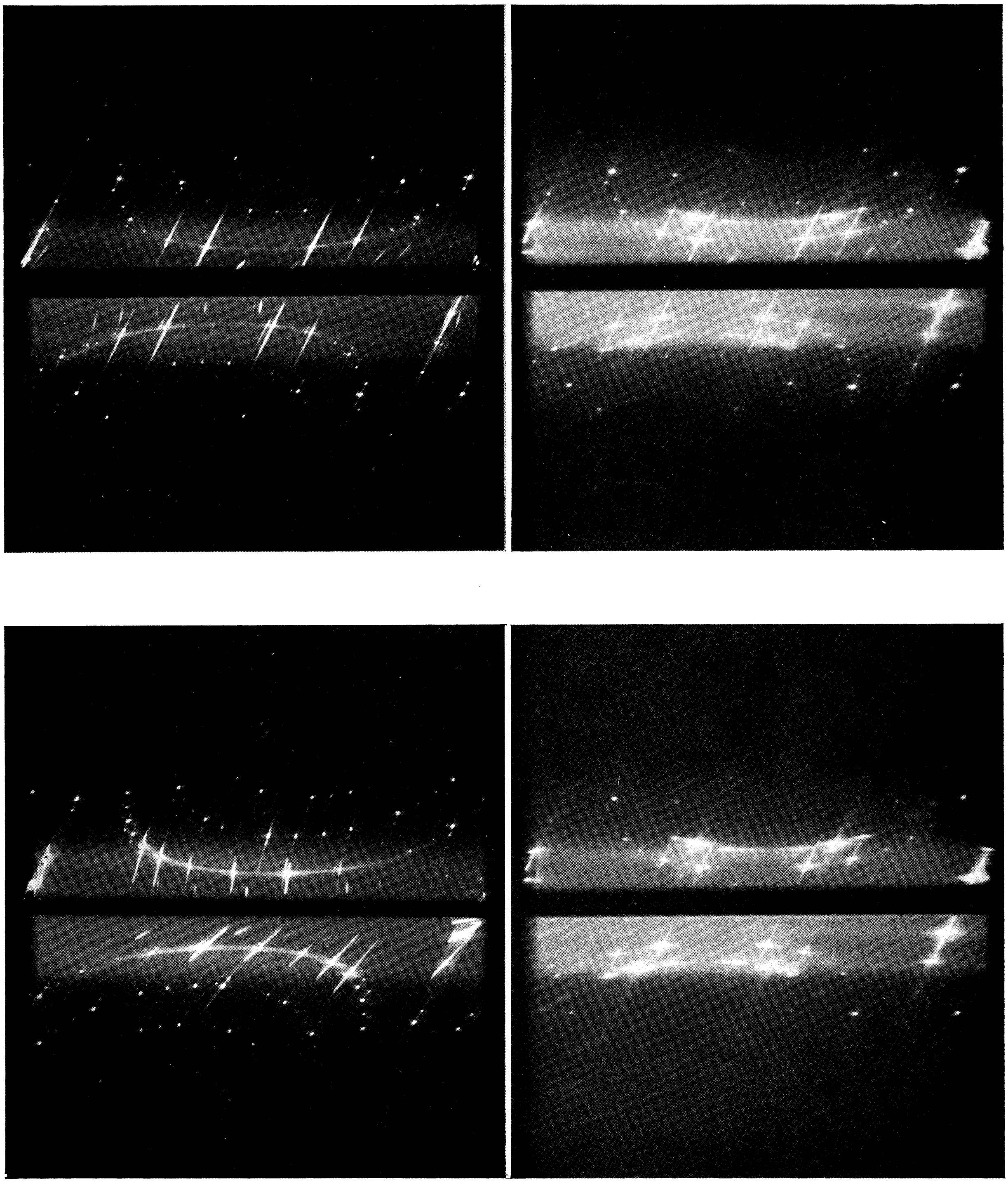
FIGURE 19. (*a*) *hll* Weissenberg photograph of untwinned anthrone (Cu*K*, 7 h exposure time). The closely spaced reflexions all in a line are the *h*10. The strongest reflexions are the 011 and 111 (the latter being further from the central horizontal line).

(*b*) *hll* of anthrone, recrystallized from hot acetic acid (Cu*K*, 6 h exposure time), unequally twinned across $(\bar{2}01)$. The *h*10, 011, 111 of the main individual are still quite obvious. Note the sharp Cu$K\alpha$ streaking connecting 110 and $\underline{110}$ (underlining indicates twin reflexion) and 310, $\underline{111}$, 111, $\underline{310}$. Traces of the Cu$K\beta$ streak are also visible.

(*c*) *hll* of anthraquinone (Cu*K*, 20 h exposure time), after heating for 6 min at 150 °C and allowing to cool. Although the 110, 210, 011, 111 (in particular) show that there is some distortion and strong thermal vibration, no twinning or streaks appear of the 19(*b*) type.

(*d*) *hll* of 50:50 anthraquinone/anthrone mixed crystal from the melt (Cu*K*, 17 h) twinned about $(\bar{2}01)$ but showing no streaks of the 19(*b*) type; rather distorted.

(*e*) *hll* of a converted specimen (Cu*K*, 5 h; after 137 h Cu*K* irradiation) showing sharp, small super-lattice reflexions. Unequal twinning on both $(\bar{2}01)$ and (001). Longer exposures did not bring up any more reflexions.



22 (*a*)

22 (*c*)

22 (*b*)

22 (*d*)

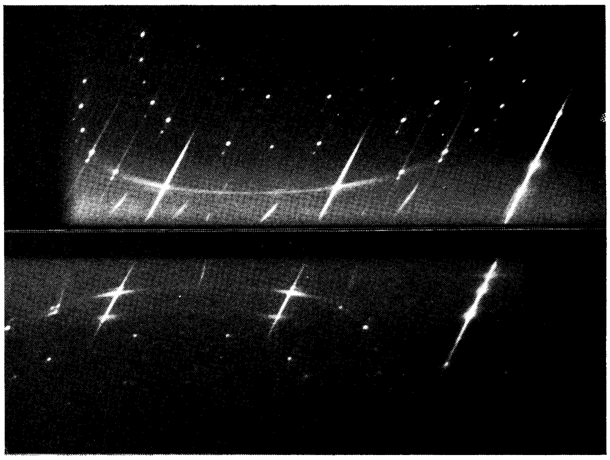
FIGURE 22. (*a*) *hk*0 Weissenberg photograph of almost fresh p.o.a. (2 to 8 h Cu*K* irradiation, that is, 6 h exposure time), showing sharp festoons out to $k = 5$.

(*b*) *hk*1 of the same specimen after 8 to 14 h Cu*K* irradiation (that is, 6 h exposure time after a previous 8 h irradiation).

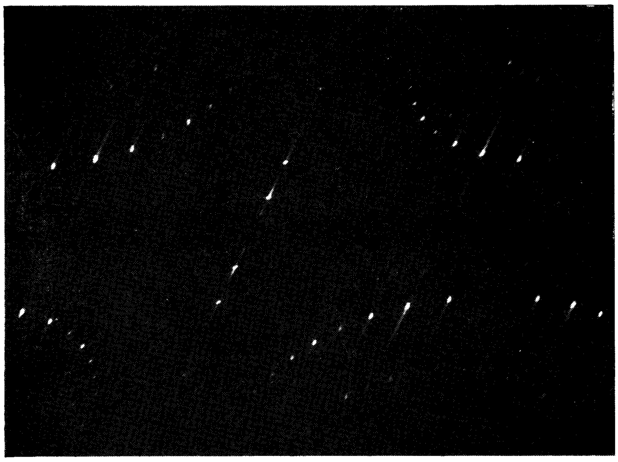
(*c*) *hk*0 of the same specimen after 14 to 20 h irradiation.

(*d*) *hk*0 of the same specimen after 50 to 56 h irradiation.

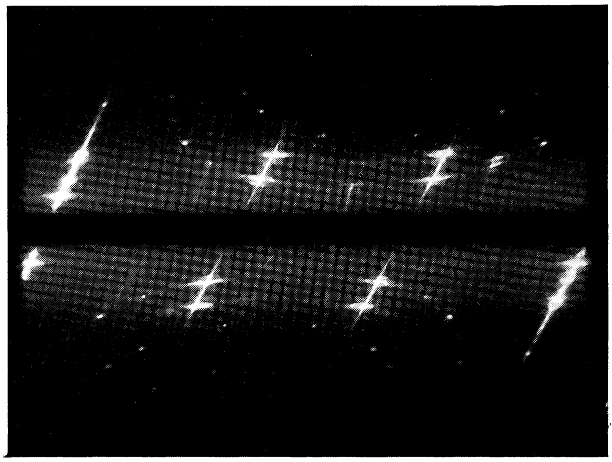
23 (*a*)



24 (*a*)



23 (*b*)



24 (*b*)

FIGURE 23. (*a*) *hk*0 of the same specimen as in figure 22 after 480 h irradiation, when only a trace of p.o.a. remains as very small, sharp 110 reflexions.

(*b*) *hk*0 of anthraquinone for comparison with figures 22(*d*) and 23(*a*). Note the presence on figures 22(*d*), 23(*a*) and 24(*b*) of *A*:*A* *h*10 reflexions where *h* is odd. These are quite strong.

FIGURE 24. (*a*) Composite 0*kl* Weissenberg photograph of almost fresh p.o.a. *above* (6 h exposure time, Cu$K\alpha\beta$), with the same after 40 h Cu*K* irradiation *below* (3 h exposure time, Cu$K\alpha\beta$). The sharp p.o.a. festoons are still visible after 40 h.

(*b*) The same after 49 to 55 h Cu*K* irradiation. As in the case of 18(*d*, *e*, *f*) and 19(*b*, *d*) the twinning across ($\bar{2}01$) produces apparent $01\frac{1}{2}$, $01\frac{3}{2}$ reflexions which are in fact $\underline{110}$, $\underline{310}$. They are weaker than the corresponding 110, 310 reflexions seen on figures 23(*a*, *b*). (This specimen was unfortunately lost before the final 0*kl* photograph, after full conversion, could be obtained.)

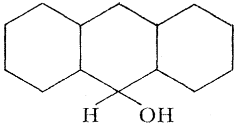
An X-ray photograph was taken of the tarry residue when it had cooled and recrystallized. It was found to give a powder pattern (figure 11 (*a*), plate 10) very similar to that of anthraquinone (figure 11 (*b*)), but containing some obviously fairly large orientated crystallites. Some further 'annealing' took place with time. Another p.o.a. crystal, however, heated for 3 h at 100 °C, although almost wholly converted (figure 12 (*a*, *b*), plate 10) showed a considerable residue of p.o.a. *powder* (cf. figure 12 (*c*)), together with strong low-angle scattering.

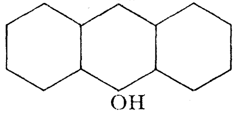
4. NATURE OF THE PRODUCTS OF DECOMPOSITION

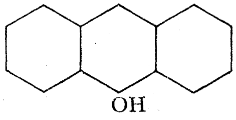
Before the above-mentioned m.p. experiments were carried out, suspicions had begun to grow that the product of decomposition was not necessarily, or not wholly, anthraquinone. Anthraquinone melts, under its own vapour pressure and with some decomposition, at 286 °C, and none of our converted specimens appeared to reach anywhere near to this temperature. To be sure, disorder and impurities could markedly lower the m.p., but the amounts would have to be very considerable to explain the lowering that takes place.

Attempts to make and to crystallize the compounds oxanthrone (IV) and 9,10-dihydroxyanthracene (V) were not successful. Either of these could be an unstable intermediate product (perhaps as uncrystallized molecules only) in the reaction, but we have no evidence that this change actually occurs, except that oxanthrone has a recorded m.p. of 167 °C. Mass spectrometer measurements would not resolve either from the p.o.a., which has the same molecular weight. Both oxanthrone and 9,10-dihydroxyanthracene are reported to decompose on melting (the latter at 180 to 187 ° C), to anthraquinone *and anthrone*, with loss of water.

The decomposition product could not be pure anthrone, because the melting point of anthrone is 154 °C. But it could be a mixture or a mixed crystal of anthraquinone and anthrone. Srivastava (1961, 1962, 1964) has shown that one crystalline form of anthrone is very similar indeed in structure to anthraquinone (figure 11 (*c*)). The unit cell has a = 15·80 Å, b = 3·998 Å, c = 7·86 Å, β = 101·7°, D_m = 1·332 g/ml., D_x(corr.) = 1·325 g/ml. for $Z = 2$ in space group $P2_1/a$. The molecules are therefore disordered in such a way as to simulate centrosymmetry.


(IV)


(V)


(VI)

Anthraquinone and anthrone are easily differentiated by their densities, by their m.p.s and by a close examination of their Weissenberg or well-resolved powder photographs. But the density of the decomposition product would always be low, and its 'm.p.' is variable but intermediate; while its Weissenberg photographs (see figure 17 (*a*, *b*); 18 (*a* to *f*), plates 12, 13) are too 'fibrous' for small intensity or spacing differences to be observable. Differentiation on the basis of powder photographs alone was inconclusive.

That the final product is actually a mixed crystal of anthraquinone and anthrone has been proved in two ways.

I. Mixed (anthraquinone: anthrone) crystals have been made and their melting points measured by Mr J. Harris (1965). They form a mixed series in all proportions (figure 13) giving a smooth m.p. curve. The intermediate m.p. found for the decomposition product of p.o.a. is easily explained in this way.

II. Mass spectrometer records have been made (by kind permission of Professor A. Maccoll, and with the assistance of Dr A. Louden and Mr M. Baldwin, on the M.S.9 in this Department) of anthraquinone, anthrone and anthracene as standards, of the photo-oxide of anthracene before and after various treatments, and after control runs with no crystals introduced. It must be borne in mind that the technique itself requires the evaporation of the material at a low pressure and at a temperature which in this case was at least 155 °C, with a certain time lapse. Each spectrogram therefore shows molecular weight peaks corresponding not only to the original substance but also to a series of breakdown products. Fortunately the series corresponding to the three standards are easily differentiated, as table 1 shows. Only the substances giving peaks which are above an arbitrarily chosen height are shown in the table, apart from a few which are regarded as of special interest. Table 2 gives comments on selected peaks and table 3 gives information, where it is available, concerning the crystals of substances identified in quantity in the M.S.9 records. Table 4 shows the comparative results on a 'mixed crystal' series, which throws some light on the reliance that can be placed on the proportions actually observed after the various treatments. Figure 14 gives a summary of the main results in abbreviated form for quick reference.

None of the structures listed in table 3 was found in the diffraction pattern of the decomposition product. If they are present, therefore, it is not in a crystalline form.† On the other hand, the diffraction patterns given by anthraquinone and anthrone or by mixed $A:A$ (figures 4 (*d*, *e*, *f*), plate 3) correspond with the pattern found (figures 18 (*a*, *b*, *c*), plate 13) which is that of a severely mosaic single crystal, with each spot drawn out along the direction of traverse. Both occur, with their respective breakdown products, in the mass spectrograms, anthraquinone as major constituent in most cases.

Apart from the information given by the m.p. determination and the mass spectrograms, however, there is one further indication that anthrone is present in some considerable quantity. All $h1l$, $h2l$ Weissenberg patterns of the decomposition product showed streaks as described on p. 18 (figure 18 (*d*, *e*, *f*) which were also found on some anthrone $h1l$, $h2l$ (figure 19 (*b*), plate 14) though not on all; but which were never found by us on anthraquinone $h1l$ patterns, even after severe heat treatment (figure 19 (*c*)).

All diffraction patterns from the decomposition product showed a heavy background at low scattering angles out to $2\theta = 28°$ ($d \sim 3{\cdot}2$ Å), which implies the presence of large numbers of disorganized molecules, either widely distributed as in a gas-like state, or in amorphous groups. Both types of inclusion appear to occur (figures 1, 3 and 12) because the

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† (1) On photographs of one crystal (figure 19 (*e*), plate 14) some satellite spots, which may have been due to an $A:A$ superstructure, did occur (see p. 18). They were not found in the majority of similar patterns. (2) Dr R. Bramley kindly made electron spin resonance spectrograms of the decomposition product of heating p.o.a. for 13 h at 85 °C. These showed a single absorption peak (width at half height about 10 G) leading to a g value of $2{\cdot}0030 \pm 0{\cdot}0005$, and a rough concentration estimate, at the time of the experiment, of 10^{-4} to 10^{-5} molar. Unfortunately no hyperfine structure was observed; and many organic molecules have g values covered by the error limits.

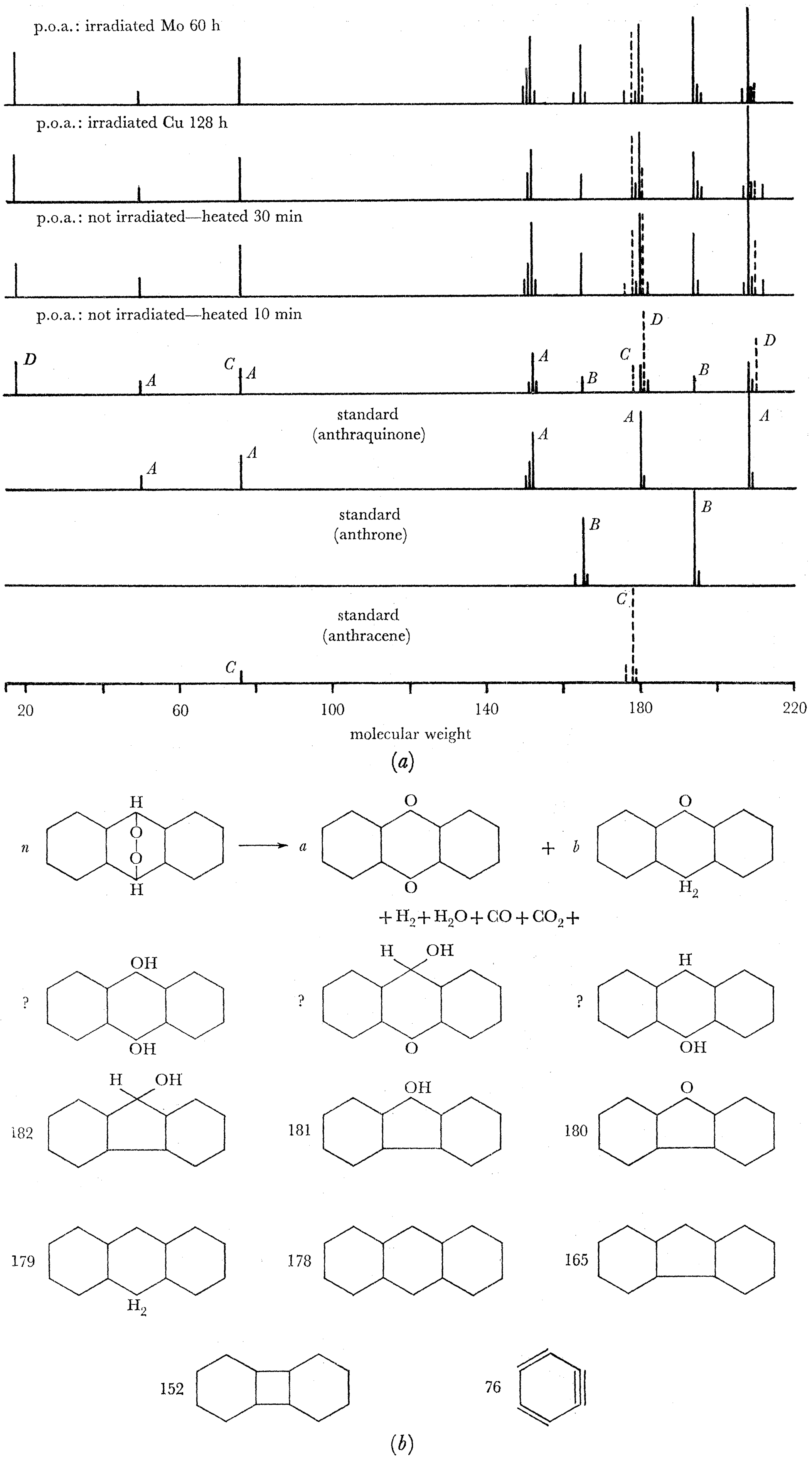

Figure 14. (*a*) Typical mass spectra, showing only the peaks above a minimum height. Peaks marked *D* are unique to p.o.a. (*b*) The results of the mass-spectral analysis.

TABLE 1. RESULTS OF M.S. 9 MASS SPECTRAL ANALYSIS OF THE PHOTO-OXIDE OF ANTHRACENE AFTER VARIOUS TREATMENTS (70 eV, 1 mmHg PRESSURE, 155 °C, EXCEPT WHERE OTHERWISE STATED)

D to *M* were all samples from one batch of p.o.a., *N* to *O* from another batch.

A anthraquinone; after 10 min in the mass spectrometer
B anthrone; (200 °C); after 10 min
C anthracene; (160 °C); after 10 min
D unirradiated p.o.a.; after 10 min
E the same after 30 min
F p.o.a. irradiated Cu*K* 125 h; after 30 min
G p.o.a. irradiated Mo*K* 60 h; (160 °C); after 5 min
H the same after 20 min
J p.o.a. irradiated Cu*K* 55 h; after 10 min
K the same after 30 min
L p.o.a. irradiated Mo*K* 83·7 h; after 10 min
M the same after 30 min
N p.o.a. (another sample) before heating; after 6 min
O Another specimen from the same batch as *N*, after heating for 24 h at 80 °C without any X-irradiation; after 10 min

In *A*, *E* to *M* the peak heights are normalized to that of anthraquinone, mol. wt. 208. Peak heights in *D* are given relative to those in *E*; while those in *N* and *O* are given relative to the main constituent, anthracene. Blank runs on *N* and *O* showed only minor traces of the various components, except for peaks 32 and 28, which may have been due to air in the apparatus (O_2 and N_2 respectively).

mol. wt.	*A*	*B*	*C*	*D* →	*E*	*F*	*G* →	*H*	*J* →	*K*	*L* →	*M*	*N*	*O*
226	—	—	—	4	5	1	1	2	—	—	—	—	15	5
212	—	—	—	2	16	1	1	1	—	—	—	—	—	—
211	—	—	—	9 [8]	13 [8]	3 [3]	4 [3]	4 [3]	—	—	—	—	6 [6]	3 [2]
210	2	—	—	56	58	20	20	18	4	3	3	3	42	16
209	16 [15]	—	—	12 [5]	22 [15]	18 [15]	18 [15]	18 [15]	16 [15]	16 [15]	17 [15]	15 [15]	9 [4]	4 [2]
208	(**100**)	—	—	(32 →	**100**)	(**100**)	(**100** →	**100**)	(**100** →	**100**)	(**100** →	**100**)	25	10
207	14	—	—	4	14	14	14	15	14	14	14	14	4	—
196	—	—	—	2	2	11	10	10	7	8	9	10	—	12
195	—	15 [15]	—	3 [3]	16 [10]	14 [8]	18 [14]	19 [14]	7 [3]	6 [3]	6 [1]	6 [1]	2 [2]	11 [4]
194	1	(**100**)	—	17	64	50	89	90	18	18	5	5	11	29
193	—	10	—	3	8	5	9	9	2	2	—	—	1	—
182	1	—	—	12 [11]	13 [11]	4 [3]	5 [3]	5 [3]	1 [0]	1 [0]	1 [0]	2 [0]	9 [2]	3 [2]
181	12 [12]	—	—	82 [4]	88 [12]	32 [10]	36 [12]	31 [11]	11 [10]	12 [10]	12 [10]	12 [10]	19 [3]	20 [2]
180	82	—	1	28	83	72	82	79	67	71	70	67	21	11
179	5	—	15 [15]	6 [5]	15 [10]	17 [10]	13 [11]	18 [11]	19 [13]	18 [12]	18 [11]	16 [11]	16 [15]	18 [15]
178	9	—	(**100**)	30	68	65	73	69	82	80	75	75	(**100**)	(**100**)
177	—	—	8 [3]	2 [0]	5 [2]	5 [1]	6 [2]	6 [2]	6 [2]	6 [2]	6 [2]	6 [2]	7 [2]	8 [2]
176	—	—	17	4	14	9	12	11	11	11	10	10	14	13
166	—	12 [10]	—	3 [2]	8 [7]	6 [4]	11 [8]	11 [8]	2 [1]	2 [2]	1 [1]	1 [1]	0 [1]	4 [3]
165	—	71	—	16	46	28	59	59	10	11	4	4	10	19
164	—	7	—	2	5	4	7	8	1	1	—	—	—	—
163	—	10	—	3	6	4	10	10	2	2	1	1	—	—
153	8 [8]	—	—	12 [5]	17 [11]	9 [5]	12 [9]	11 [9]	6 [4]	6 [4]	6 [4]	7 [4]	8 [3]	5 [2]
152	60 [3]	—	6	42 [2]	81 [4]	54 [3]	71 [4]	69 [4]	45 [3]	47 [3]	46 [3]	44 [3]	29 [2]	16 [1]
151	27	—	7	17	34	26	37	36	23	25	24	22	14	9
150	12	—	5	7	16	7	18	18	11	12	12	10	7	4

TABLE 1 (*cont.*)

mol. wt.	*A*	*B*	*C*	*D*	→	*E*	*F*	*G*	→	*H*	*J*	→	*K*	*L*	→	*M*	*N*	*O*
139	—	6	—	2		5	3	7		7	—		—	—		—	2	2
126	9	—	—	6		12	9	11		11	6		6	6		6	4	2
118	—	—	—	8		9	1	—		—	—		—	—		—	27†	2
115	—	3	—	3		5	3	2		5	—		—	—		—	2	3
105	—	—	—	3		6	2	5		2	—		—	—		—	8	2
94	—	—	—	—		—	—	—		—	10		18	27		22	—	—
90	5	3	—	4		9	8	6		6	7		7	7		7	6	2
89	1	—	14	8		13	14	13		13	14		14	14		14	19	13
88	—	2	6	2		6	7	4		4	9		8	7		7	9	7
82	—	9	1	2		6	6	7		8	3		2	—		—	—	4
77	6 [2]	—	—	9 [2]		5 [3]	8 [3]	11 [3]		10 [3]	6 [3]		6 [3]	5 [3]		6 [3]	11 [2]	5 [1]
76	36	—	10	25		52	46	47		43	43		45	43		41	29	19
75	13	2	3	10		20	15	16		15	13		14	13		12	9	6
74	10	2	—	7		13	10	7		8	6		8	7		7	5	4
63	9	6	—	13		20	15	15		15	11		12	12		11	12	9
51	5	3	—	10		16	8	9		9	5		6	6		6	10	5
50	15	2	—	12		20	14	13		13	11		12	11		11	8	5
44	5	—	—	4		3	29	4		3	10		11	28		22	6	22
39	3	3	—	7		10	6	7		7	5		6	7		6	5	5
32	—	—	—	—		—	2	—		—	11		7	6		7	(21)†	(23)†
28	6	—	—	5		6	18	11		9	140†		136†	54†		25†	(41)†	(48)†
18	5	2	—	32		33	50	52		39	129		122	91		97	56	44
17	1	—	—	8		8	10	11		8	26		24	19		19	12	11

† Possibly, but not necessarily contamination. Air would give 32 (O_2) and 28 (N_2).

( )† Found on previous blank runs and therefore certainly contamination, already present in the mass spectrometer.

[15] Numbers in square brackets give the isotope abundance of the compound immediately following; thus any peak M, due to a $^{12}C_{14}$ compound, will be accompanied by 15% $M+1$ because of the probability that one carbon out of the fourteen will be ^{13}C.

TABLE 2. FORMULAE CORRESPONDING TO THE PRINCIPAL MOLECULAR WEIGHTS SHOWN IN TABLE 1; WITH COMMENTS

mol. wt.	formula and comments
226	$C_{14}H_{10}O_3$. This occurs in very small quantity and only when a fair amount of the p.o.a. is also present. It is formed from p.o.a. by addition of free oxygen, probably when anthrone or anthracene is also being formed
210	$C_{14}H_{10}O_2$ (I, IV or V)
208	$C_{14}H_8O_2$ (II). This, the main anthraquinone peak, is relatively important in all samples but increases markedly with time in the 'fresh' p.o.a. sample, as the sample decomposes
194	$C_{14}H_{10}O$ (III). This is the main anthrone peak and is noticeably less important (*a*) in the fresh p.o.a. sample; (*b*) in the samples *J, K, L, M* in which very little p.o.a. was left. It could also be anthranol (VI), but this would not explain the diffraction results
181	($C_{14}H_{13}$ or) $C_{13}H_9O$. This is clearly a breakdown product of p.o.a., and not of *A*, *B* or *C*. The second of the two formulae given is the more likely, and it corresponds with the loss of CHO(29) from the p.o.a. molecule
180	($C_{14}H_{12}$ or) $C_{13}H_8O$, 9-fluorenone, is an important breakdown product of anthraquinone, by loss of CO; and it appears in quantity in those spectra where the parent anthraquinone is also plentiful
178	$C_{14}H_{10}$, anthracene, increases with time as the fresh p.o.a. sample *D* is heated and is evidently an important breakdown product of the p.o.a. It is the main decomposition product in the samples *N* and *O*; the reason for this is not known
166	$C_{13}H_{10}$ } These characteristic breakdown products of anthrone, from which they are derived by loss of CO or CHO, occur in amounts proportional to those of the parent anthrone found in the spectrogram
165	$C_{13}H_9$
152	$C_{12}H_8$. Biphenylene is derived from anthraquinone by the loss of 2(CO); or from p.o.a. by the loss of 2(CHO); or from anthracene by loss of C_2H_2 (26); but it is not a breakdown product of anthrone. It occurs in considerable quantities in the spectrograms *D* to *M*
76	C_6H_4. Benzyne is an interesting breakdown product of anthraquinone and (to a lesser extent) of anthracene, but not of anthrone. It occurs in all spectrograms, except *B*
44	CO_2 or C_2H_4O } The amounts of these are extremely variable in the spectrograms *D* to *O*, but H_2O always occurs in considerable quantity
28	CO, N_2 or C_2H_4
18	H_2O
17	OH

TABLE 3. CRYSTALLOGRAPHIC INFORMATION CONCERNING FLUORENONE, ANTHRACENE, FLUORENE AND BIPHENYLENE

Fluorenone $C_{13}H_8O$ (Iball 1936)
Pbca; $Z = 16$; $D = 1{\cdot}276$ g/ml.; molecule bent
$a = 16{\cdot}0$ Å, $b = 12{\cdot}5$ Å, $c = 18{\cdot}63$ Å

Anthracene $C_{14}H_{10}$ (Robertson 1933; Mason 1964)
$P2_1/a$; $Z = 2$; $D = 1{\cdot}26$ g/ml.; molecule planar
$a = 8{\cdot}56$ Å, $b = 6{\cdot}04$ Å, $c = 11{\cdot}16$ Å, $\beta = 124{\cdot}7°$

Fluorene $C_{13}H_{10}$ (Iball 1936; Brown & Bortner 1954)
Pnam; $Z = 4$; $D = 1{\cdot}202$ g/ml.; molecule planar
$a = 8{\cdot}57$ Å, $b = 5{\cdot}70$ Å, $c = 18{\cdot}87$ Å

Biphenylene $C_{12}H_8$ (Waser & Lu 1944)
$P2_1/a$; $Z = 6$; $D = 1{\cdot}25$ g/ml.; molecule planar
$a = 19{\cdot}6$ Å, $b = 10{\cdot}5$ Å, $c = 5{\cdot}84$ Å, $\beta = 91° 20$

distribution found has a continuous background but with annular regions of high intensity, some of which may correspond, especially on rotation or Laue patterns which still show some p.o.a. spots, to p.o.a. powder lines (figures 12 (*a*, *b*, *c*)). We may visualize the crystal, therefore, at an advanced stage of decomposition, as composed of crystallites of mixed anthraquinone and anthrone molecules, with orientations generally distributed in a nearly

Table 4. Comparison of mass spectra data for (I) anthraquinone, (II) 70 % anthraquinone, 30 % anthrone; (III) 30 % anthraquinone, 70 % anthrone; (IV) anthrone

II and III were formed from the melt. All these four specimens were tested using the probe, whereas *A* to *M* of table 1 were volatilized in a hot box. The results show that in such mixed crystals as II and III, the anthrone and anthraquinone are readily distinguishable, but that the anthraquinone breakdown appears to be more complete than that of the anthrone, so that the 208 peak is much lower than expected, relative to 194.

mol. wt.	I	II	III	IV
210	2	—	—	—
209	17	5	3	—
208	(100)	35	16	—
207	14	4	2	—
195	—	3	12	16
194	—	(30)	(70)	(100)
193	—	2	6	8
181	11	6	1	—
180	82	43	13	—
179	3	1	—	—
178	2	—	—	—
169	10	—	—	—
166	—	4	5	13
165	—	27	34	80
164	—	3	3	8
163	—	6	3	12
153	6	6	—	—
152	50	42	9	—
151	21	19	4	—
150	11	9	—	—
139	—	4	3	8
126	7	7	—	—
125	2	2	—	—
90	7	—	—	—
89	—	—	—	3
87	3	—	—	3
86	2	—	—	2
83	—	—	2	3
82	—	—	6	7
77	9	4	1	—
76	35	27	7	1
75	12	15	3	2
74	9	13	2	3
63	10	9	3	7
62	—	4	1	3
51	7	7	2	3
50	15	22	3	3
39	5	6	2	4
32	(9)?	—	—	—
28	(45)?	—	—	—

Gaussian way about the original p.o.a. orientation, but cemented together by disorganized molecules and by very small and quite disorientated crystallites of the original, intermediate (if any) and final products. To judge from the behaviour, previously described, of crystals observed on the hot stage of a microscope, they may also contain some trapped gaseous products of decomposition which break up the crystal in order to escape, when it is heated rapidly, but which can escape gradually or remain entrapped if it is irradiated without additional heating.

5. ANALYSIS OF THE GEOMETRY OF THE CHANGES SHOWN ON WEISSENBERG PHOTOGRAPHS

5·1. *hkl Weissenberg patterns;* $k = 0, 1$

The original p.o.a. crystals gave excellent *h*0*l*, *h*1*l*, *h*2*l*, Weissenberg (hereafter W.) photographs (figure 15 (*a*), plate 11) on which no hint of disorder was observable. Subsequent *h*0*l* W. photographs showed no streaking (apart from the usual white radiation streaks) but new (*A*:*A*) spots appeared which were easily differentiated from the original p.o.a. spots because they were always somewhat elongated along the direction of traverse. At the same time or even earlier the p.o.a. spots became less sharp (figure 15 (*b*)), although they never (before disappearing altogether) became quite so drawn-out as the new reflexions (figures 17 (*a*, *b*), plate 12), which remained of approximately the same lengths from the time they appeared until they had replaced the p.o.a. altogether (figures 18 (*a*, *b*, *c*), plate 13). The new crystal was never really 'single', and this made it extremely difficult to unravel its exact orientation relative to the original p.o.a. Apart from its severely mosaic character, which made precise measurement of angles impossible, it was always twinned on two non-equivalent twin planes, although the individuals could be of different relative sizes in different specimens (figures 18 (*a* to *f*)), and usually only three of the four possible individuals were detected.

One set of *A*:*A* reflexions (which will at first be called 00*l*′, irrespective of whether they are in fact *h*00 or 00*l*) appeared at 2°, within the obtuse β, from the original p.o.a. 00*l* reflexions. The *A*:*A* pattern was twinned about the {00*l*′} reflexions (figures 18 (*a* to *c*)). In principle it should be possible to decide fairly easily whether 00*l*′ is *A*:*A* *h*00 or 00*l*.

(1) With a good anthraquinone crystal, the main distinguishing feature is that 003, although weak, is present; whereas 600, with approximately the same spacing, is almost unobservable. The $|F|_{\text{obs.}}$ are:

$$200:400:600:800 = 9{\cdot}5:8{\cdot}3:0{\cdot}35:3{\cdot}0$$

$$001:002:003:004 = 7{\cdot}7:7{\cdot}3:2{\cdot}6:5{\cdot}3$$

But this distinction is not possible on the *h*0*l* W. photograph of the decomposition product, because 600 and 003 are then not, in general, observable at all; and because another possible twinning on ($\bar{2}$01) would in any case even up their intensities. In anthrone 600 and 003 are more nearly equal in intensity, even on an untwinned crystal.

(2) If rotation photographs are taken about the original p.o.a. [100] and [001], the new layer-line distances should distinguish between $a = 15{\cdot}8$ Å and $c = 7{\cdot}9$ Å of *A*:*A*. The original application of this test appeared to show that 00*l*′ was *A*:*A* *h*00, since the

intermediate 1st, 3rd, 5th layer-lines apparently tended to disappear from a p.o.a. [100] rotation photograph (implying that the p.o.a. *a* axis 15·9 Å had changed to *A*:*A* $c = 7\cdot9$ Å); while the p.o.a. [001] rotation photograph clearly developed layer-lines corresponding with a 15·8 Å identity distance.

However, a strongly exposed p.o.a. [100] rotation photograph showed weak 1st, 3rd, etc., layer-lines which did *not* disappear even after 485 h Cu*K* irradiation, being just as strong then as after 130 h irradiation. And it was realized that twinning about $(\bar{2}01)$ would be bound to enhance the even layer-lines of a true 15·8 Å identity distance. (See figure 5 (*e*).)

Similarly, the 15·8 Å identity distance observed on the p.o.a. *c* rotation photograph after conversion could be due to the twinning on $(\bar{2}01)$.

In fact, it was not possible either from the *h*0*l* W. photograph, or from rotation photographs, to determine with certainty the identity of $(00l')$, which we shall call twin plane I, and it was not until a much later stage of the investigation that it became clear that twin plane I must be *A*:*A* (001), and not (100) as had at first been deduced.

The evidence comes from a comparison of *h*1*l* W. photographs of untwinned anthraquinone, untwinned and unequally-twinned anthrone and such doubly-twinned *A*:*A* crystals as show unequal twinning on both twin planes. The untwinned anthrone (figure 19 (*a*), plate 14) and anthraquinone (figure 19 (*c*)) allow an unequivocal identification of *h*10 and 01*l* (*h*10 are closely spaced) and show a 111 reflexion about as intense as 011. The unequally-twinned anthrone (figure 19 (*b*)) shows 011 and 111 very clearly, but also shows fine streaks through 110 and $\underline{110}$ (twin reflexion in $01\frac{1}{2}$ position) and through 310, $\underline{111}$, 111 and $\underline{310}$ (the latter in the $01\frac{3}{2}$ position).† The twinning here is across $(\bar{2}01)$ which we shall call twin plane II. Figures 18 (*d*, *e*, *f*), 19 (*e*), which are all *h*1*l* W. photographs of partly or wholly converted *A*:*A*, show the same twinning across $(\bar{2}01)$ giving an apparent doubling of the *c* axis and the same, though coarser, streaks. The $(\bar{2}01)$ twinning is unequal in each case and it is still possible to identify the 011 and 111 of the major twin. In all three cases, however, there is also twinning across (001). In figure 18 (*d*) this twin is very weak, in figures 18 (*e*, *f*) the two individuals are nearly equal. Figures 18 (*a*, *b*, *c*) show the corresponding *h*0*l* photographs. Figures 18 (*a*, *b*) are of fully converted products, but figure 18 (*c*) shows the intermediate stage, with p.o.a. (001) very close to the twin plane which is now known to be *A*:*A* (001). It must be remembered that *h*1*l* p.o.a. and *h*1*l* *A*:*A* W. photographs have to be taken at different equi-inclination angles because *b* has changed in length; and the intermediate stage is therefore best observed on the zero level.

The larger twin, giving more intense spots, is always found to be orientated relative to the original p.o.a. so that its *h*00 reflexions lie at about 4°, in obtuse β, from *h*00 of p.o.a. (figures 17, 18 (*c*) and 20). The changes of angle observed are consistent with the change from p.o.a. ($\beta = 108\cdot2°$) to a mean somewhere between anthraquinone ($\beta = 102\cdot5°$) and anthrone ($\beta = 101\cdot7°$).

No particular variation of the relative size of twins or the importance of twin planes I and II with treatment (irradiation by Cu*K* or Mo*K*; heating) could be observed. As an example, figure 17 (*b*) shows *h*0*l* for a crystal given a total of about 84 h irradiation by

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† Underlining indicates a twin reflexion.

Mo*K* (40 kV, 20 mA; within lead cover over window) followed by a $5\frac{1}{2}$ h Weissenberg exposure to Cu$K\alpha\beta$ (30 kV, 15 mA). The following reflexions are all easily visible simultaneously:

Photo-oxide of anthracene

200	$\bar{8}01$	$\overline{10}02$	$\bar{8}03$	$\bar{8}04$	$\bar{8}05$	$\bar{2}07$ and some
400	$\bar{4}01$	$\bar{8}02$	$\bar{6}03$	$\bar{6}04$	$\bar{2}05$	weaker higher-index
600	$\bar{2}01$	$\bar{6}02$	$\bar{2}03$	$\bar{4}04$	005	reflexions. No
	001	$\bar{4}02$	003	004	205	twinning
	201	$\bar{2}02$	203	404	405	
	401	002				
		202				

(P.o.a. crystals do occasionally twin on (001). One batch was invariably twinned. But apparently single crystals were chosen for these experiments):

Anthraquinone–anthrone

200	(001)	$\bar{6}01$	($\bar{2}03$)	$\bar{4}02$	($\bar{4}02$)	$\bar{6}03$	($\bar{6}03$)	$\bar{2}04$	($\bar{8}01$)
400	(002)	$\bar{4}01$	($\bar{2}02$)	$\bar{2}02$	($\bar{4}01$)	$\bar{2}03$	($\bar{6}01$)	004	(800)
800	(004)	$\bar{2}01$	($\bar{2}01$)	002	(400)	203	(601)		
		001	(200)	202	(401)				
		201	(201)	and some weaker high-index reflexions. The					
		401	(202)	indices in parentheses are those of the twin					
		601	(203)	across ($\bar{2}01$)					
		801	(204)						

There is also seen in figure 17 (*b*) a twin across (001) which has less than one-eighth of the intensity of the main individuals.

It is of some interest that the p.o.a. [101], [001] practically coincide in direction with the [$10\bar{2}$], [104] respectively of the *twin A:A across* ($\underline{001}$) (figure 20), and that there are simple numerical relations between identity distances along corresponding directions. There seems to be no geometrical reason for the existence of this form of anthraquinone or anthrone twinning (which has not been found in either substance alone or in the 50:50 mixed crystal) *apart from its geometrical relation with the original p.o.a.* The possibility of ($\bar{2}01$) twinning (which does often occur in pure anthraquinone and anthrone) is obvious from the pseudo-symmetry (figure 26 (*a*)).

The $h1l$ streaks, which are perpendicular to the twin plane II (figure 21) can be geometrically explained only on the basis of some special form of limited disorder, involving short-range order such as platelets parallel to ($\bar{2}01$) which have internal order, but with disorder of successive platelets. They appear to be diagnostic of anthrone and are not characteristic of anthraquinone. They are receiving further study. Figure 19 (*e*), which was referred to in the footnote on p. 10, shows unequal twinning on both twin planes I and II, but also shows some sharp, small and as yet not fully explained reflexions in positions which would correspond with indices ($\frac{1}{2}\,1\,\frac{1}{4}$, $\frac{3}{2}\,1\,\frac{3}{4}$, $\frac{5}{2}\,1\,\frac{1}{4}$ and $\frac{3}{2}\,1\,\frac{1}{4}$). These spots, which obey the same twin laws as the main structure, appear to be due to a 'superstructure' of unit-

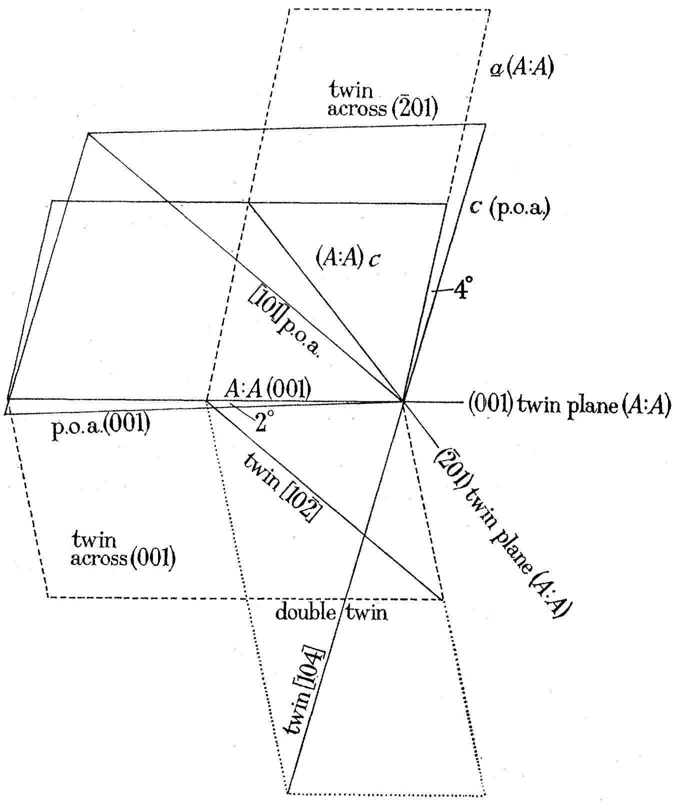


FIGURE 20. Diagram showing some of the geometrical relationships of the unit cells of the original p.o.a., the main $A:A$ and its twins. The detailed structural relationships of these twins has been considered in a separate publication elsewhere (Lonsdale 1966).

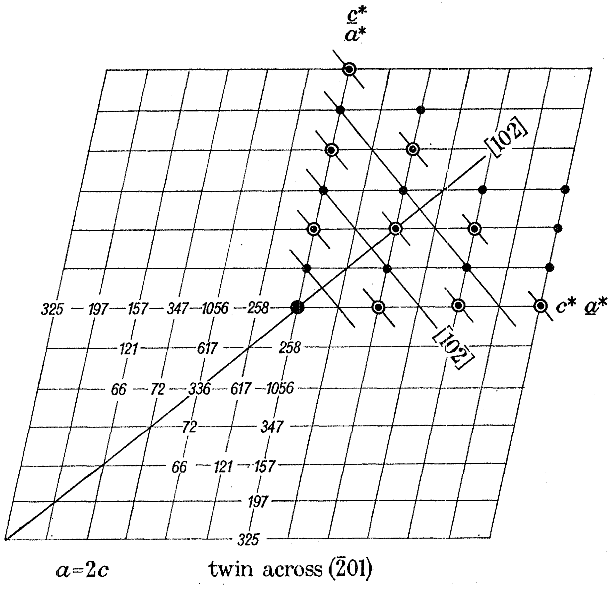


FIGURE 21. Reciprocal net, hll, showing observed streaking and the relative intensities of the hll reflexions in acute β^*. The single reflexions are shown as black dots. Reflexions of the main individual and its twin across $(\bar{2}01)$ which coincide are shown ringed. Streaks correspond with extension along the direction $[10\bar{2}]$. (Compare figure 28.)

cell dimensions $2a$, b, $4c$ (approx. $31{\cdot}6\times 4{\cdot}0\times 31{\cdot}6$ Å) as compared with $A{:}A$. But their number is too few to be able to determine the space group, especially as the 'superstructure' is also apparently twinned, and there was no evidence from the mixed m.p. curve observed by Harris (1965) that any such superstructure exists. It may only occur under very special conditions of crystallization, as well as requiring a definite numerical ratio of anthraquinone to anthrone molecules. It was not possible, with one crystal only, to carry out a mass spectrometer analysis.

5·2. *hkl Weissenberg patterns;* $h = 0, 1, 2$; $l = 0, 1, 2$

These can be discussed together, since the $(\bar{2}01)$ twinning tends to make them similar. In the discussion of the early experiments (p. 5) it was mentioned that *hk*0 Weissenberg photographs showed sharp continuous p.o.a. constant *k* festoons. These are seen (figure 22 (*a*), plate 15), out to $k = 5$ and they also occur on *hk*1 (figure 22 (*b*)), *hk*2, 0*kl*, 1*kl*, 2*kl*. The gradual disappearance of the p.o.a. constant *k*—index festoons and of the *hk*0 and *hk*1 p.o.a. reflexions is accompanied by the appearance of *hk*0, *hk*1 $A{:}A$ reflexions and constant *k* festoons, not quite so well defined, however (figures 22 (*c*, *d*)), which do not disappear (figure 23 (*a*), plate 16) even after a very long irradiation. The final trace of p.o.a. {110} reflexion has also not disappeared after 485 h irradiation. There is clearly a considerable amount of low-angle diffuse scattering due to disorganized molecules. The general similarity of the *hk*0 conversion product and of *hk*0 anthraquinone can be seen by comparing figures 23 (*a*) and (*b*).

The 0*kl* Weissenberg photographs, as would be expected from this mesomorphic phase, show p.o.a. constant *k* festoons just as sharp as those on *hk*0 photographs. These disappear in a similar way, as the 0*kl* $A{:}A$ reflexions and festoons appear. If there is no twinning, the *hk*0 and 0*kl* anthraquinone patterns are easily distinguishable, because $a = 2c$. Specimens equally twinned across $(\bar{2}01)$ would give indistinguishable patterns; but the converted specimens are usually unequally twinned, and the 0*kl* pattern can be distinguished by the relative weakness of the twin *hk*0 reflexions where *h* is odd.

The extension of the reflexions along the direction of traverse of the camera, that is, the mosaic angle of the crystals, appears to be similar for all three *h*0*l*, *hk*0, 0*kl* Weissenberg patterns. The product of decomposition, therefore, is not so much fibrous, as distributed in *all* directions about the original orientation with a mosaic angle of up to 15° or over.

6. Discussion of the decomposition mechanism

The original p.o.a. structure is shown in projection in figures 25 (*a*, *b*, *c*). The intermolecular distances are as shown in table 5.

6·1. *Formation of isolated chains of molecules*

The X-ray evidence proves that as a result of X-irradiation or of heating, the crystal of photo-oxide first breaks down to give some isolated chains of molecules parallel to [010] (which retain their exact periodicity along the chain); and then breaks up into somewhat disordered crystallites, so that an oscillation pattern is obtained from a stationary crystal. Table 5, with figures 25 (*a*, *b*, *c*), indicate why this should happen. The importance of CH ··· O 'hydrogen bonding' has been pointed out by Sutor (1962, 1963) and by

TABLE 5. INTERMOLECULAR DISTANCES FOR WHICH $C—C < 3{\cdot}75$ Å; $C—O < 3{\cdot}75$ Å; $O—O < 3{\cdot}40$ Å; $O—H < 2{\cdot}85$ Å; $H—H < 2{\cdot}80$ Å

(Data provided by Dr C. J. Brown. Hydrogen positions are assumed, taking C—H = 1·08 Å.)

atom of molecule at *xyz*	to atom	of molecule at	distance (Å)
O1	O1	$1-x,\ 1-y,\ \bar{z}$	3·18
O1	C9		3·35
O1	H9		2·68
C6	C4	$1-x,\ 1-y,\ 1-z$	3·74
C6	C14		3·66
O1	C3	$\frac{1}{2}+x,\ \frac{1}{2}-y,\ z$	3·70
O1	H3		2·79
O2	C3		3·75
O2	H3		2·82
H5	H5	$1-x,\ \bar{y},\ 1-z$	2·33
H5	H10		2·46
H2	H8	$-\frac{1}{2}+x,\ \frac{3}{2}-y,\ z$	2·49
H3	H8		2·68
C2	O1	$\frac{1}{2}-x,\ \frac{1}{2}+y,\ \bar{z}$	3·43
H2	O1		2·46
C2	O2		3·44
H2	O2		2·79
H7	H6	$\frac{3}{2}-x,\ \frac{1}{2}+y,\ 1-z$	2·67
along [010] direction:			
O2	C8	$x,\ -1+y,\ z$	3·51
O2	H8		2·73
O2	C9		3·41
O2	H9		2·49
C4	C1		3·74
C10	C8		3·62
H10	H8		2·76

Ferguson & Tyrrell (1965). Lonsdale & Smith (1941) observed diffuse thermal streaking on Laue photographs of benzil which indicated that the CH ··· O contacts along the [100] [010] and [110] directions (Brown & Sadanaga 1965) were less easily stretched than the van der Waals contacts in other directions. Now along the [010] direction in anthracene photo-oxide crystals there is one CH ··· O contact of length 3·41 Å with an H ··· O distance of 2·45 Å (assuming C—H = 1·08 Å) which means that the bond is very little bent; and a rather more bent CH ··· O contact of length 3·51 Å with H ··· O 2·73 Å; whereas the shortest H ··· H distance is 2·76 Å. Between molecules in *neighbouring* [010] chains there are short contacts:

CH ··· O	3·35 Å, H ··· O	2·68 Å, much bent	
	3.43	2·46 Å, little bent	
	3·44	2·79 Å, much bent	
O ··· O	3·18 Å		
H ··· H	2·33, 2·46, 2·49 Å		

The first three of these will tend to hold the structure together against any repulsion due to the last four (together with the general attractions and repulsions of longer van der Waals forces). But if X-irradiation should tend to ionize the O or H atoms, or if thermal

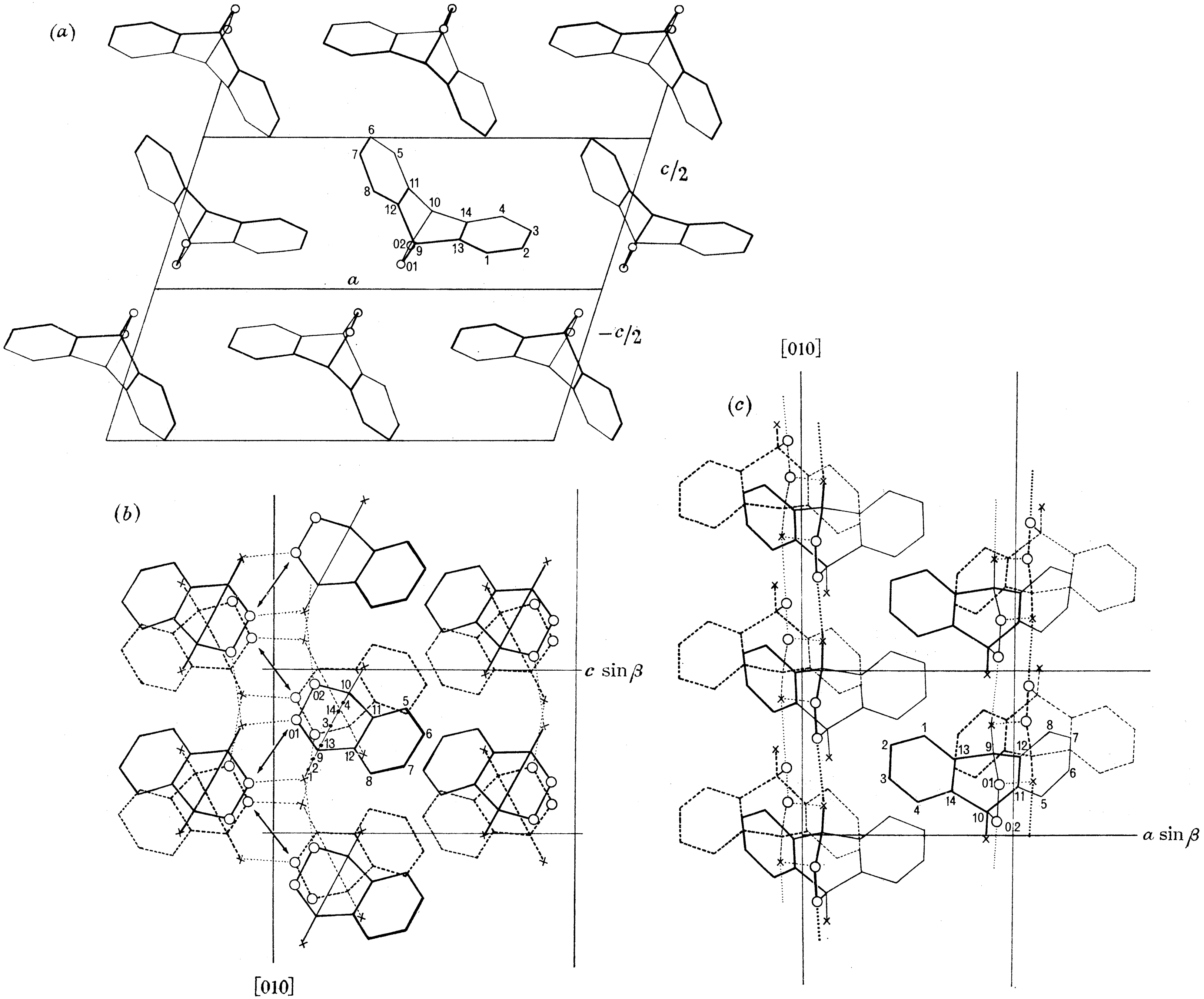


FIGURE 25. (*a*) Structure of p.o.a.: [010] projection. The standard molecule *xyz* is numbered to correspond to table 4.
(*b*) [100] projection.
(*c*) [001] projection.

vibration should tend to shorten the O ··· O, H ··· H distances, or if both these occur simultaneously, then the effect of the resulting repulsion may be sufficient to break down the forces holding neighbouring [010] chains together. And if this happens simultaneously for all contacts around any particular [010] chain, that chain will lose its phase relation with its neighbours, while retaining its own periodicity, which is not similarly affected by thermal vibration or X-irradiation, since there are no short contacts between *like* atoms *along* [010].

Once a number of [010] chains around any particular crystallite have broken away, it becomes easier for moderate disorientation of the whole crystallite to occur; and this is what seems to happen.

6·2. *Chemical reactions in isolated chains*

When, however, isolated [010] chains exist of molecules which are effectively held together *only* by CH ··· O contacts, then thermal vibration (especially if accompanied by some ionization) will result in one or more of the following effects.

(*a*) In the absence of restraining side contacts and in the presence of attraction by CH of neighbouring molecules, the CO—OC bridges of single molecules (which as figure 6 (*a*) shows, are in a state of considerable thermal vibration and will be much more so at higher temperatures or if ionized) will break. The violence of this effect will tend to throw off H 9, H 10, and these hydrogen atoms will either be caught up by neighbouring molecules in the same or other chains, or will eventually find their way out of the crystal or will help to form smaller molecules, such as H_2O, which become trapped in the structure. The mass spectrometer records (table 1) show that some of these effects must happen there and *may* have also happened in the solid-state reaction previously, for samples *F–M*.

(*b*) The attraction of O 2, especially if enhanced by ionization, may tend to detach H 9 from a neighbouring molecule; which having lost one hydrogen atom will the more easily suffer rupture of its CO—OC bridge, flinging off the other hydrogen (H 10) in the process. If the breakdown shown in columns *D*, *E* of table 1 is similar to that which occurs in the crystal, then this kind of process, involving $C_{14}H_9O_2$ as an intermediate product, could explain the relatively high proportion of 209 in *D* and *E* as compared with that in the record *A* of the standard anthraquinone (table 1). Either process, (*a*) or (*b*), must literally involve a 'chain reaction', the breakdown running along the isolated chains.

6·3. *Recrystallization of the decomposition product*

In either case (and it may be that heating or X-irradiation respectively would favour one process rather than the other) the molecules in one chain would now be anthraquinone, or possibly oxanthrone or 9,10-dihydroxyanthracene. The molecules of anthraquinone would have straightened out and come closer together (figures 26 and 27) and it must be expected that the oxygens would have a large out-of-plane vibration relative to the anthracene nucleus. This, however, is exactly what does occur in ordinary anthraquinone (El Sayed 1965; Lonsdale, Walley & El Sayed 1966) and it will not therefore hinder the contraction of the chains of molecules along [010] (thus explaining the appearance of new festoons and the absolute identity of [010] directions in the initial and final product) and simultaneous recrystallization in directions normal to [010] (figure 28) which involves really large movements of many chains of molecules. It is not to be expected, however, that

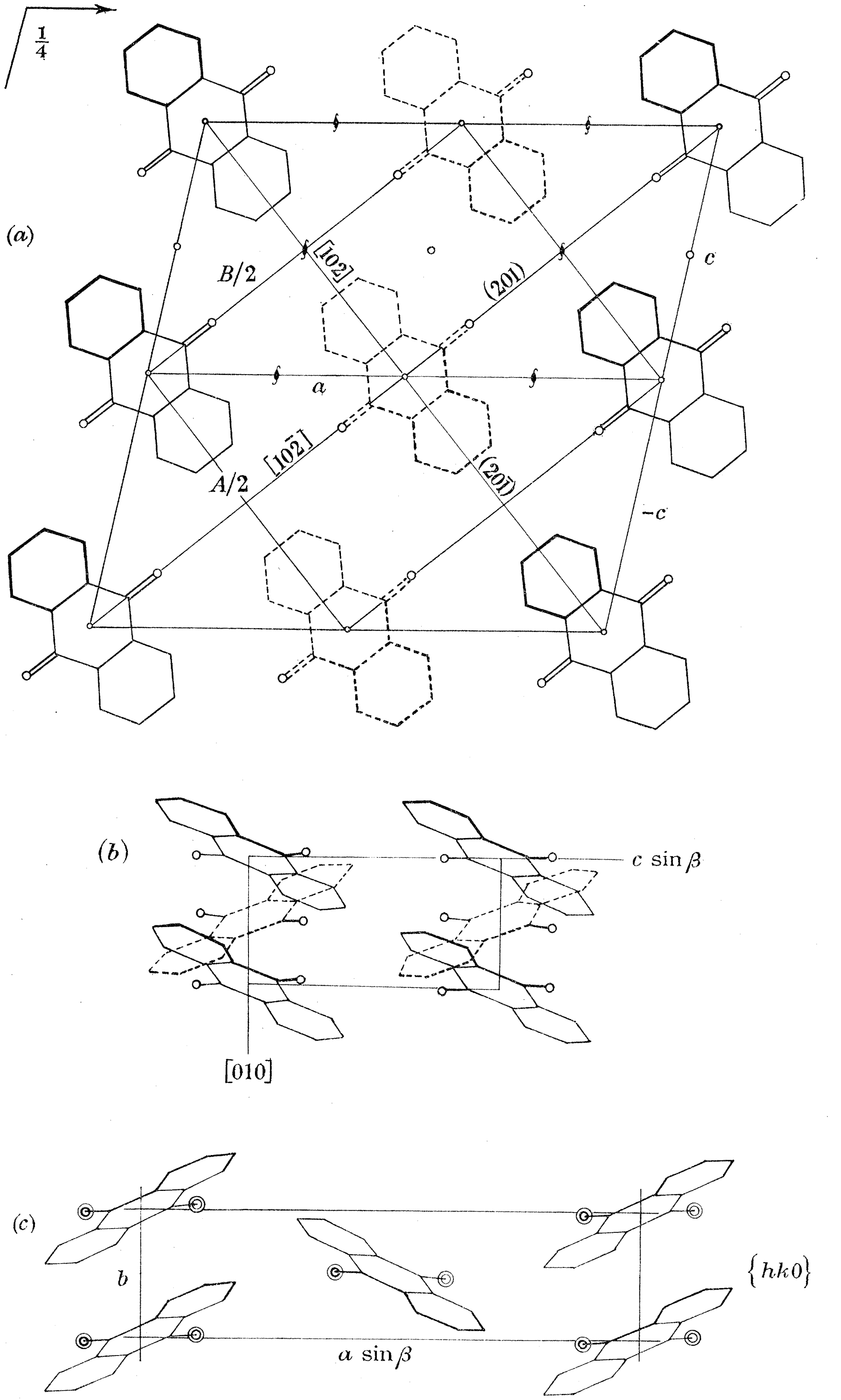


FIGURE 26. (*a*) Anthraquinone: [010] projection. The tilt of the molecular normal is 27·2° to [010] in $(\bar{2}01)$ and 2° to [010] in (201). The oxygen atoms lie in (201), which is why the 201 reflexion varies most from anthraquinone to anthrone. (Compare figure 13, plate 11.)

(*b*) [100] projection.

(*c*) [001] projection.

the new orientation will be precise; and a distribution of up to 15° or more about the original [010] direction is in fact found.

The repeat distances of the molecules along [010] are quite different for p.o.a. (5·8 Å) and for anthraquinone (4 Å) (figures 25, 26 and 27); and this transformation will certainly involve the breaking up of [010] chains into short lengths in the same general direction, which explains the deterioration of sharpness of the layer-line streaks and festoons of the final relative to those of the initial product.

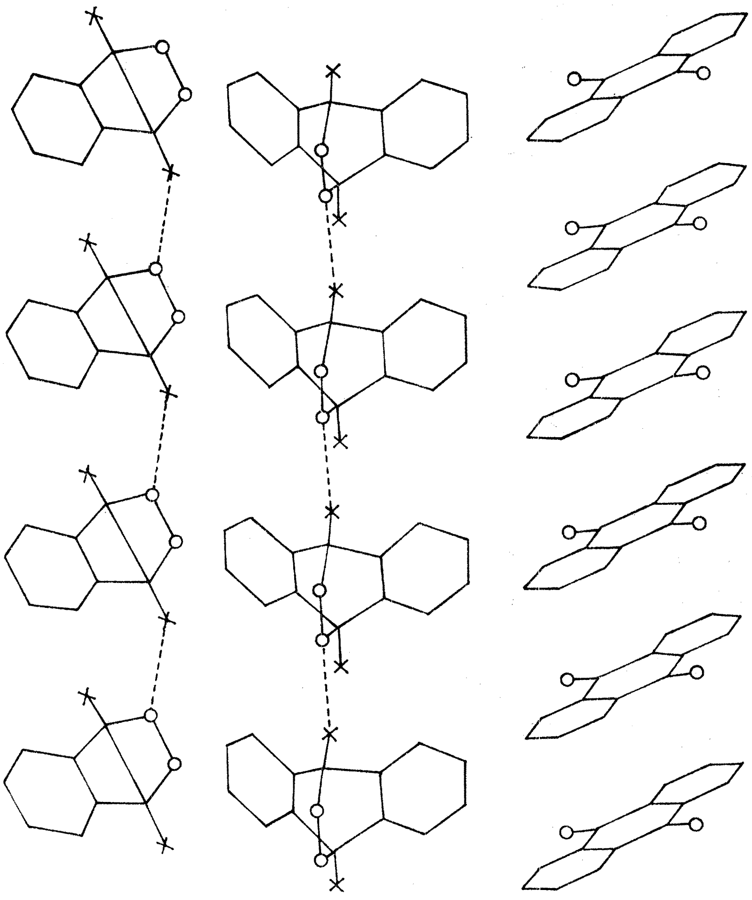


FIGURE 27. Strings of molecules along [010], showing the appearance of the anthraquinone molecules as seen along [100] or [001] by comparison with the photo-oxide of anthracene strings. In the case of anthrone there may be some ordering of the asymmetrical molecules along this direction (Srivastava 1961).

There is a general resemblance between the structures of p.o.a. and anthraquinone in the [100] direction. The *a* lengths are almost equal and both crystallize in space group $P2_1/a$, although the centrosymmetrical anthraquinone molecules lie on centres of symmetry and the photo-oxide molecules are displaced from the centres. Nevertheless, the similarity is sufficient for recrystallization to proceed with a near coincidence of the [100] axes (figure 20).

In the [001] directions, however, there is an almost complete change of axial length (11·4 to 7·9 Å), although the directions themselves are not far apart, and with a slight adjustment of [100] they can come even nearer. Geometrically, therefore, the main decomposition crystals are those for which the [001] correspond in direction as closely as possible to that of the original crystal. But twinning is easy, first on ($\bar{2}01$) because of the $a = 2c$ relationship for anthraquinone and the strongly pseudo-orthorhombic character of its structure, and secondly on (001) because of the special relations between directions and identity distances in the photo-oxide unit cell and in the twinned anthraquinone unit cell which were mentioned on p. 18. It is possible that the 2° shift of the a axis is indeed partly conditioned by these secondary twin relationships.

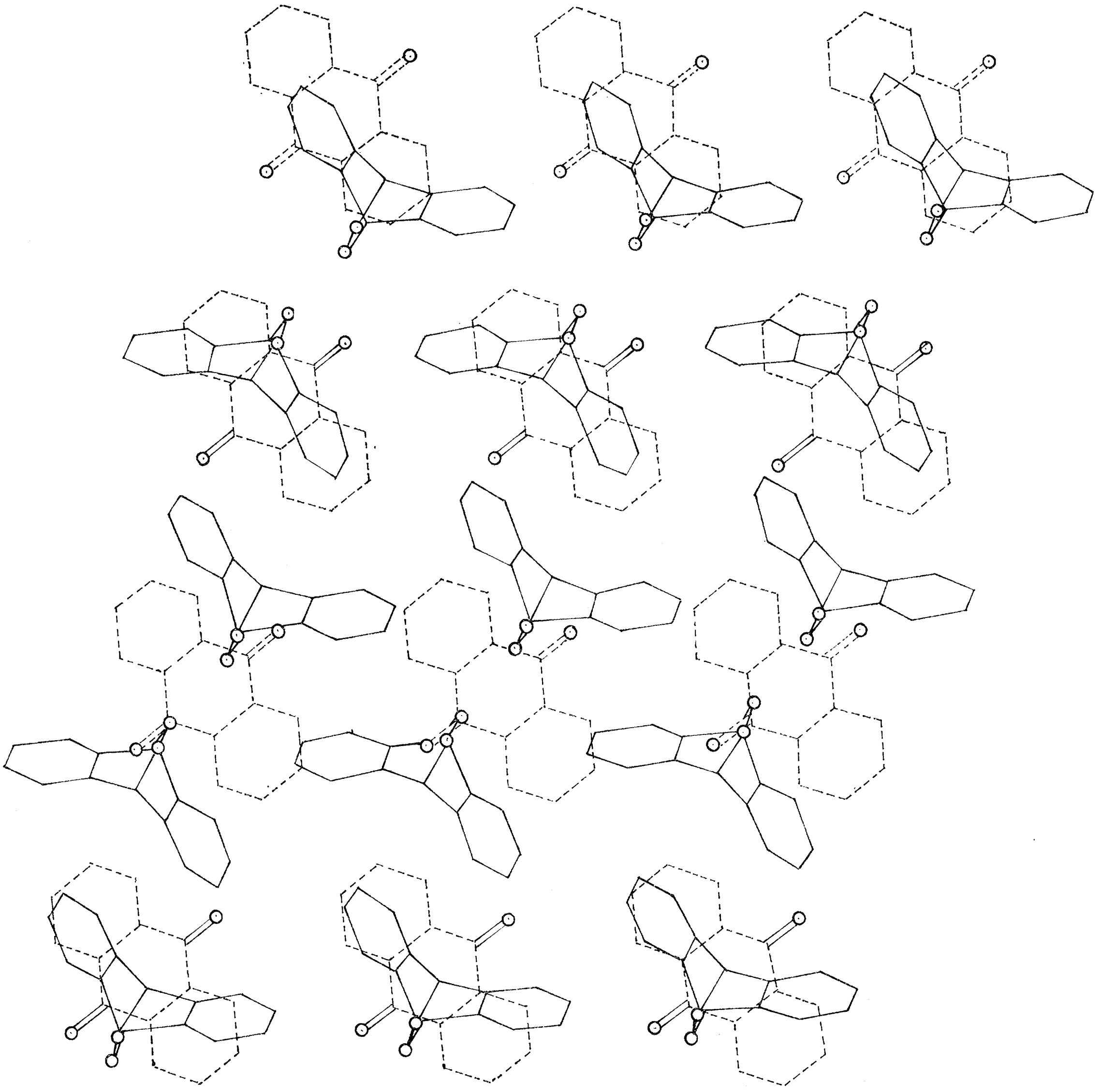


FIGURE 28. A possible superposition of the [010] projections of p.o.a. and of anthraquinone. The reaction clearly requires big movements of some strings of molecules (the strings being normal to this projection).

One may say, therefore, that this reaction takes place in a single crystal to 'single crystal' form: (i) because chains of the photo-oxide molecules change individually into chains of anthraquinone molecules at a fairly slow rate; and (ii) because there are sufficient resemblances between the two unit cells for the one to change into the other (or into one of its twins) given sufficient time for the non-crystalline products of the decomposition to be removed or segregated and sufficient chains of anthraquinone molecules formed in the same neighbourhood. It will be seen from figure 29 that the twins formed can be isolated from one another in the first place, and probably are, although they may grow together as the reaction proceeds.

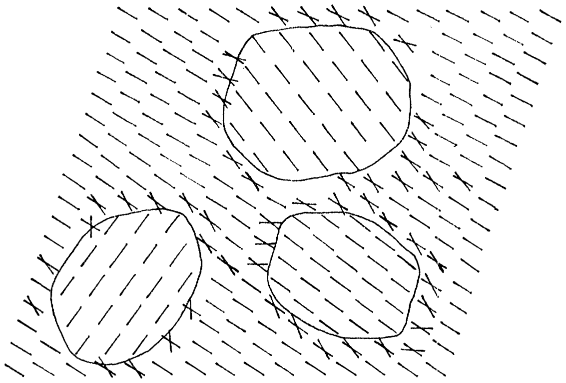
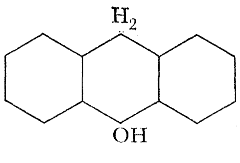


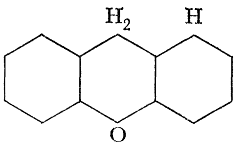
FIGURE 29. Diagrammatic representation of the formation of isolated [010] chains, disorientated or displaced relative to the main p.o.a. matrix; and the consequent isolation of p.o.a. crystallites which are then free to rotate slightly out of position. Isolated A:A crystallites are also shown, the smaller of the two being a twin across (001) of the larger. In the perpendicular [010] direction the A:A molecules are much more closely spaced than are those of p.o.a. and each crystallite of A:A as it is formed introduces some 5 % free space.

The mass spectrometer records, the m.p., and the disorder streaks seen on *hll* W. photographs prove, however, that anthraquinone is not the only crystallizable decomposition product. The formation of an anthrone molecule involves the loss of one oxygen atom by the photo-oxide molecule and the transfer of one hydrogen atom. It seems certain that in this case also, several processes may occur simultaneously in isolated chains. It is relevant here to consider the proportions of molecules 195, 193 in the mass spectrometer records relative to that of anthrone 194 (table 1).

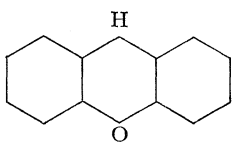
Peak 195, which has to be corrected for the ^{13}C isotope abundance in anthrone, could correspond to VII or to various forms of VIII. Any of these could be an unstable intermediate product in the solid-state reaction product, as could also IV, V or VI. In general, the proportion of 195 (corrected) relative to 194 is higher in the 'photo-oxide' M.S. records than in the standard anthrone record. This is not true of 193 (IX).



(VII)



(VIII)



(IX)

The similarity of crystal structure of anthraquinone and anthrone ensures that if both are formed together, they will easily form mixed crystals; and if IV or V were an intermediate stage it would ensure the complete mixing of the A:A product, with the formation of the considerable amount of H_2O which is indeed found from the M.S. record. We do not yet know whether single strings along [010] are invariably either anthraquinone or anthrone or whether the two kinds of molecule can occur in the same [010] string. The diffuse $k = \frac{1}{2}$ streaks found for anthrone by Srivastava (1961) do not occur here. There is not, therefore, the short range order along [010] strings that occurs in anthrone, but there is some kind of ordering in $(\bar{2}01)$ platelets required to explain the streaking in $h1l$ W. photographs.

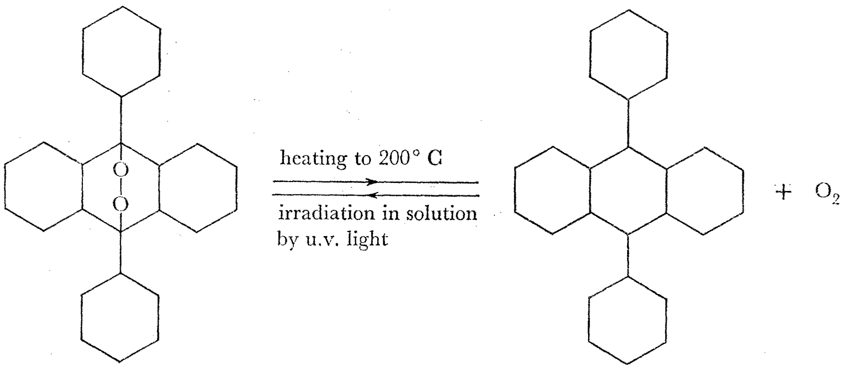
None of the other breakdown products found on the M.S. records appear to occur in a crystallized form in the final product, but they may well be present as single molecules or amorphous groups. The questions now to be considered are: where are they, and what happens to the gaseous products of decomposition?

6·4. *Spatial requirements of p.o.a. and of A:A*

A comparison of unit-cell dimensions shows that the total space occupied per molecule has been reduced from 254 Å^3 per p.o.a. molecule to 242·5 Å^3 for each anthraquinone or anthrone molecule; so that *A*:*A* crystallites 'imprisoned in' or replacing the p.o.a. matrix will leave some 5% 'free space', since the whole crystal has not changed its shape at all (figure 16). Or if the actual measured density of 1·356 g/ml. is taken as a basis of calculation, the original 'average volume' occupied by each p.o.a. molecule is even greater: 259·5 Å^3. This would leave 17 Å^3 unoccupied space per molecule: 6·5% 'free space' after conversion has taken place. Since this space will generally consist of bubbles or cracks, there will be ample room for some included disorganized material, or for the escape, when the conversion takes place sufficiently slowly, of H_2, H_2O, CO molecules and of any other gaseous products of decomposition.

7. BEHAVIOUR OF RELATED COMPOUNDS

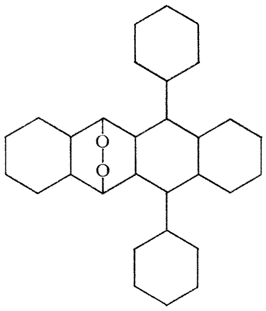
Dufraisse & Gérard (1935) reported that when the p.o.a. decomposed violently on heating, it did so without giving up any oxygen. They contrasted this behaviour with that of the photo-oxide of 9,10-mesodiphenylanthracene (X), which if heated to 200 °C gave up all its oxygen and regenerated the hydrocarbon (XI) from which it had been formed



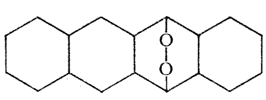
(X) (XI)

(Dufraisse & le Bras 1937). Dufraisse & Loury (1935) had reported previously that the photo-oxide of diphenylnaphthacene (XII) did not give up its oxygen on heating

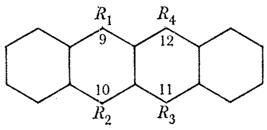
Dufraisse & Horclois (1936) stated that the photo-oxide of naphthacene (XIII) decomposed with explosive violence at 120 °C, without melting, leaving a reddish resin. They condensed the products of the explosion of 0·2350 g of the original substance by means of liquid air. Instead of the 20·3 ml. of O_2 that would have been collected if the decomposition had been similar to that of X, they obtained only 1·55 ml. of gas (21 °C, 965 mm pressure) which they believed to consist of CO and H_2. The resinous products of decomposition had no sharp melting point.



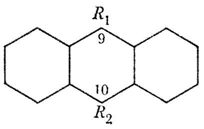
(XII)



(XIII)



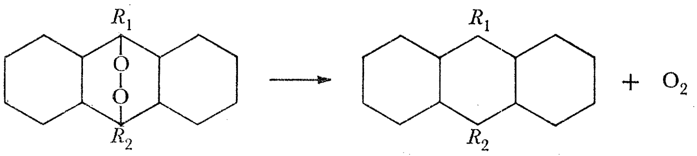
(XIV)



(XV)

Both XII and XIII may well undergo a reaction similar to that described in this paper. Our attempts to study them have so far been frustrated by the difficulty of growing good small single crystals.

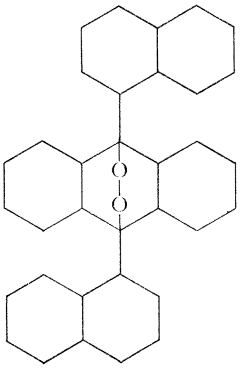
In a review paper Dufraisse (1939) stated that the thermal dissociation of 9,10-photo-oxides of hydrocarbons of the types XIV and XV is strongly influenced by the nature of the substituents R_1 and R_2. If R_1 and R_2 are both hydrogen, no O_2 is lost on heating, but for R_1, R_2 = CH_3, C_6H_5, $C_{10}H_7$ the release of O_2 could be 80 % or more of the calculated total. Where $R_1 = H$ and $R_2 = C_6H_5$ some O_2 is given off, but at a temperature rather higher than is the case when neither constituent is H.



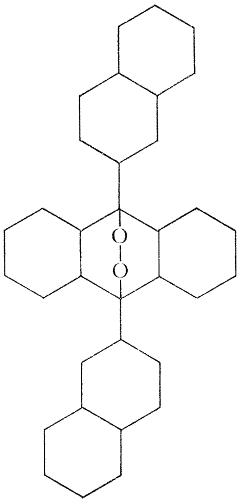
The two photo-oxides of diα- and diβ-naphthyl 9,10-anthracene (XVI, XVII) were studied quantitatively by Dufraisse *et al.* by collecting the products of decomposition. For the β-compound, 0·1015 g of the photo-oxide were decomposed giving 0·0943 g of the pure hydrocarbon (m.p. 380 °C, identical with that of the original hydrocarbon from which the photo-oxide was made) and 0·0070 g of O_2, which is 94 % of that theoretically recoverable.

The pattern of these decomposition processes seems now to be reasonably clear. If the substituents R_1 R_2 attached to C9, C10 are both hydrogen atoms, the result of heating (and probably of X-irradiation also, in all such cases) is to break the oxygen bridge and to cause the loss or transfer of some or all of the hydrogen atoms, the oxygen either being retained in ketonic or possibly in enolic form, or combining with H_2 to give water, or perhaps being lost in combination as CO, CHO, etc. Sometimes it does occur as free O_2

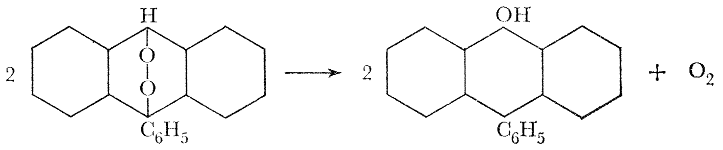
and may be seen on the M.S. record at 32. If R_1, R_2 are large groups they remain attached, and when the oxygen bridge breaks, as it does on more drastic heating, it is oxygen that is lost; there are no other free atoms with which it can combine. If one of the substituents is hydrogen and the other a large monovalent hydrocarbon group, then some but not all of the oxygen is lost, though only at an even higher temperature. It would seem possible that in such a case the reaction would be (say),



(XVI)



(XVII)



but this is not, as yet, tested.

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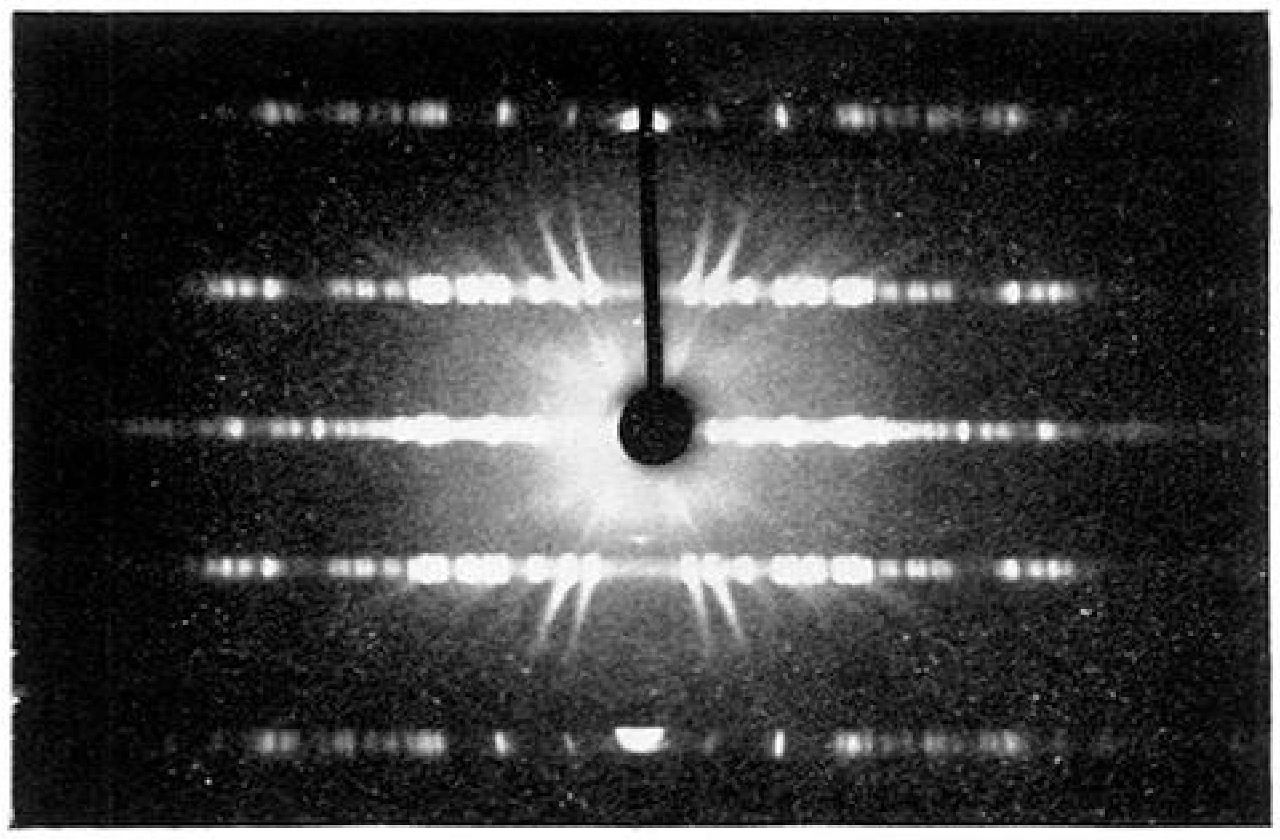

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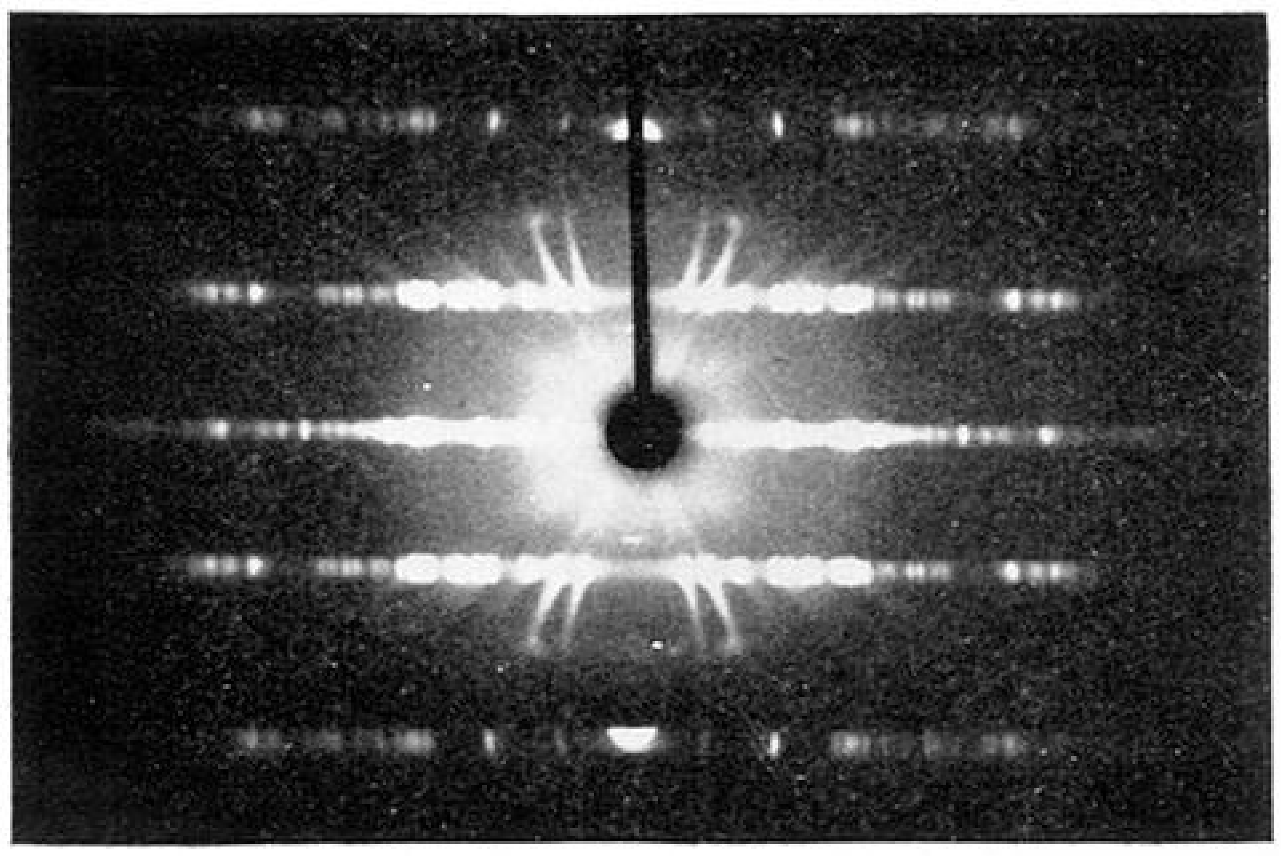

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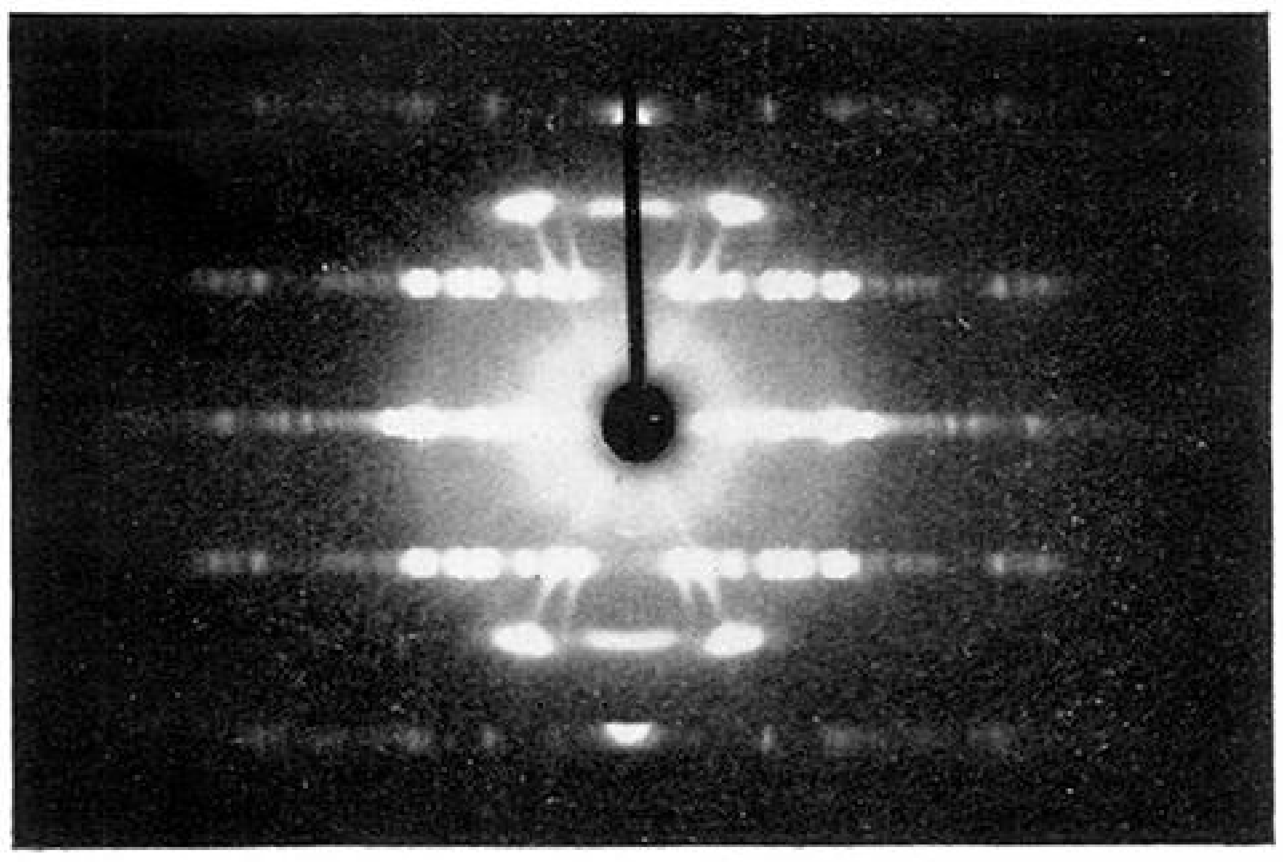

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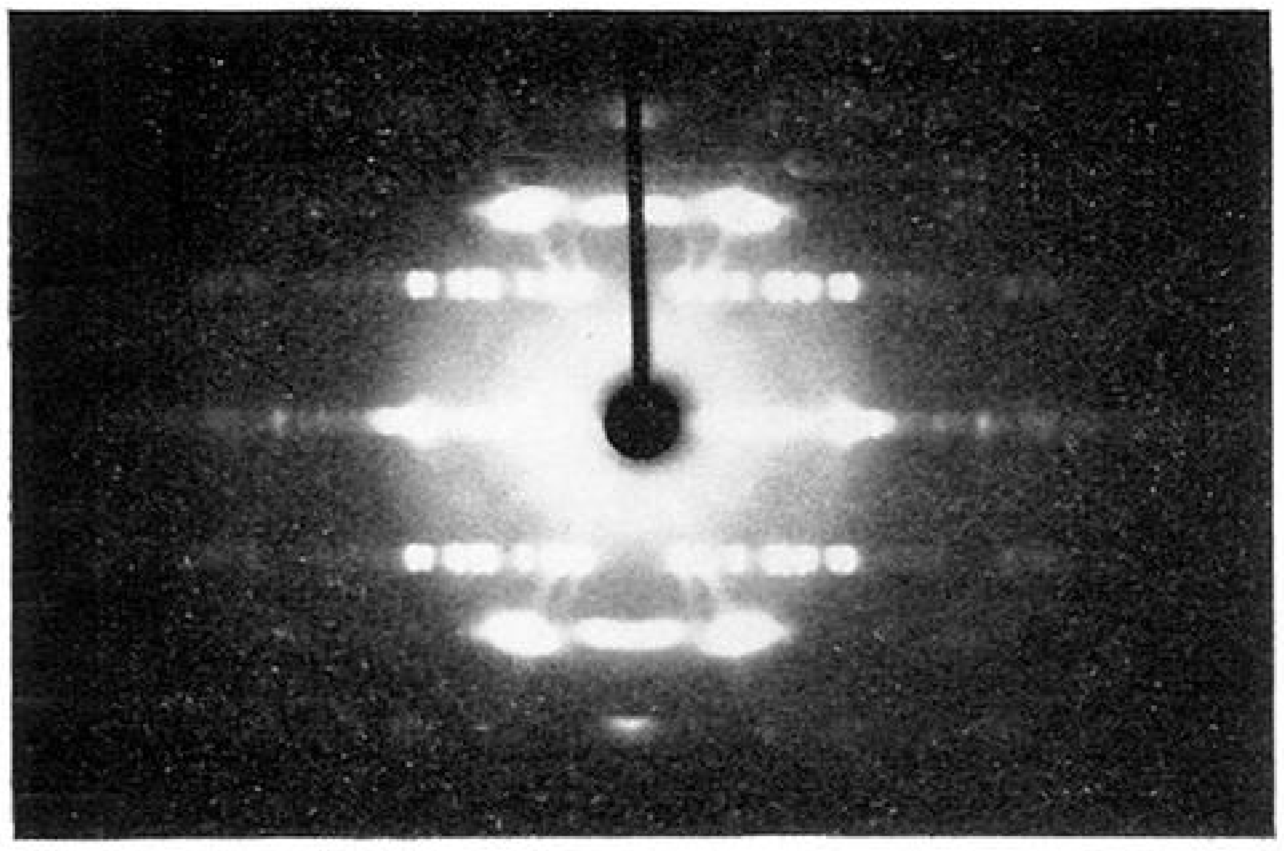

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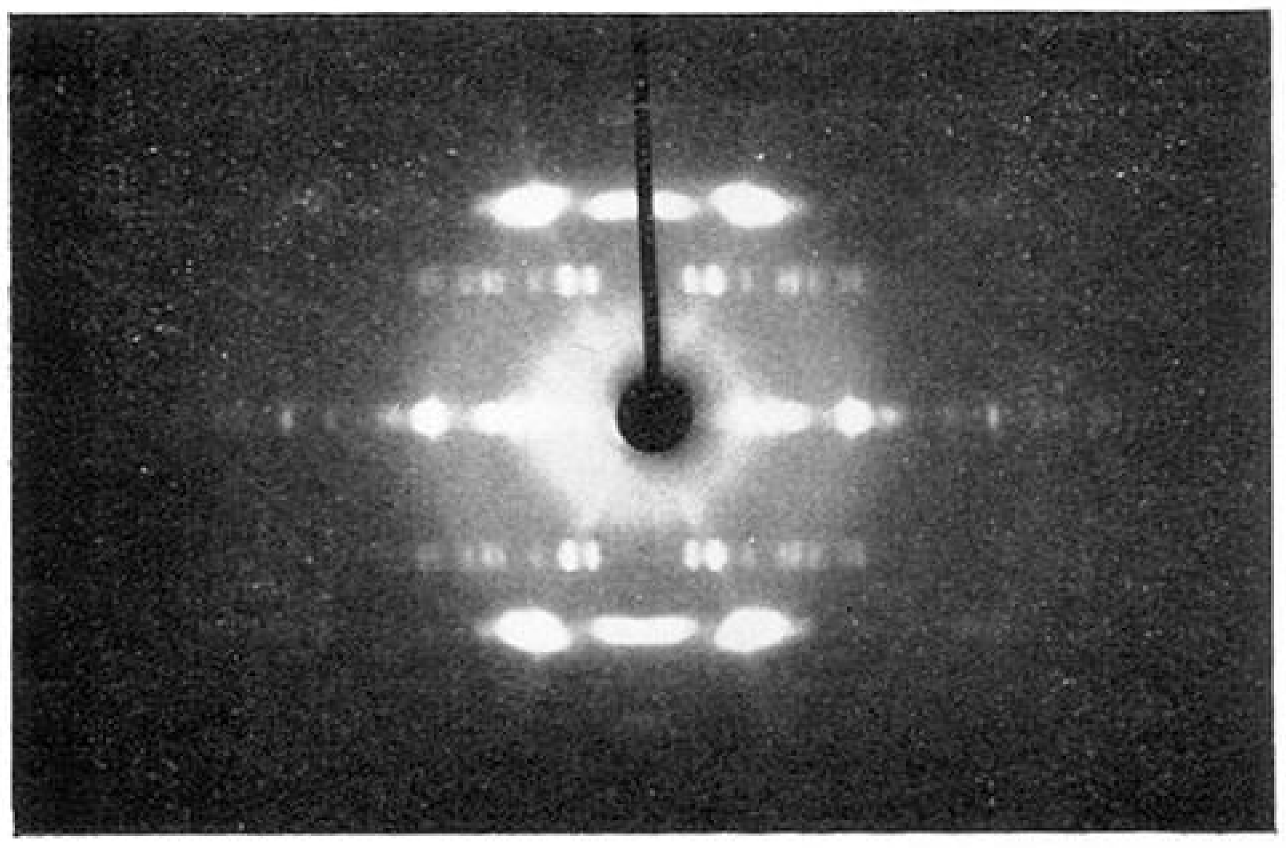

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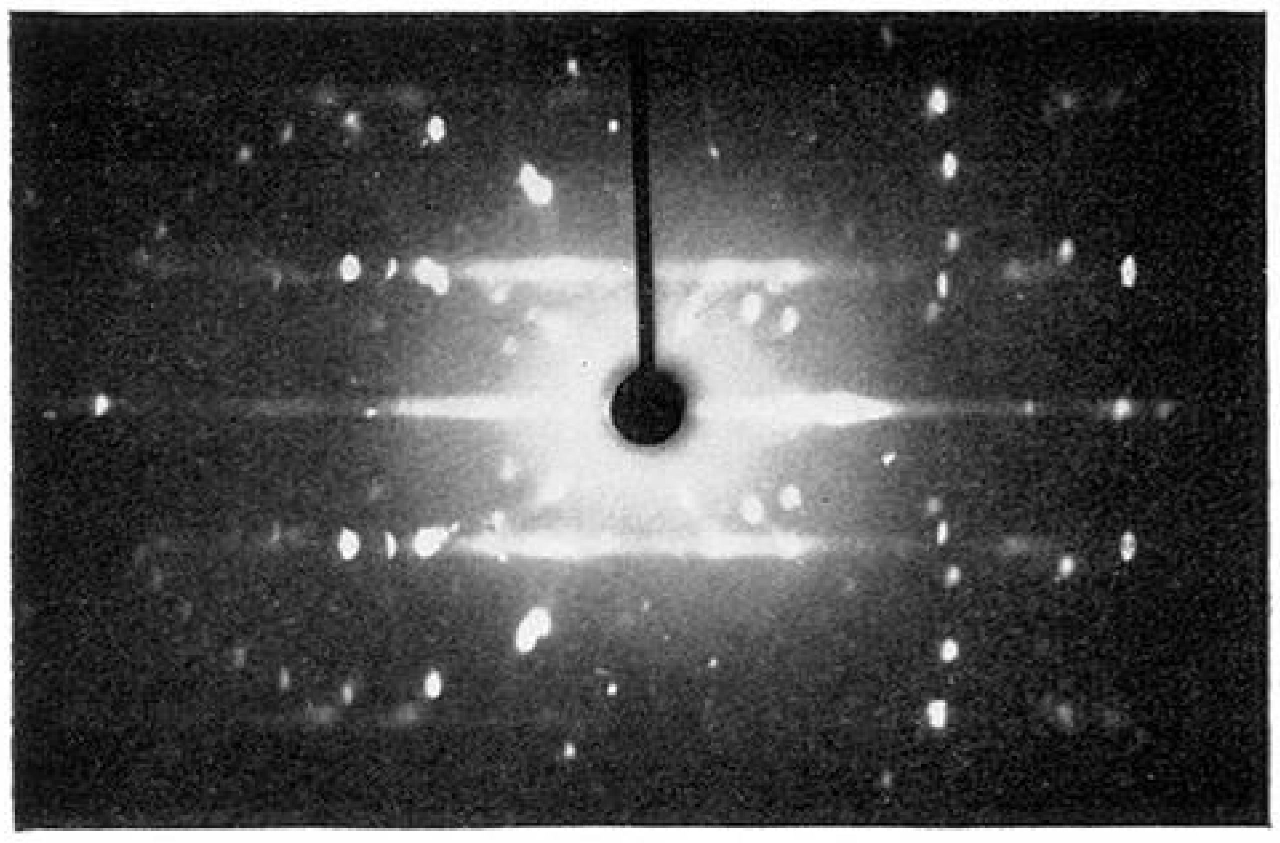

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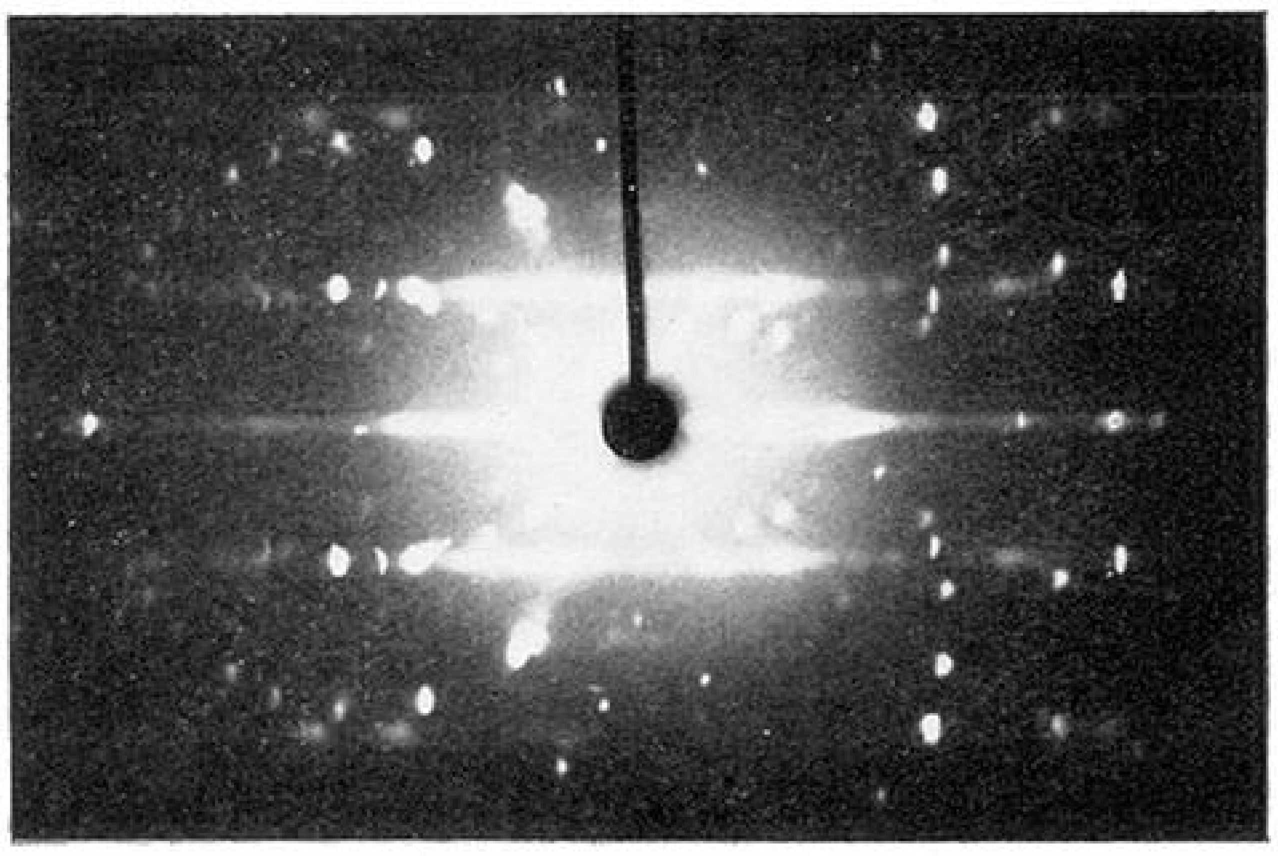

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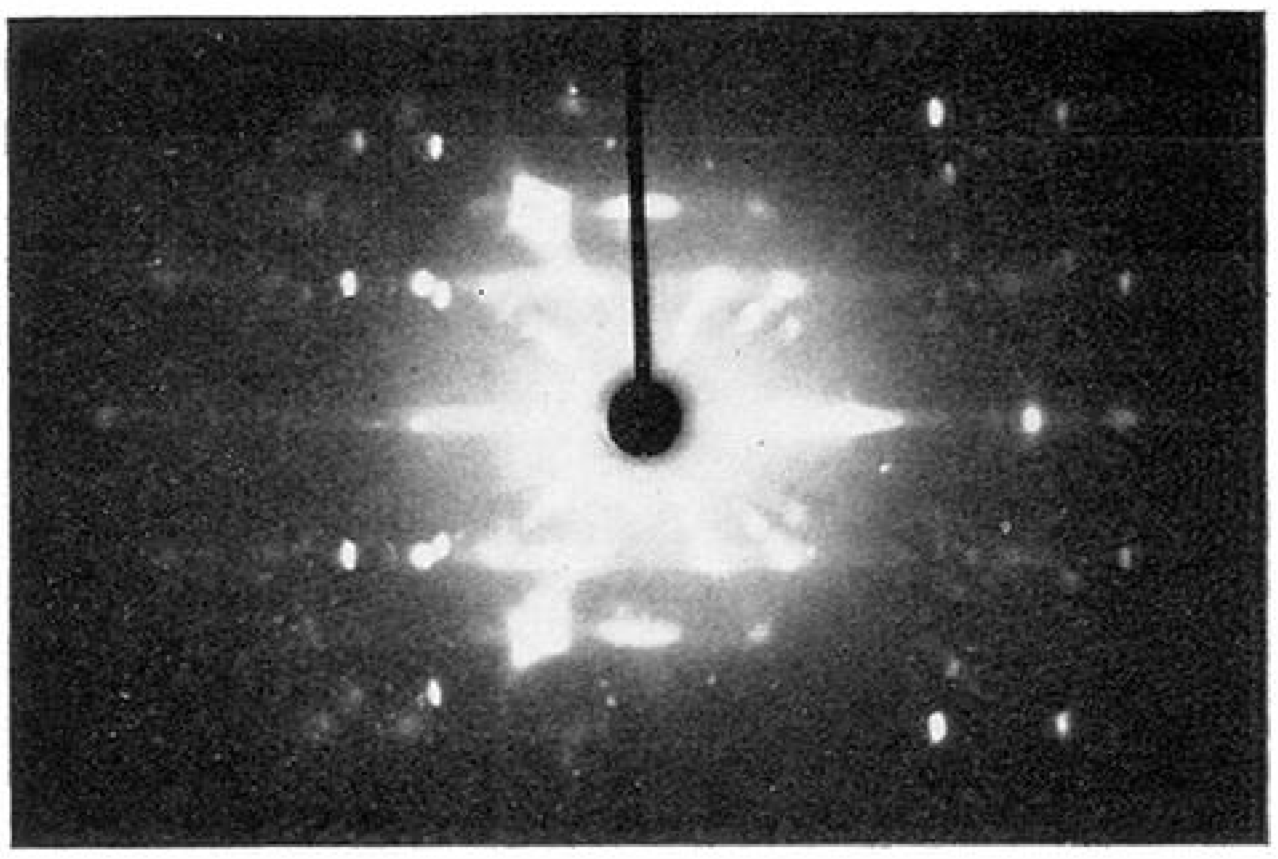

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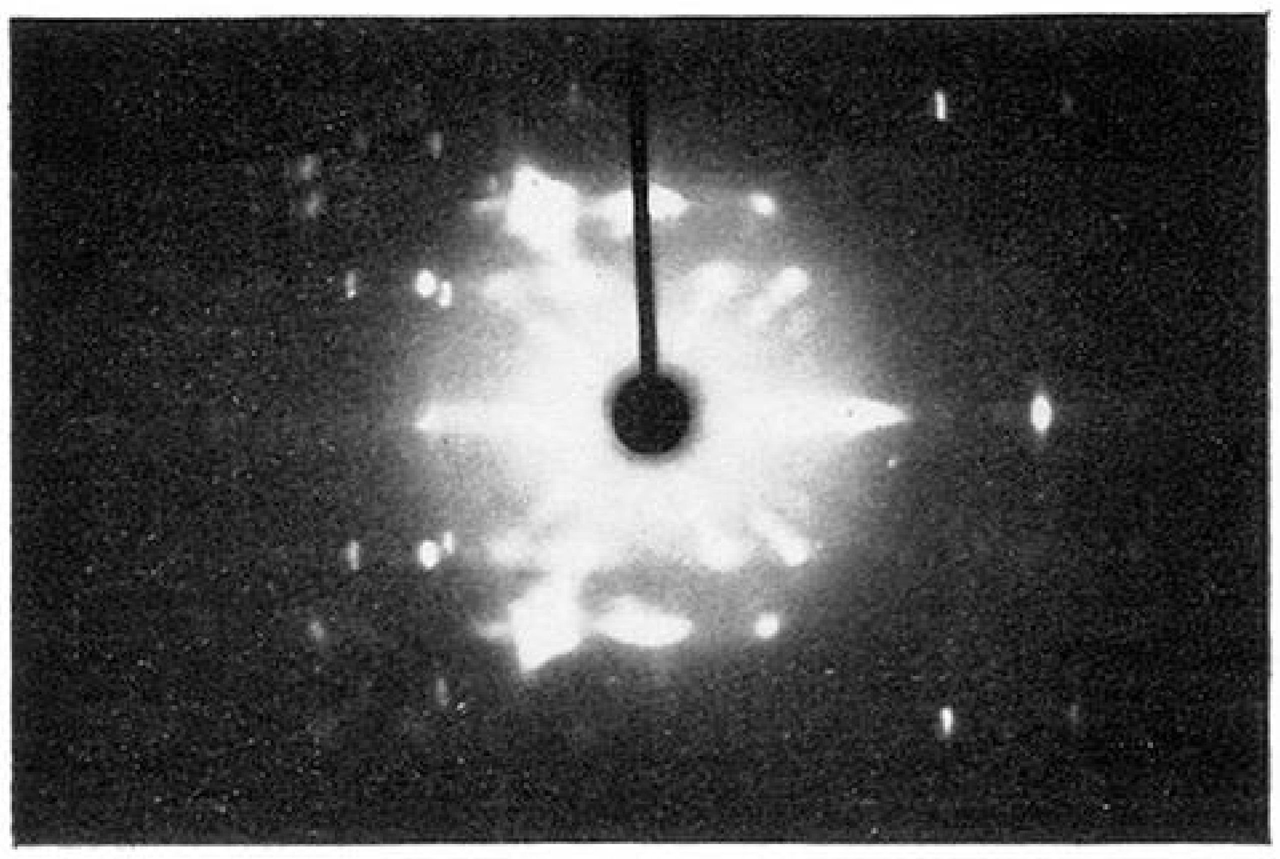

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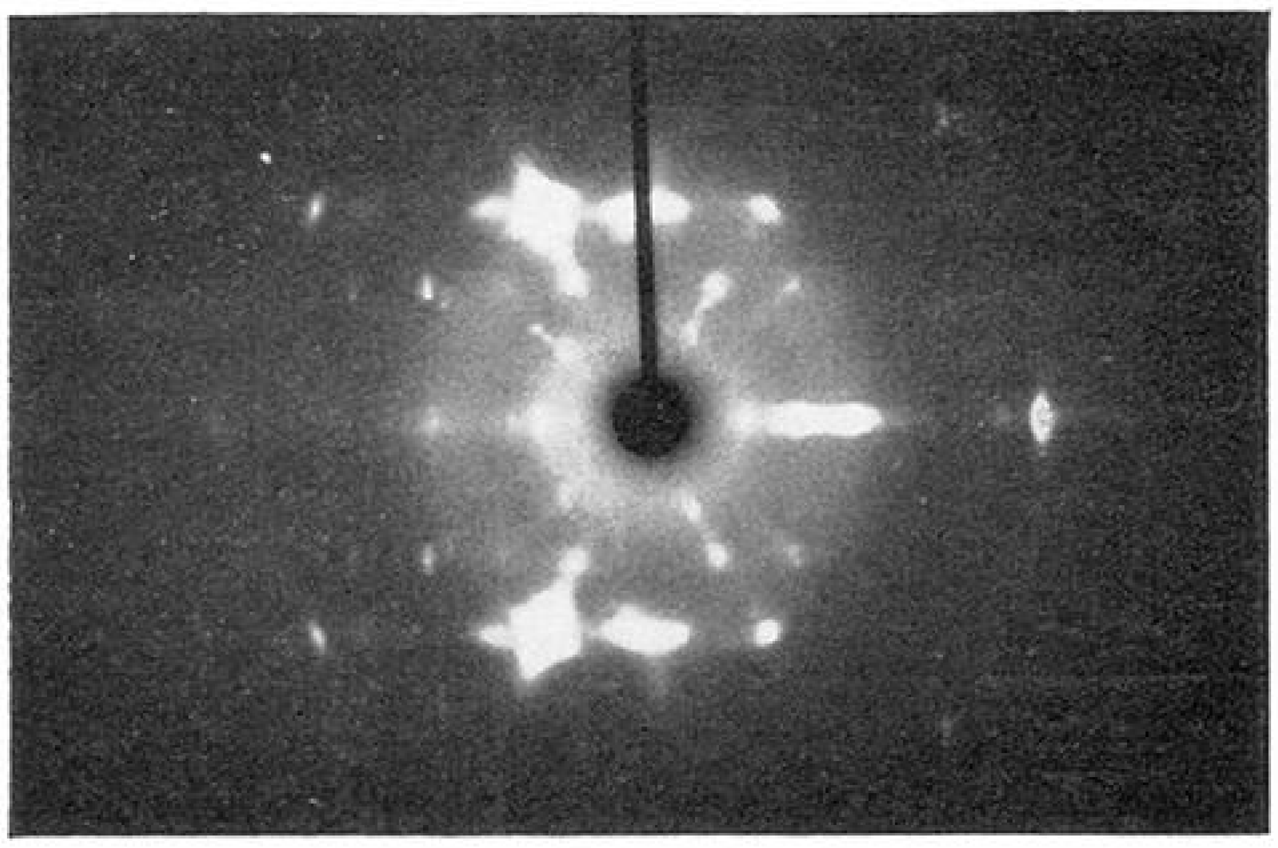

1 (*j*)

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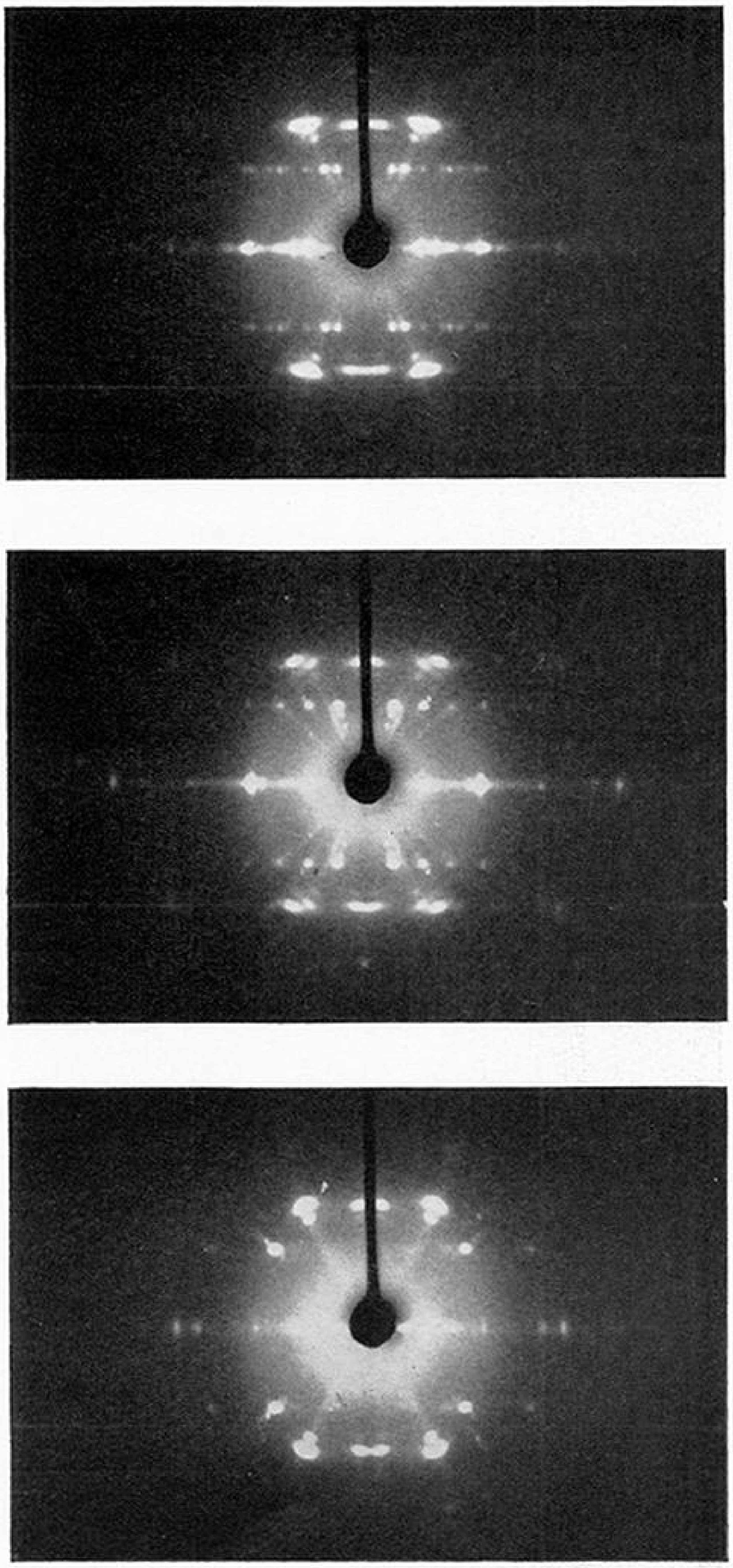


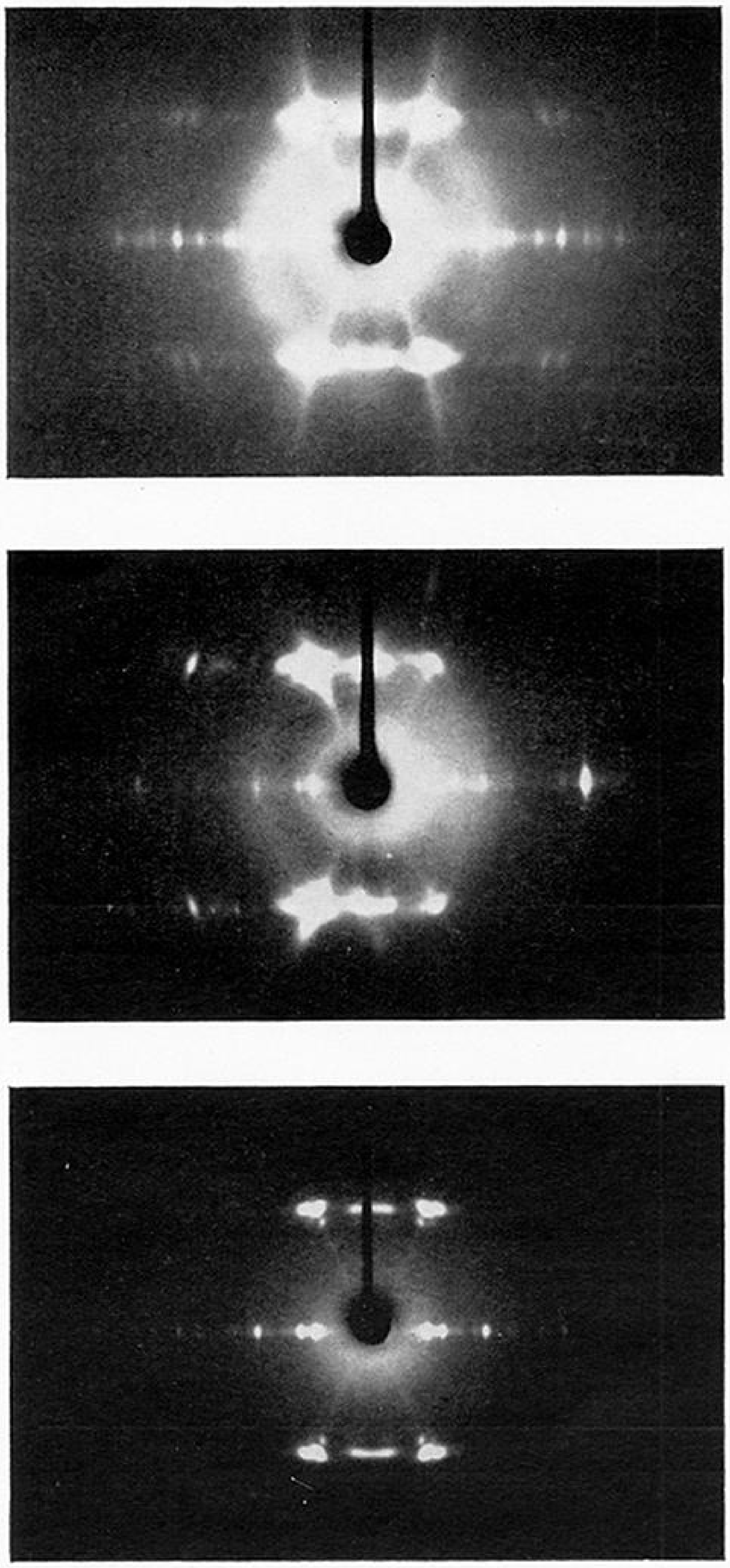


FIGURE 2. (*a*) Rotation about [010] of another crystal, after a total 55·7 h Cu*K* irradiation (specimen randomly selected from a sample placed inside a lead cap over an X-ray tube window).

(*b*, *c*) Two corresponding 'stills', mutually orthogonal, [010] vertical (56·2 and 56·7 h total irradiation respectively) which show clearly (since there should be no planes of symmetry intersecting in monoclinic [010] that the original p.o.a. was or has become twinned, and that the final *A*:*A* is also twinned or consists of crystallites which bear to one another the relationship of twinned individuals (compare figure 20).

FIGURE 3. (*a*) Completely converted crystal. Rotation about [010], Cu*K*, 30 min exposure, after total 125·3 h Cu*K* irradiation, inside lead cap; showing considerable disorder, and also diffuse rings due to very small (colloidal sized) crystallites and near amorphous groups.

(*b*) 'Still' photograph corresponding to 3(*a*). The crystal position is identical with that for figure 1(*f* to *j*) and a similar fibrous character is evident.

(*c*) Cu*K* [010] rotation of another crystal nearly completely converted after 60 h Mo*K* irradiation inside lead cap to X-ray tube window. 30 min exposure. The differences between 3(*a*) and 3(*c*) are not associated with the radiation used but with the perfection of the original crystal. Many similar photographs have been obtained under all conditions.

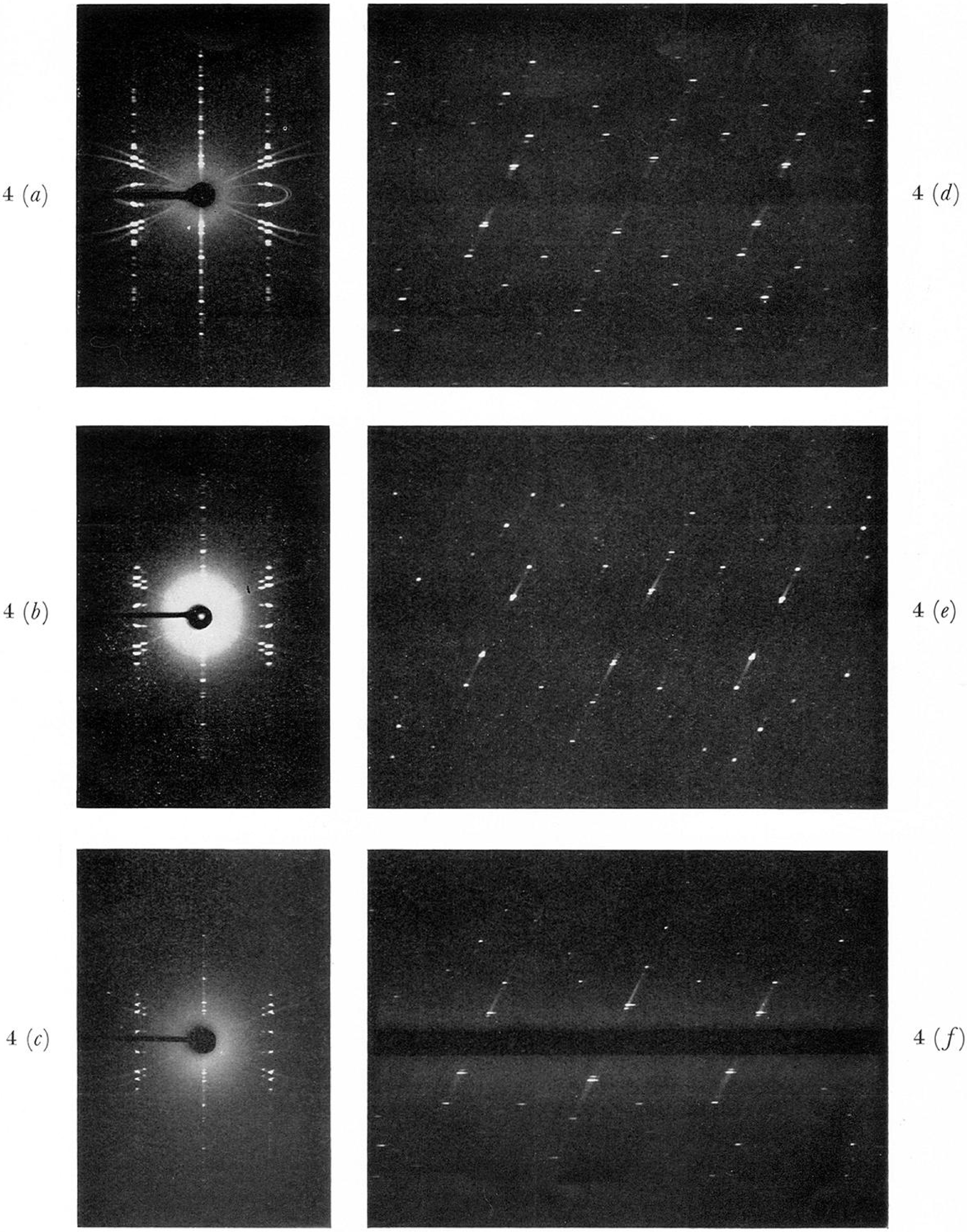
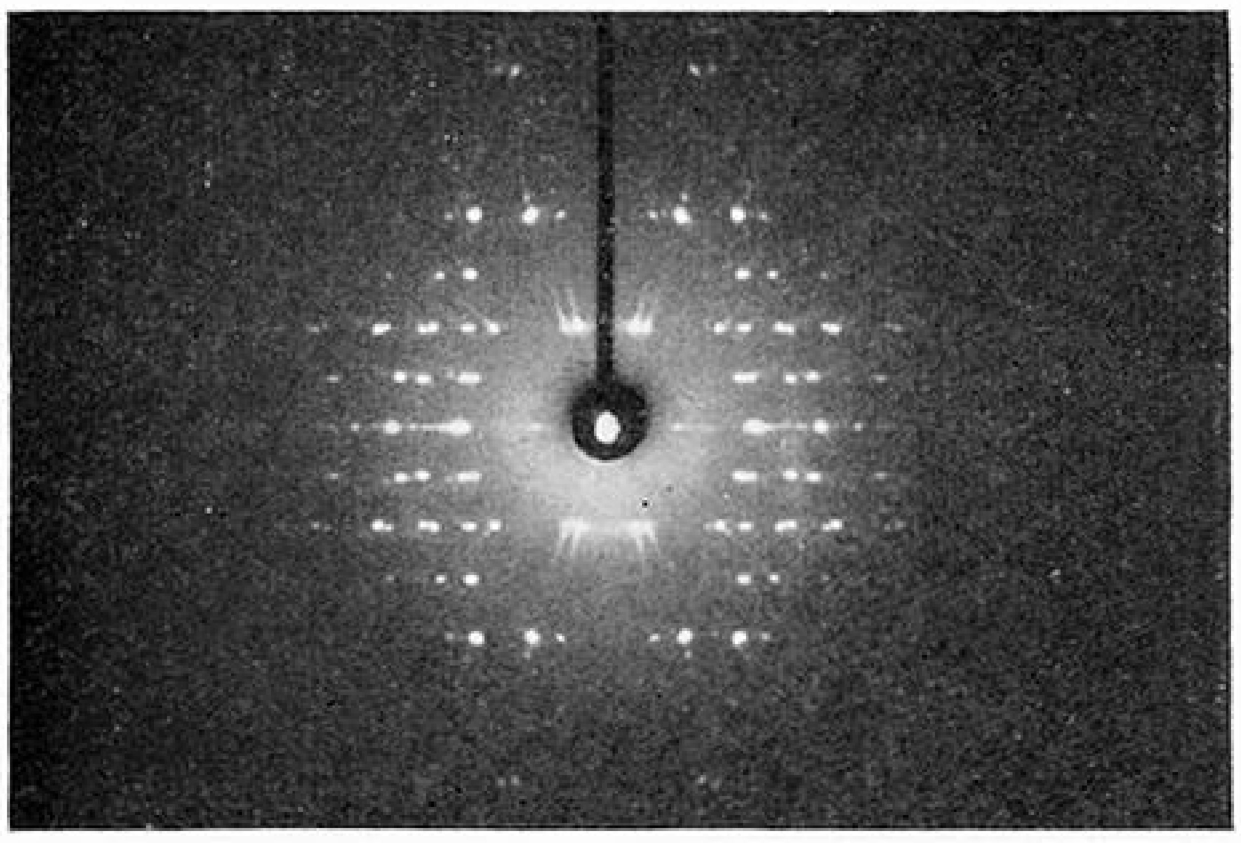


FIGURE 4. (*a*) Cu*K* [010] rotation of anthraquinone, recrystallized from benzene.

(*b*) The same of anthrone, recrystallized from hot ethyl alcohol.

(*c*) The same of 50:50 anthraquinone:anthrone, recrystallized from the melt in a capillary tube (J. W. Harris 1965).

(*d*, *e*, *f*) Weissenberg *h*0*l* photographs corresponding to (*a*, *b*, *c*).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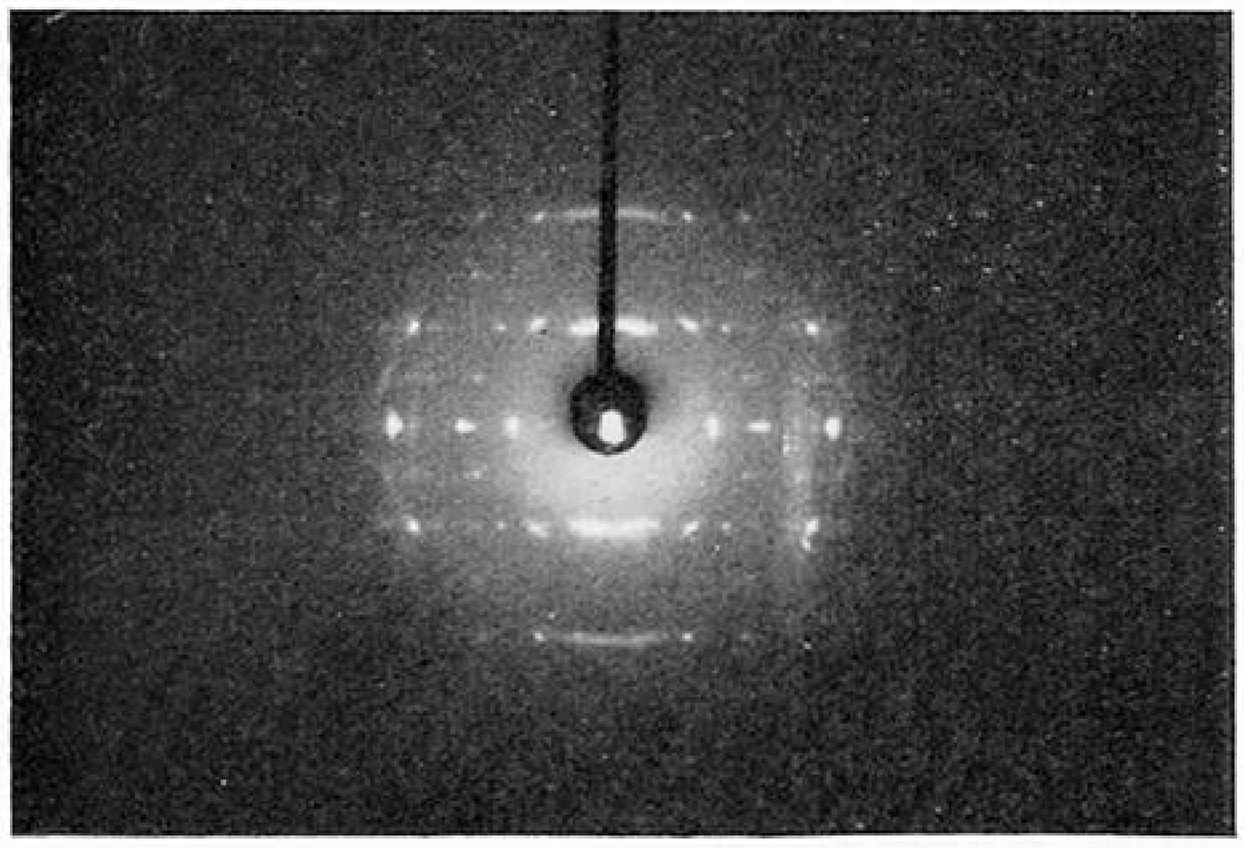
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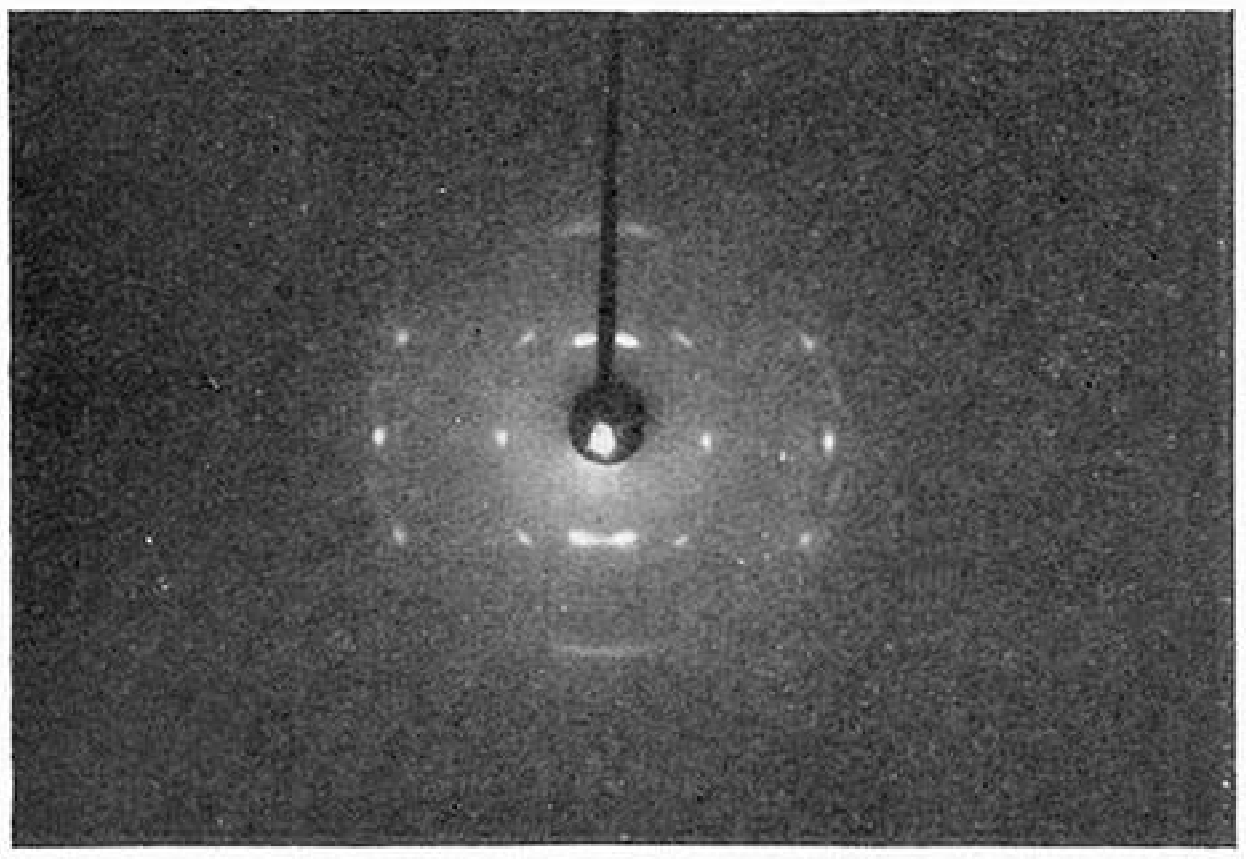
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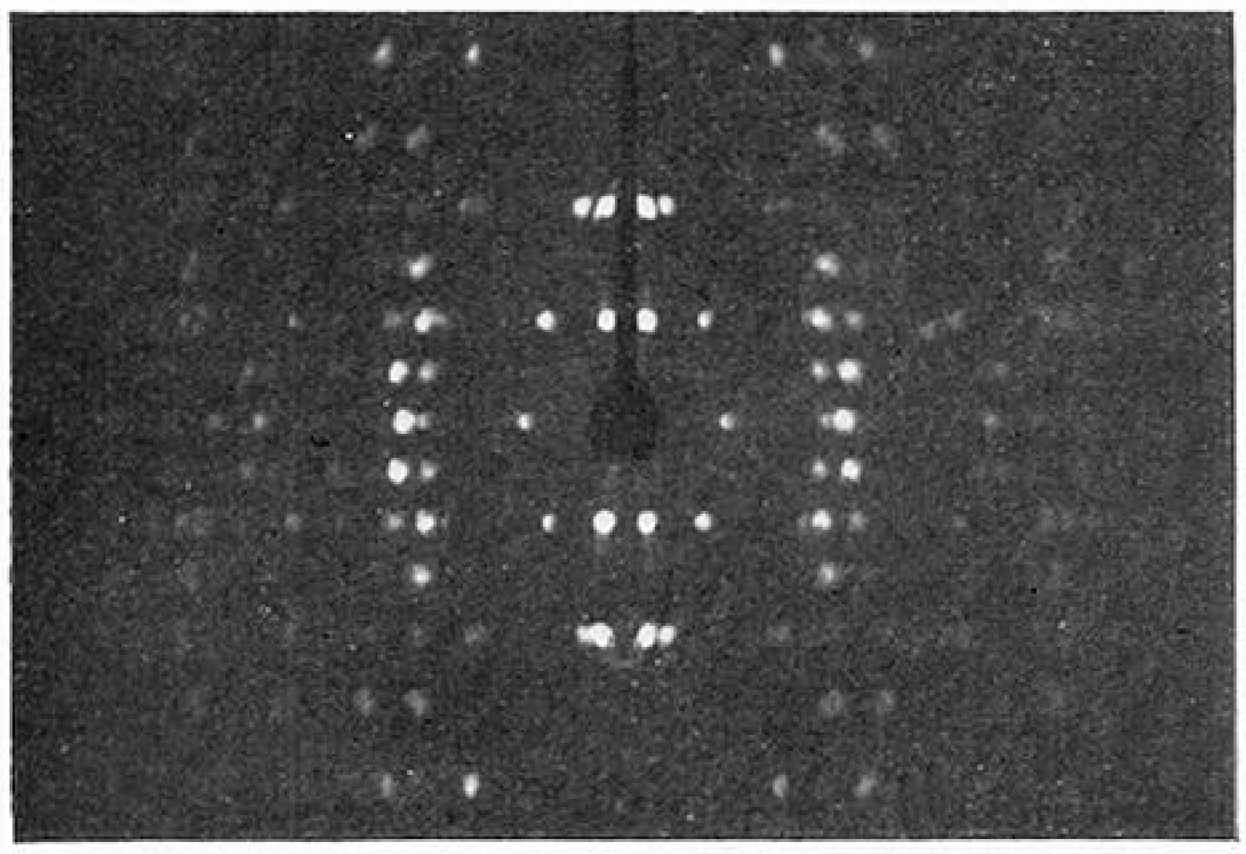
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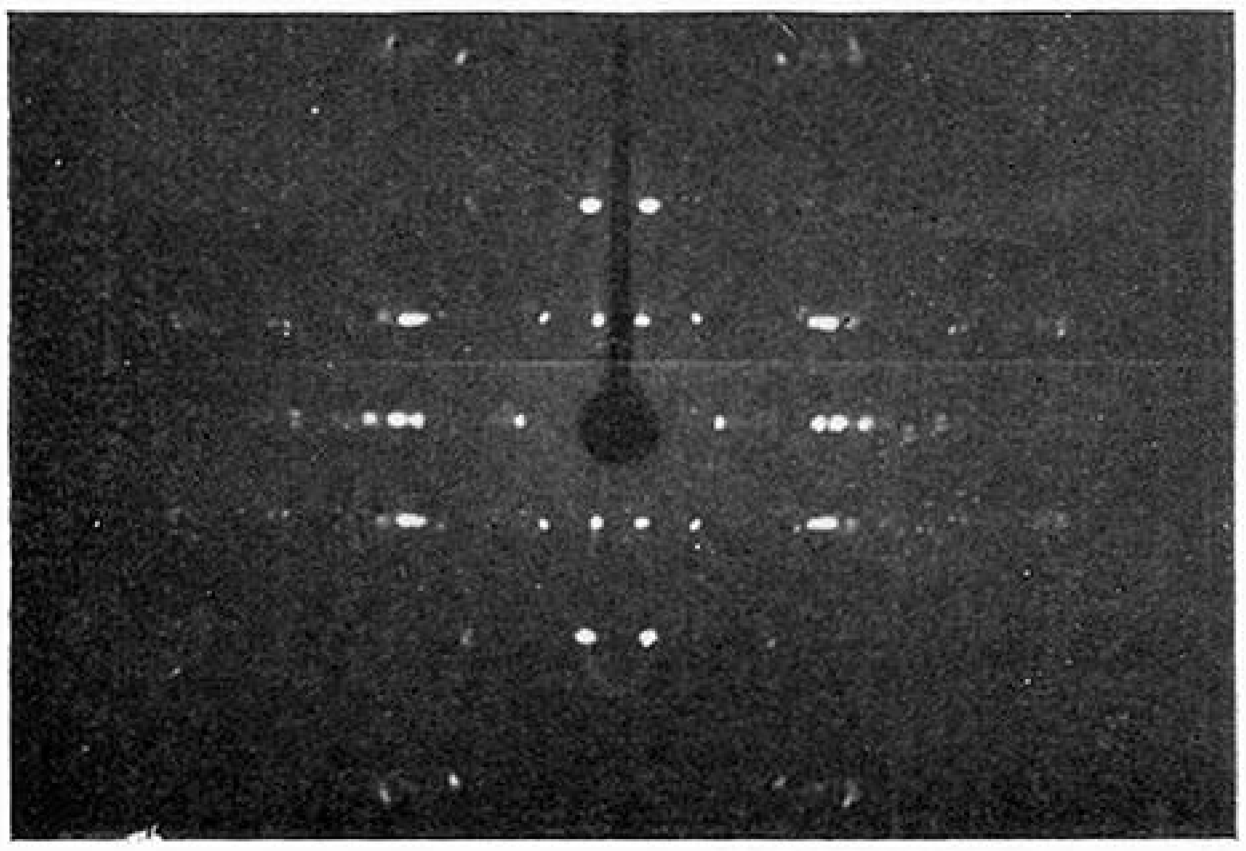
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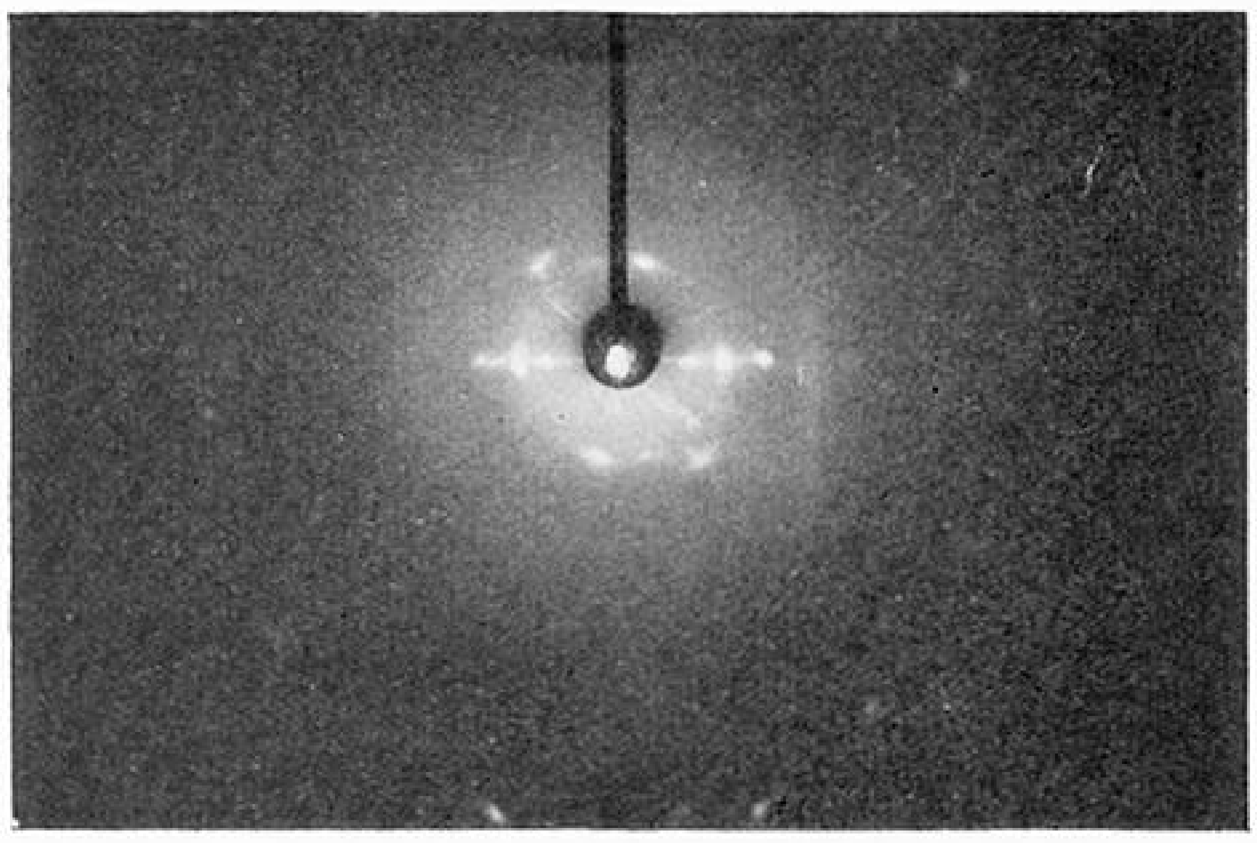
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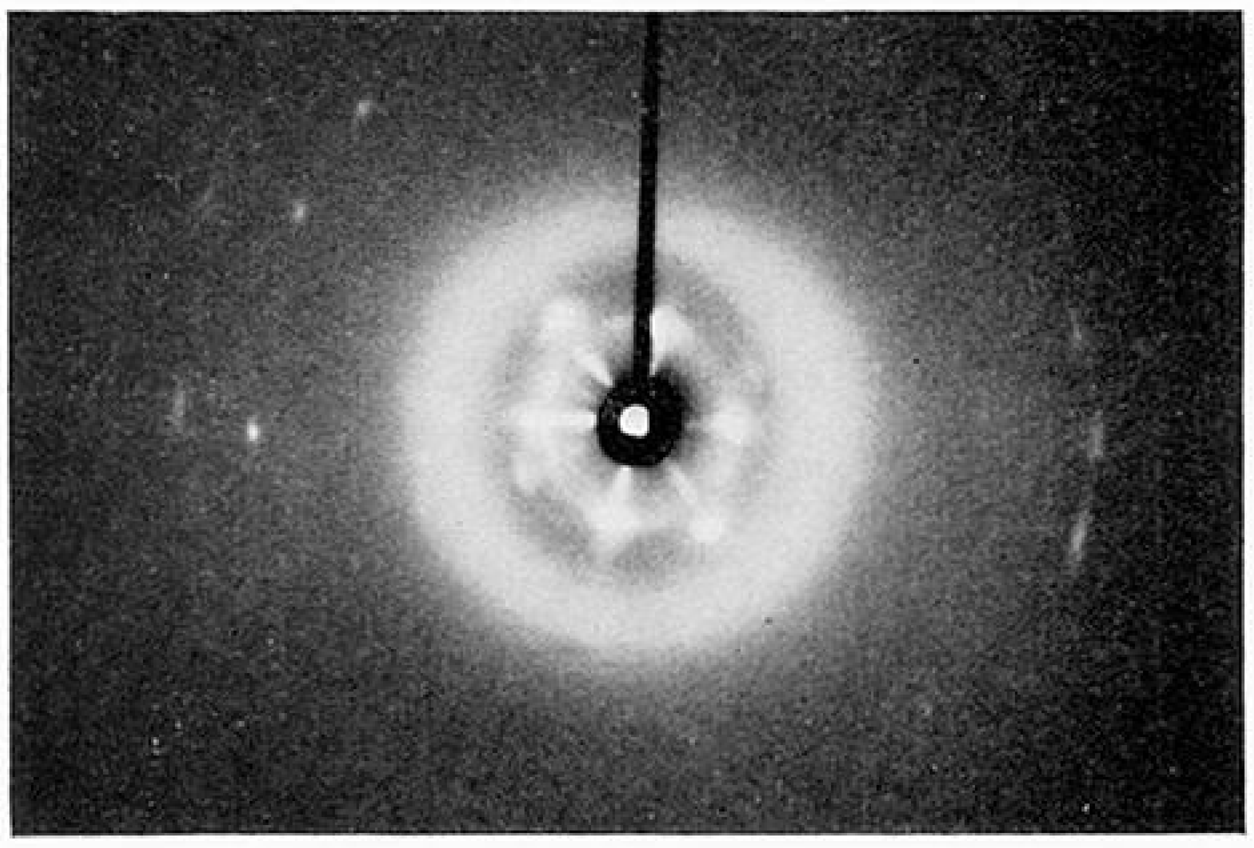
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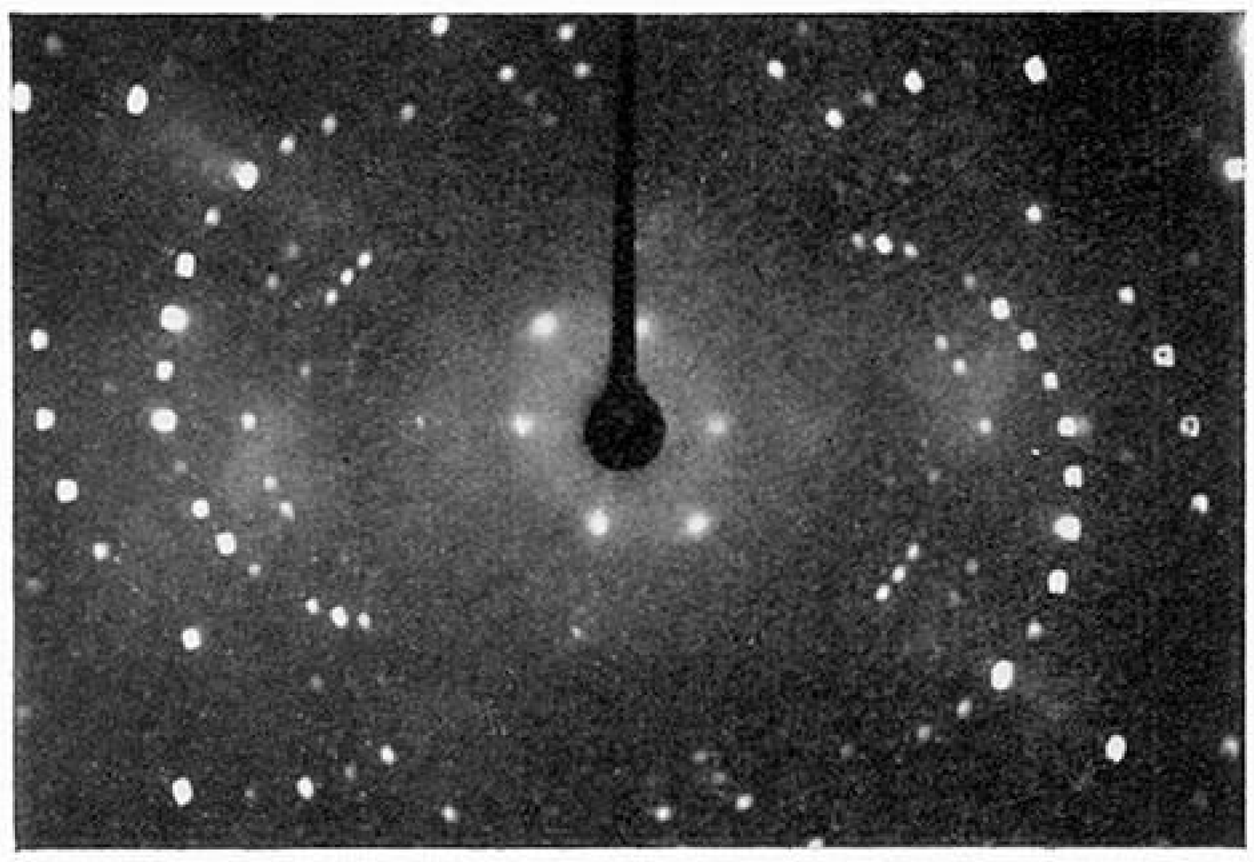
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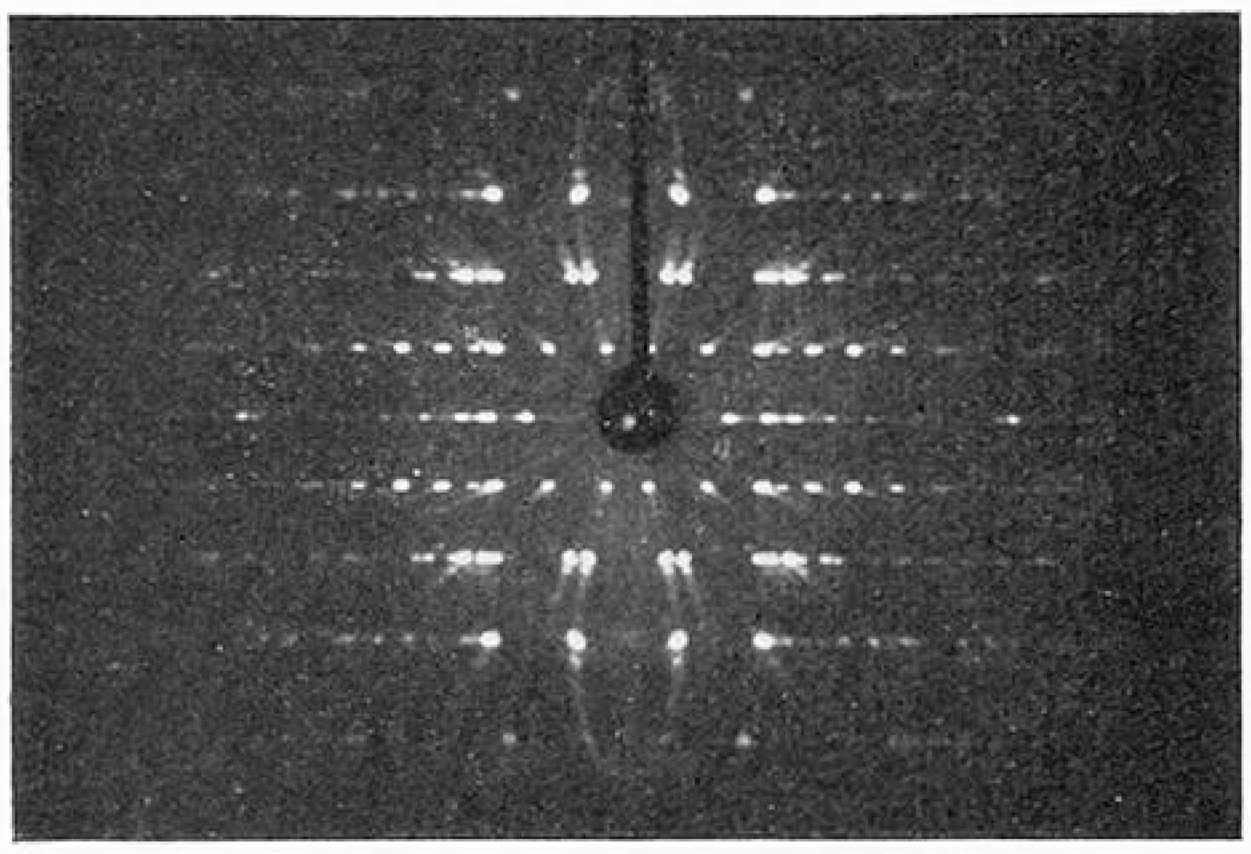
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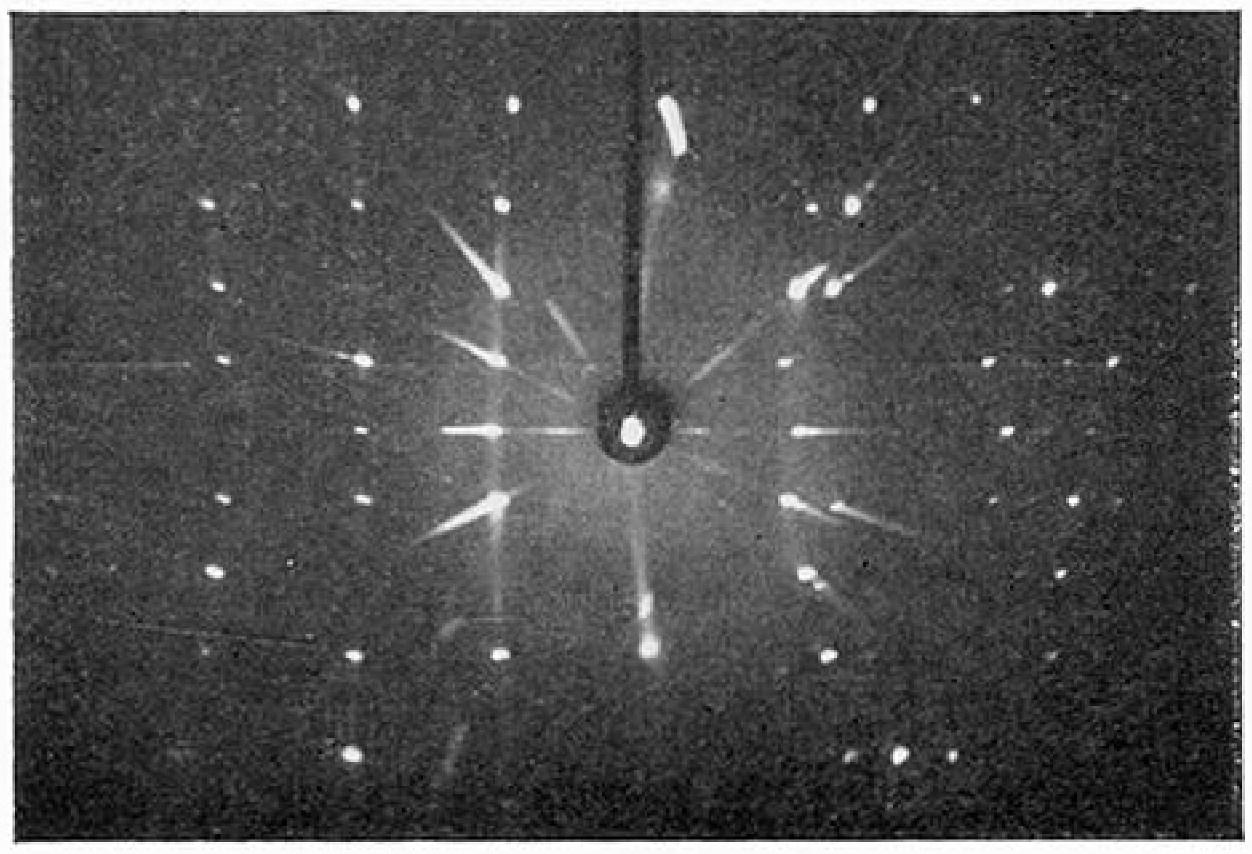
5 (*j*)

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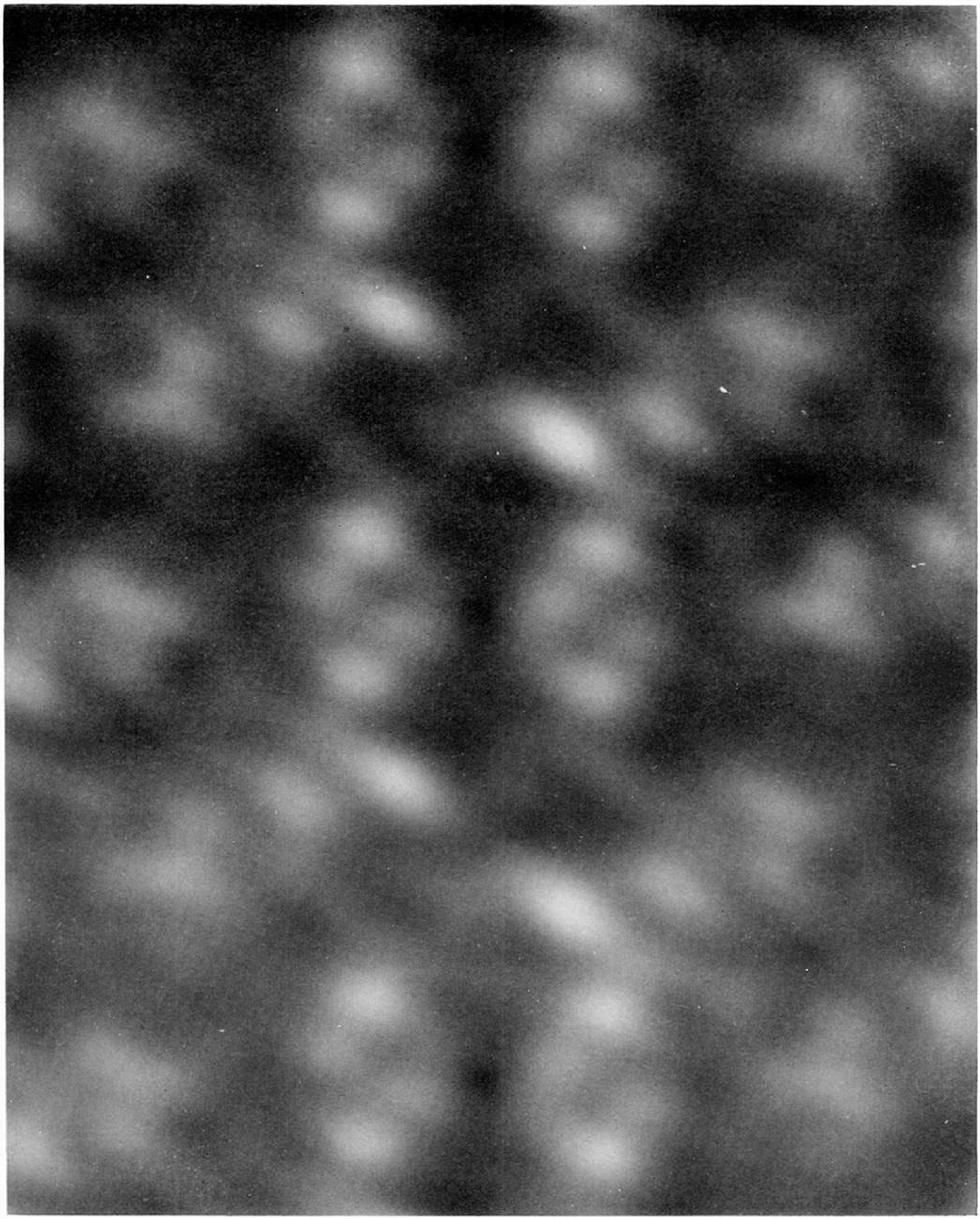


Figure 6 (*a*). An optical synthesis, made on the von Eller photosommateur, of the p.o.a. [010] projection from room-temperature (20 °C) data. Note the lack of resolution along the O—O bridge (one oxygen is superimposed on a carbon atom of the central ring), and the general diffuseness of the side rings.

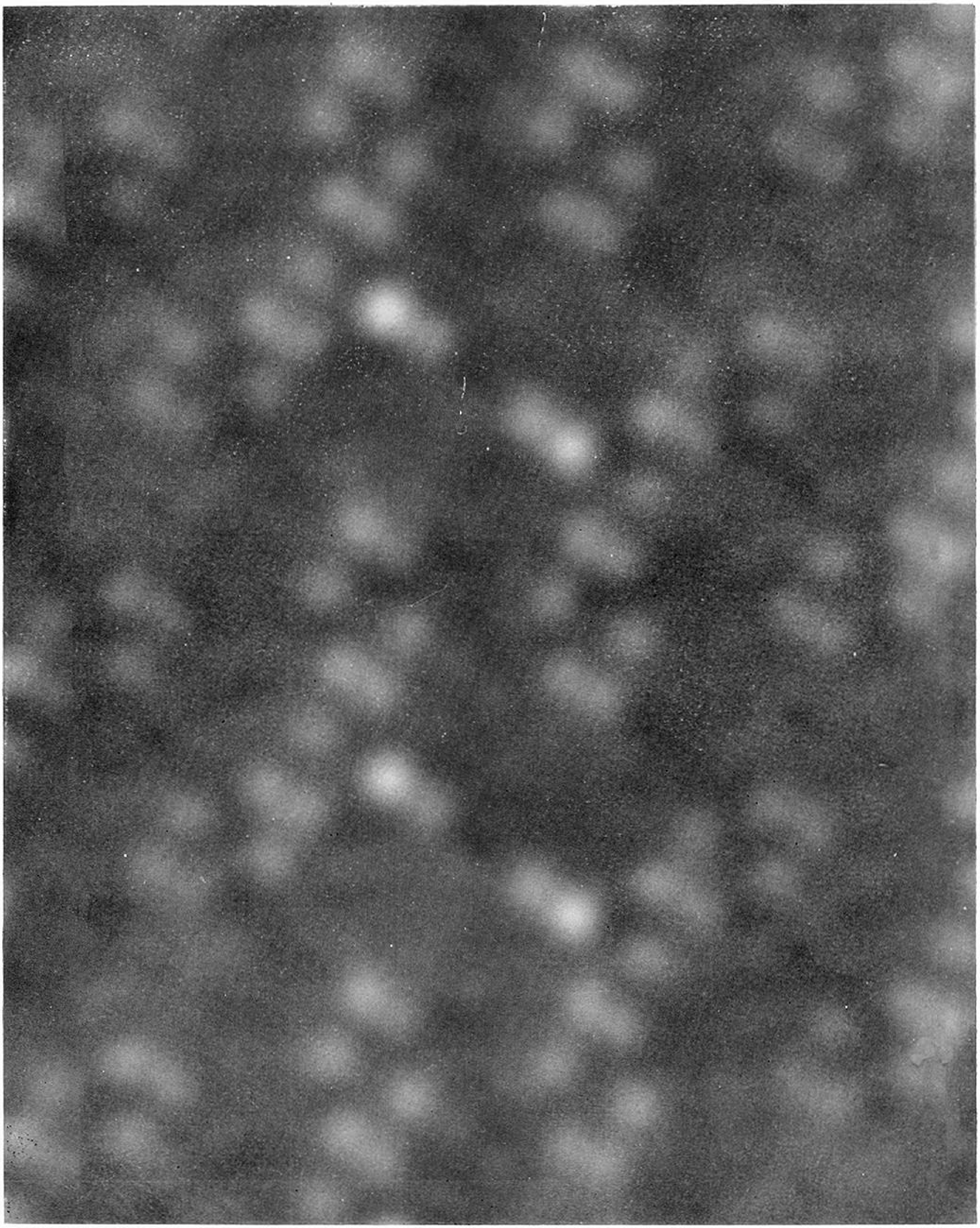
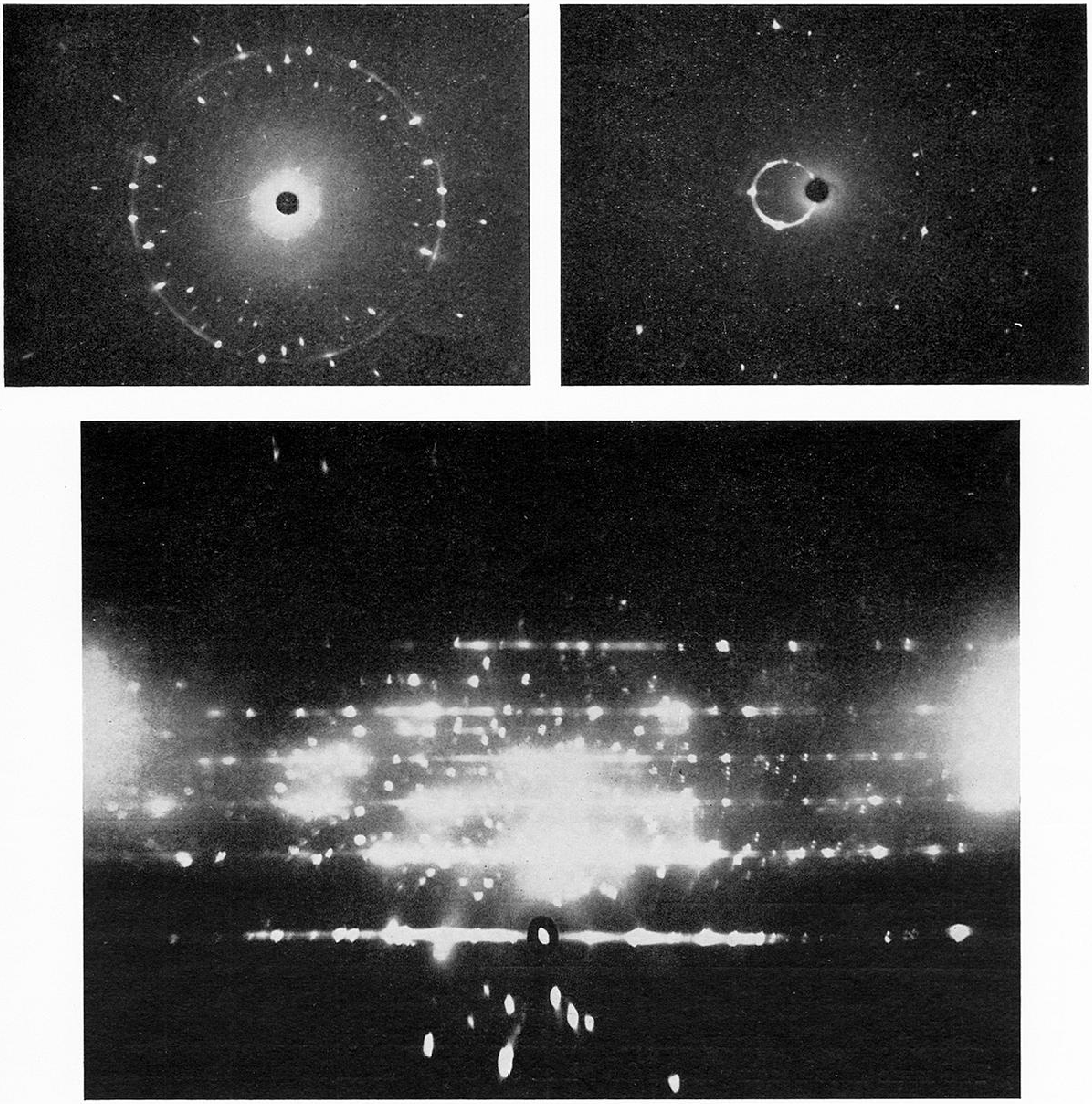


FIGURE 6(*b*). The same from low-temperature data (near to the boiling point of liquid nitrogen). The atoms are now well resolved.


7 (*a*)

7 (*b*)

7 (*c*)

FIGURE 7. (*a*) Laue photograph, on a flat film, of nearly fresh p.o.a., [001] vertical; incident (white + Cu*K*) radiation along [010]. A nearly continuous ring due to CuKα is seen, enhanced in the position of thermal diffuse spots and accompanied by traces of the Cu$K\beta$ ring. A second ring of larger diameter can be clearly seen on the film, but is not reproducible. These rings correspond with one-dimensional regularity along the [010] direction, first and second orders.

(*b*) The same with [010] tilted a little out of line with the incident X-ray beam. The ring of zero order now shows and is very intense. Compare the oscillation pattern figure 5(*j*), which is nearly at right angles to this ([001] vertical, [010] nearly normal to the incident beam).

(*c*) Inclined-beam Laue photograph of a large crystal of nearly fresh p.o.a., showing layer-line streaks for $k = 0 \cdots 5$.

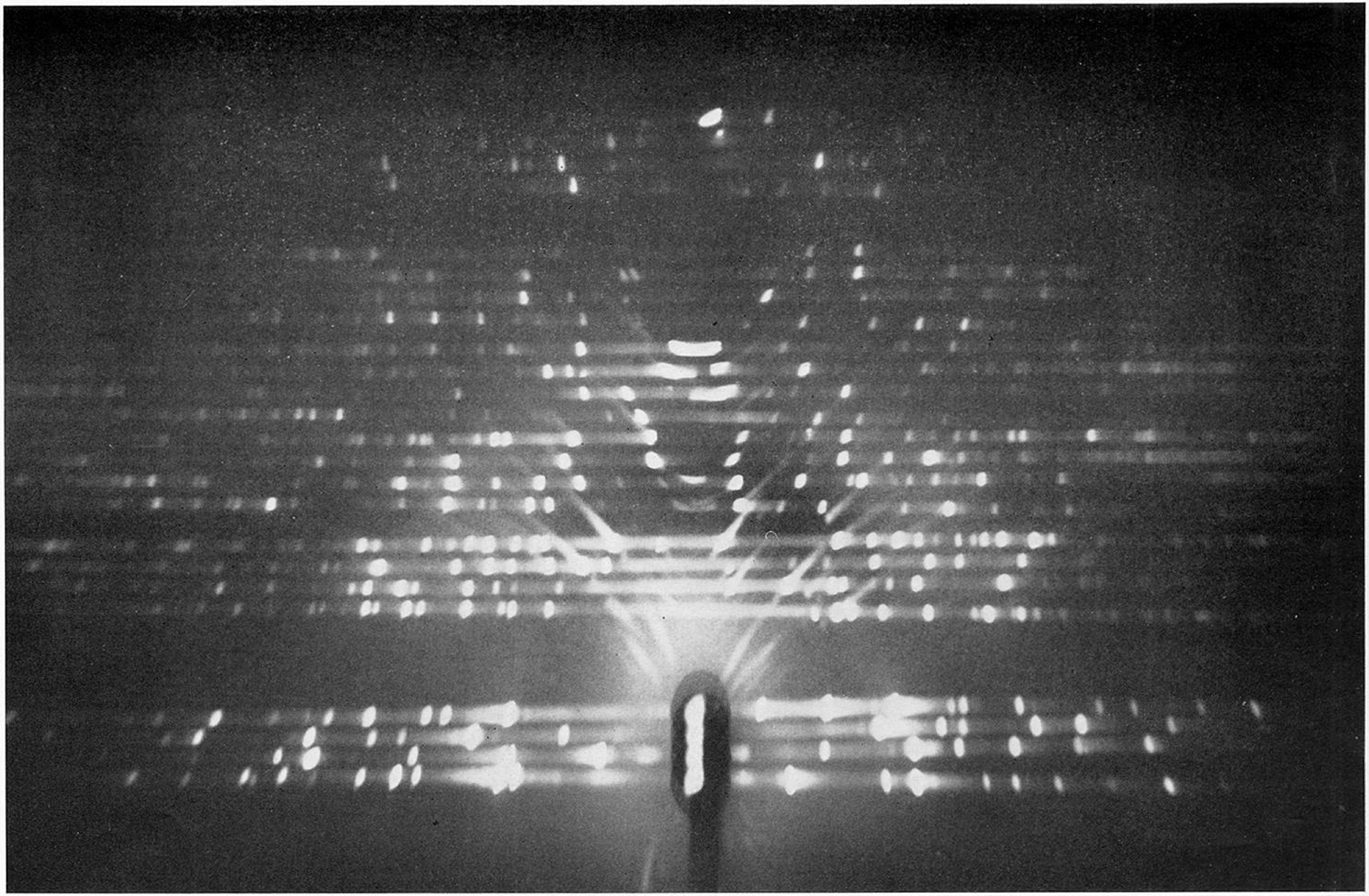
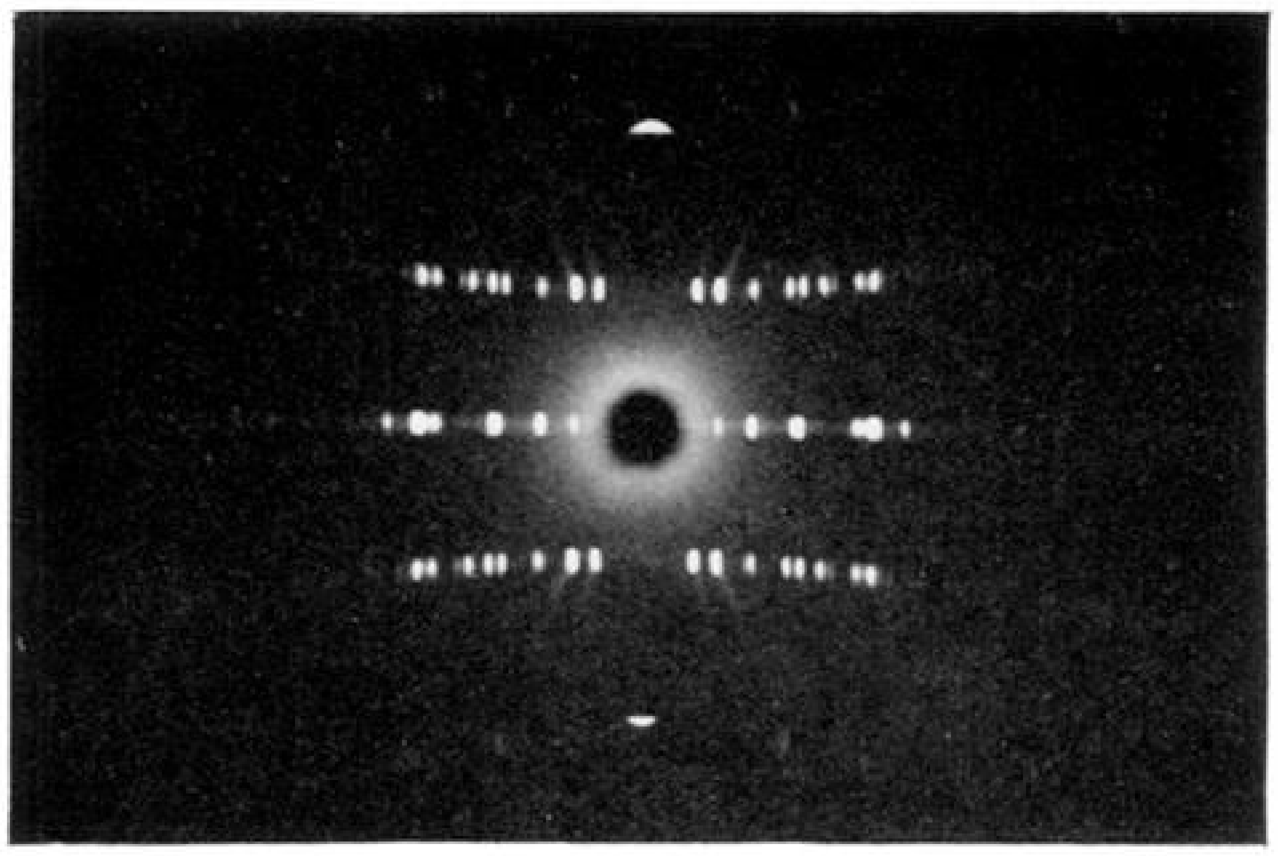
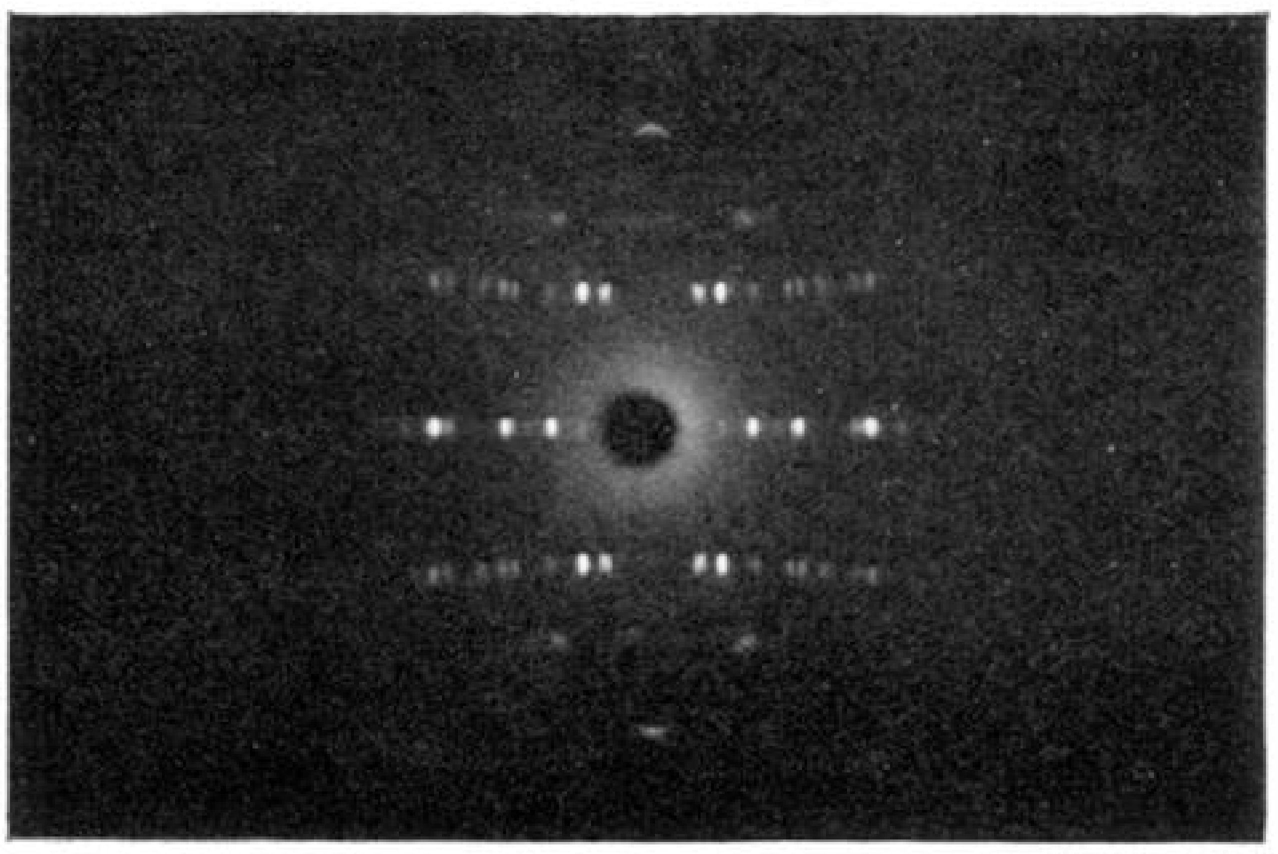


FIGURE 8. Four out of a set of eight superimposed 'inclined beam' 29° oscillation photographs (Milledge 1963), taken on two films, with the film shifted between each setting and the crystal moved by 180°/7 so that no. 8 repeats no. 1. [010] vertical, white + Cu*K* radiation.

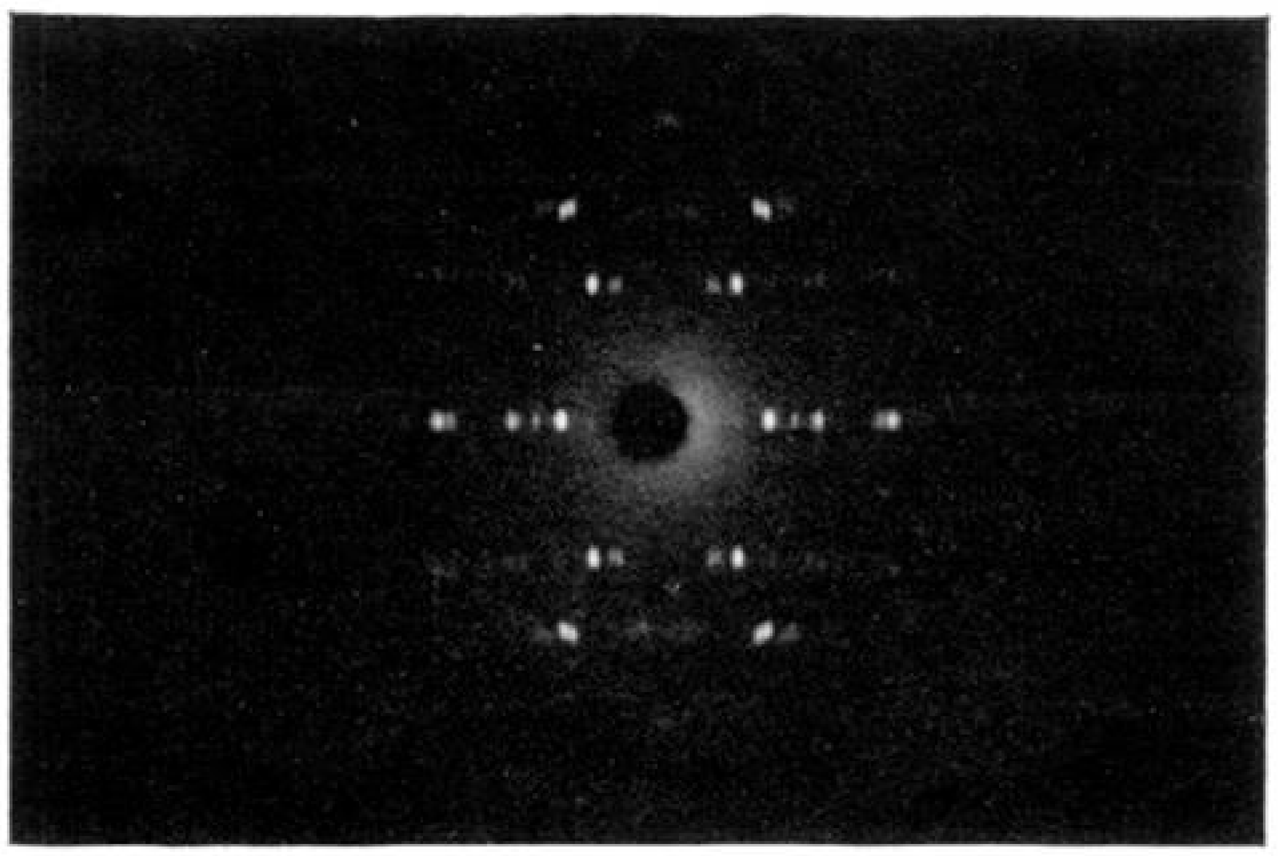
9 (*a*)



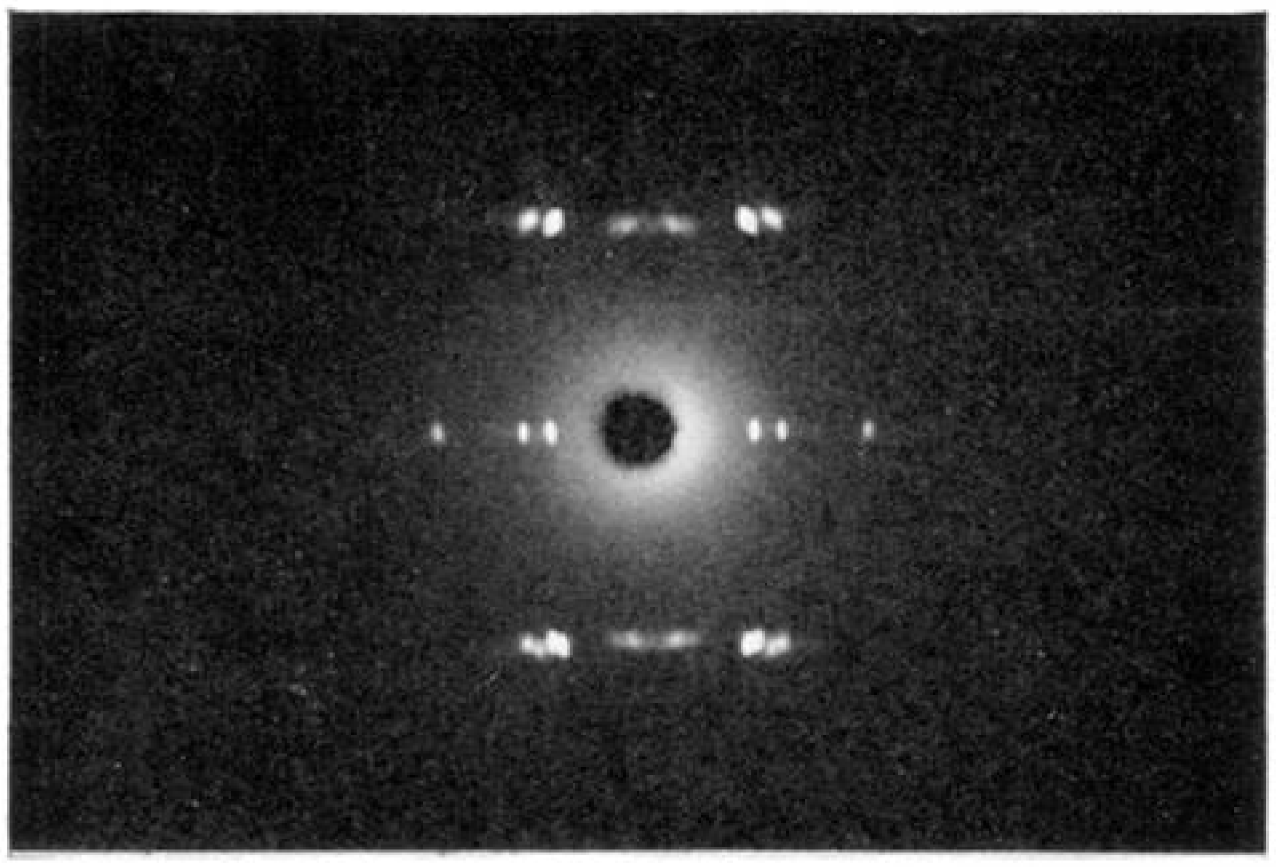
9 (*b*)



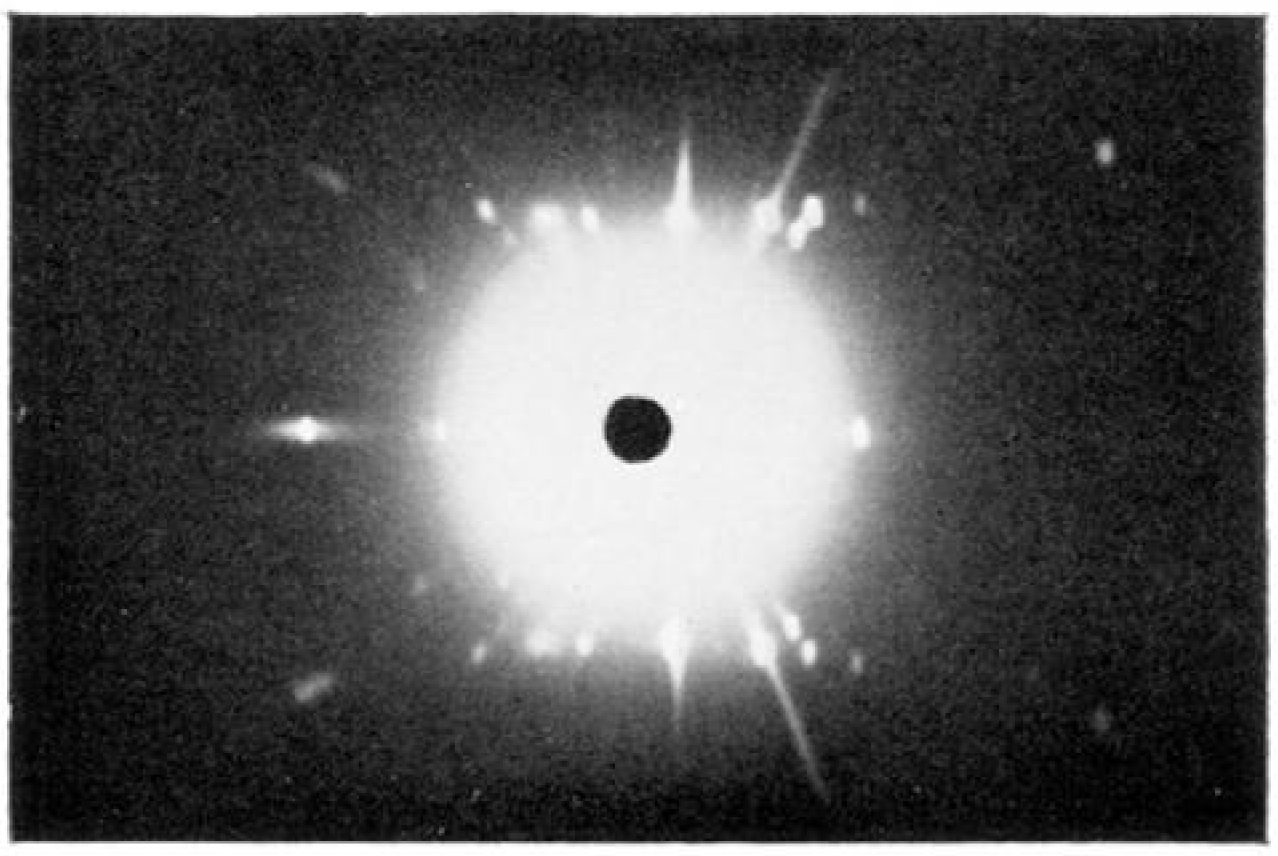
9 (*c*)



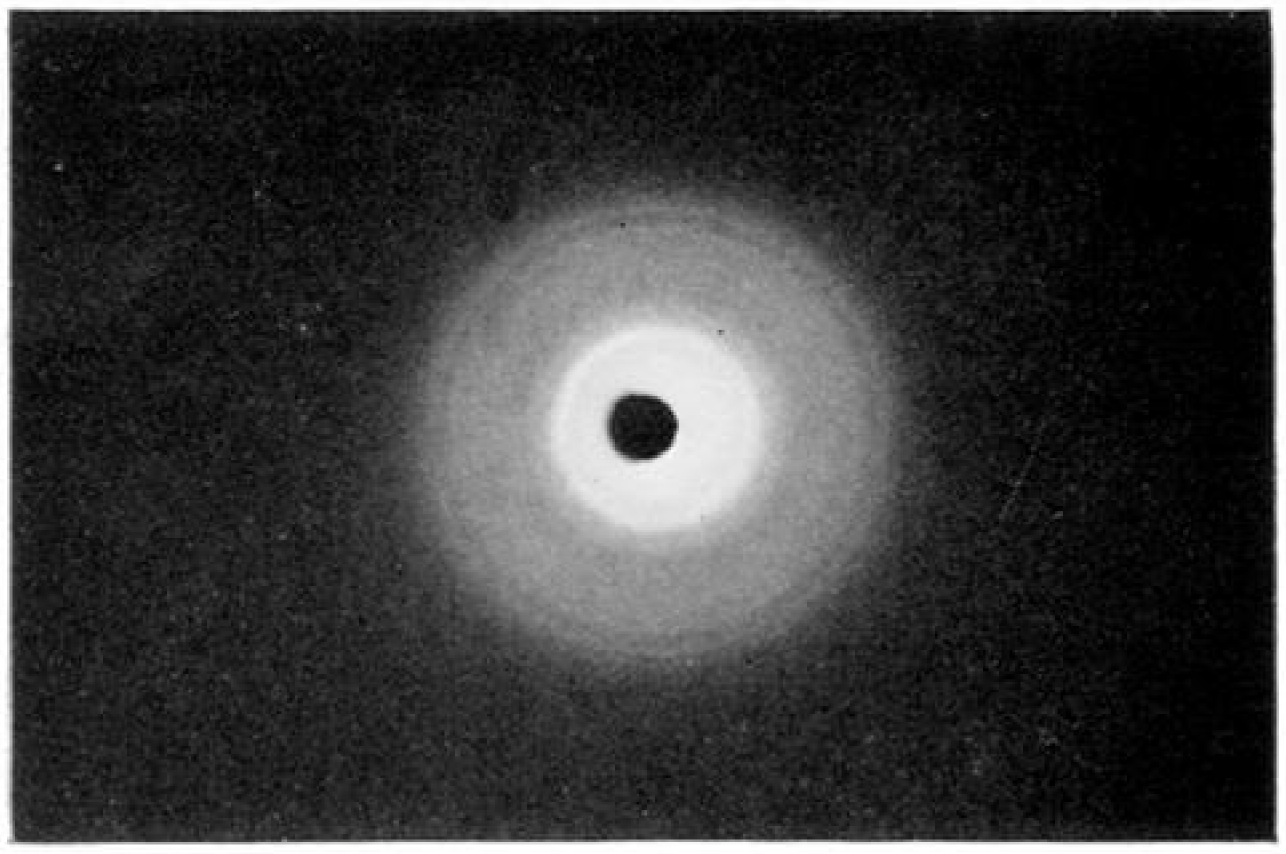
9 (*d*)



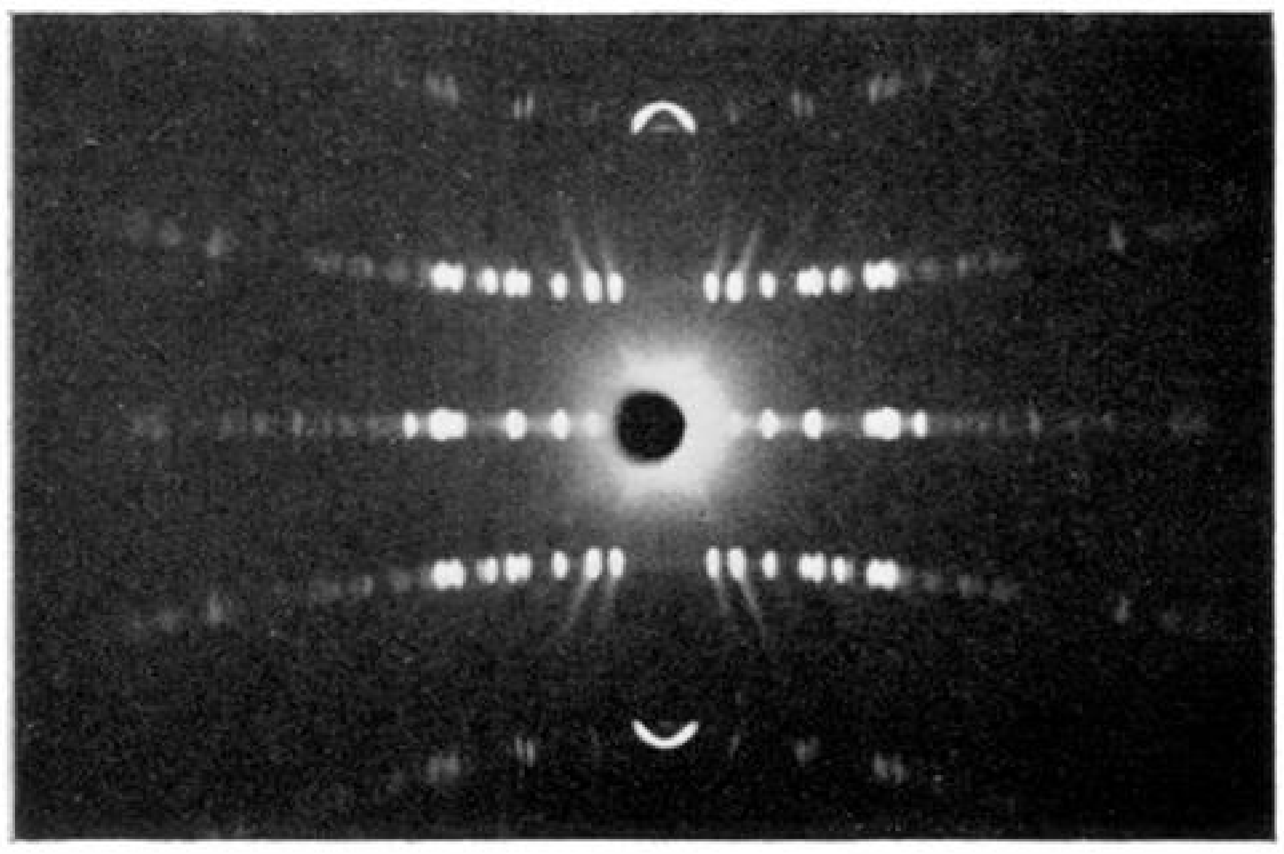
9 (*e*)



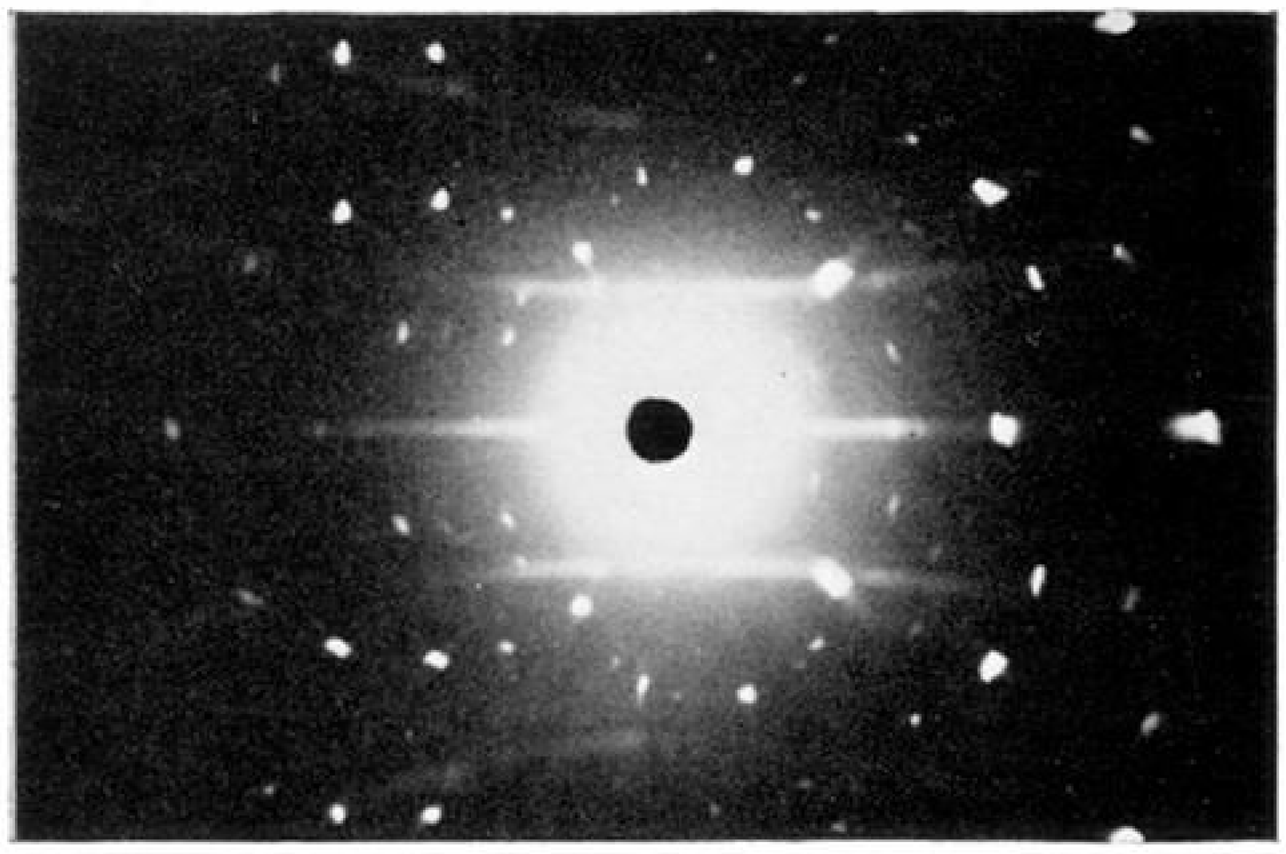
10 (*a*)



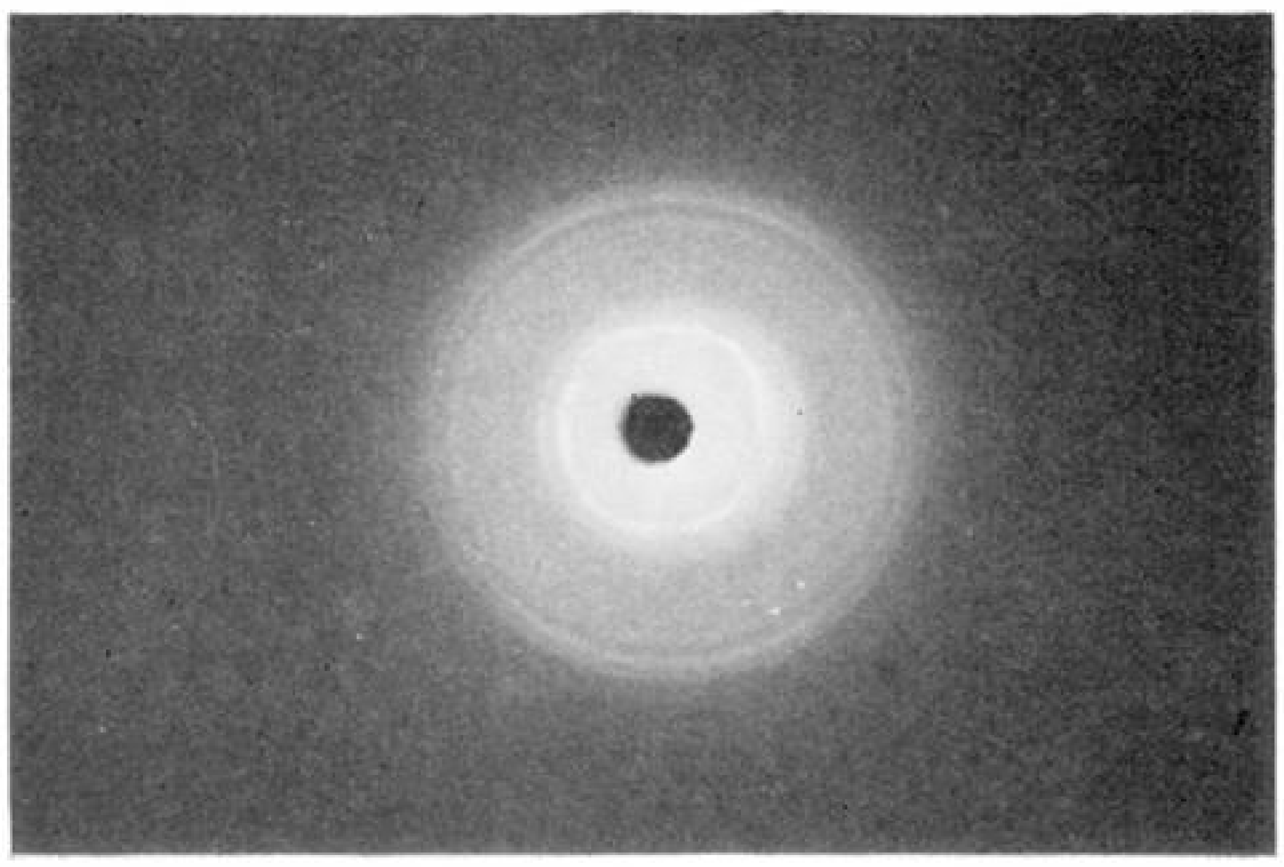
10 (*b*)



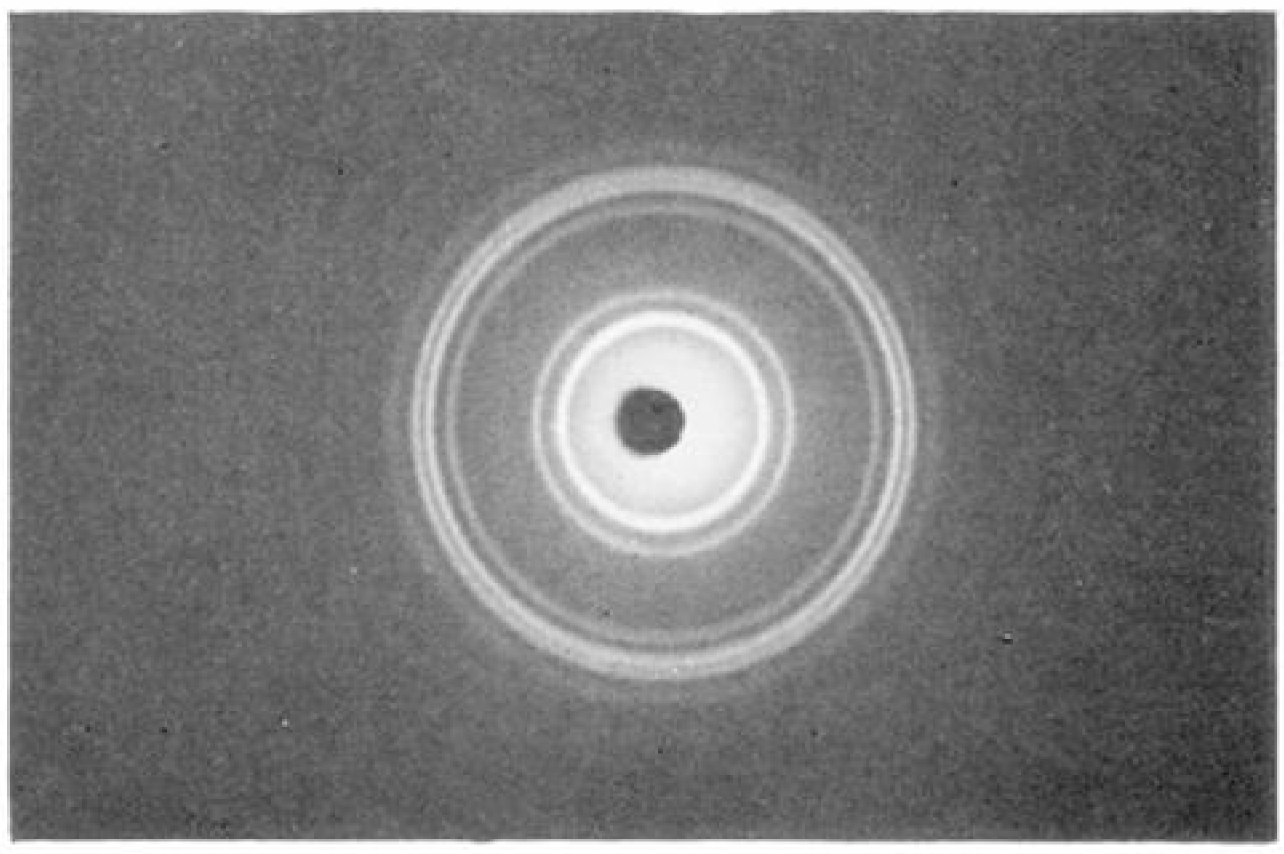
10 (*c*)



10 (*d*)

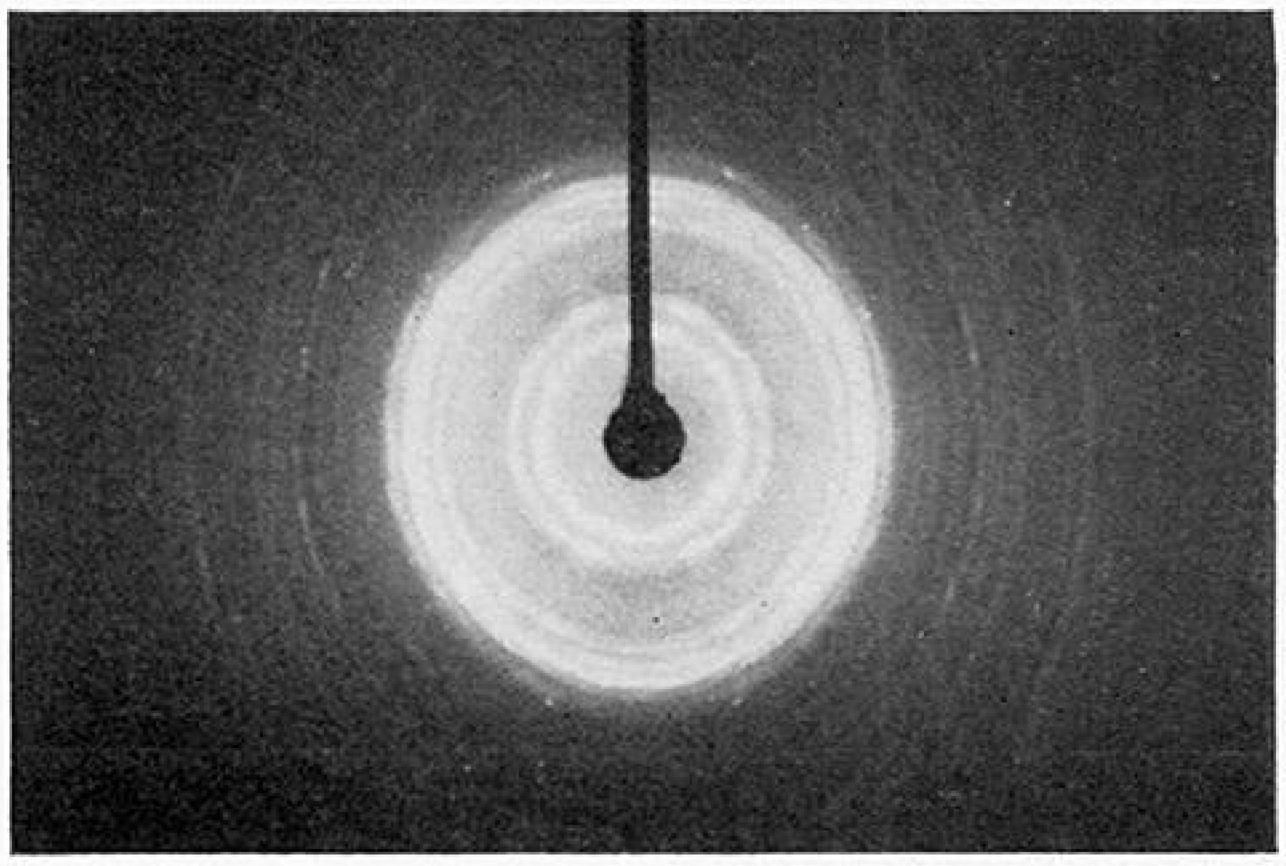


10 (*e*)

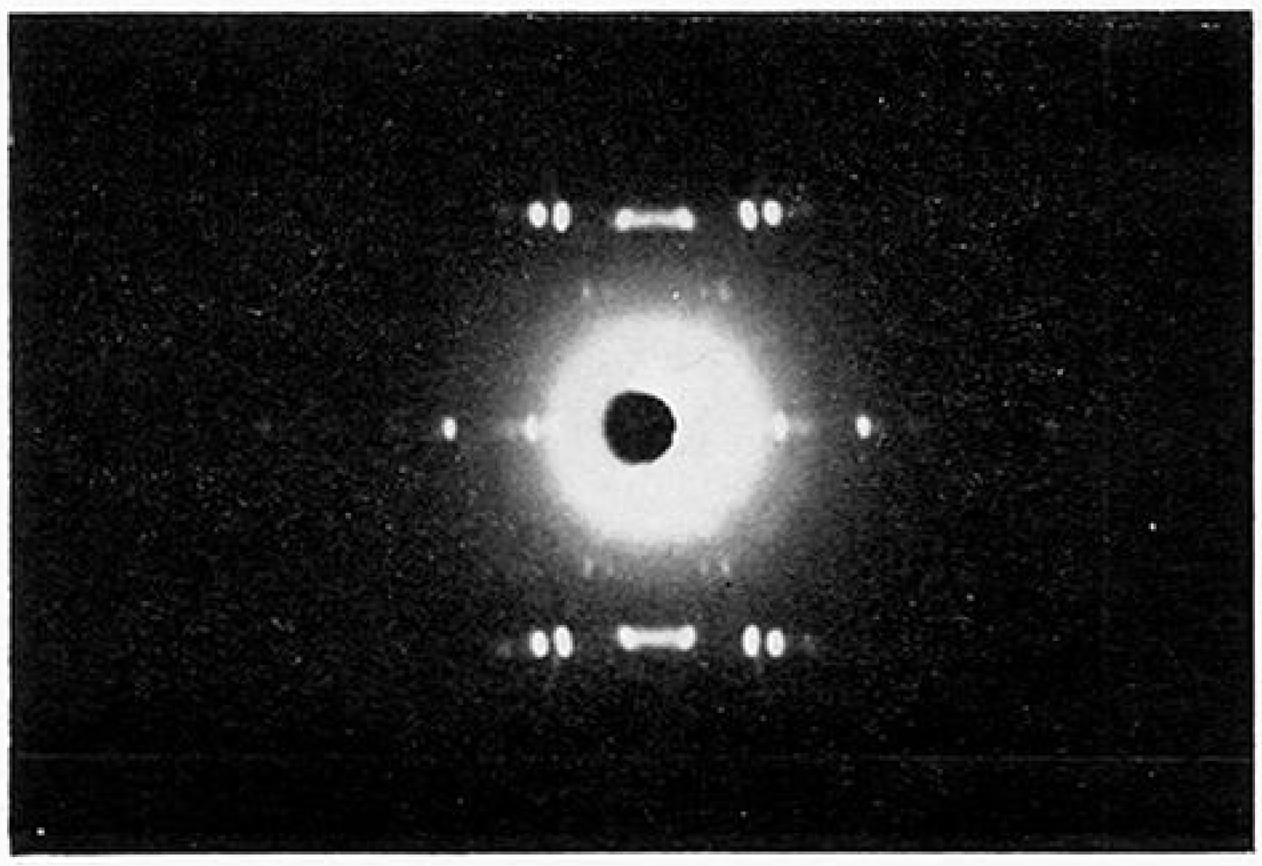


For legend see facing page.

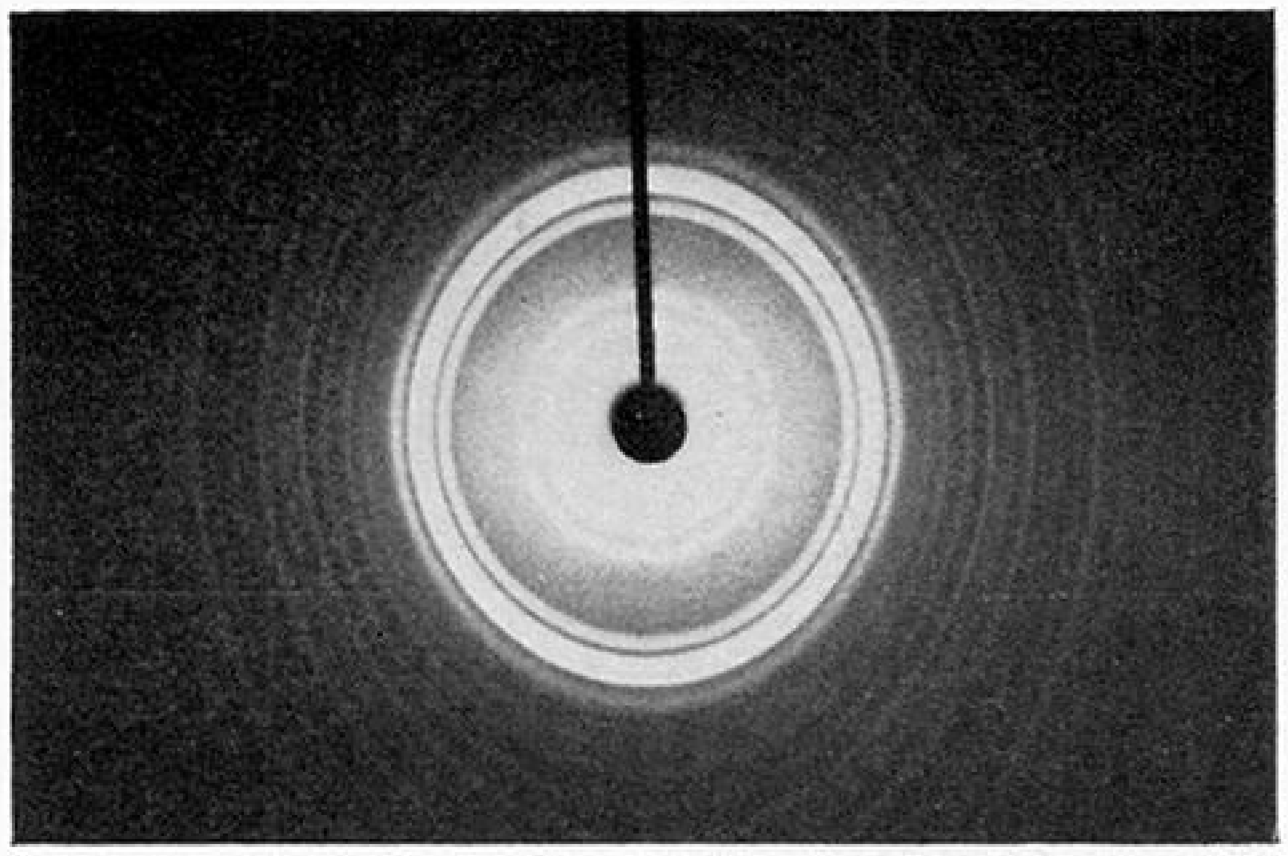
11 (*a*)



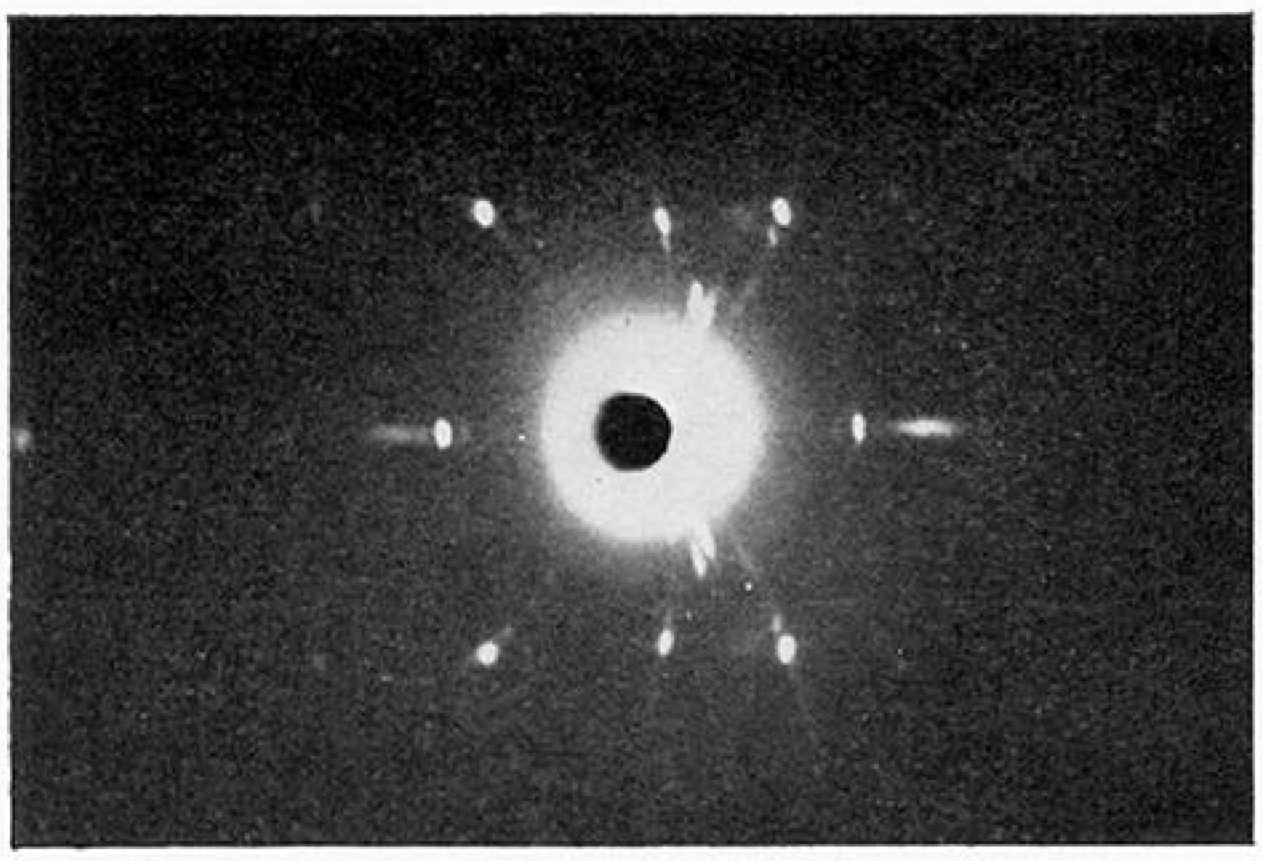
12 (*a*)



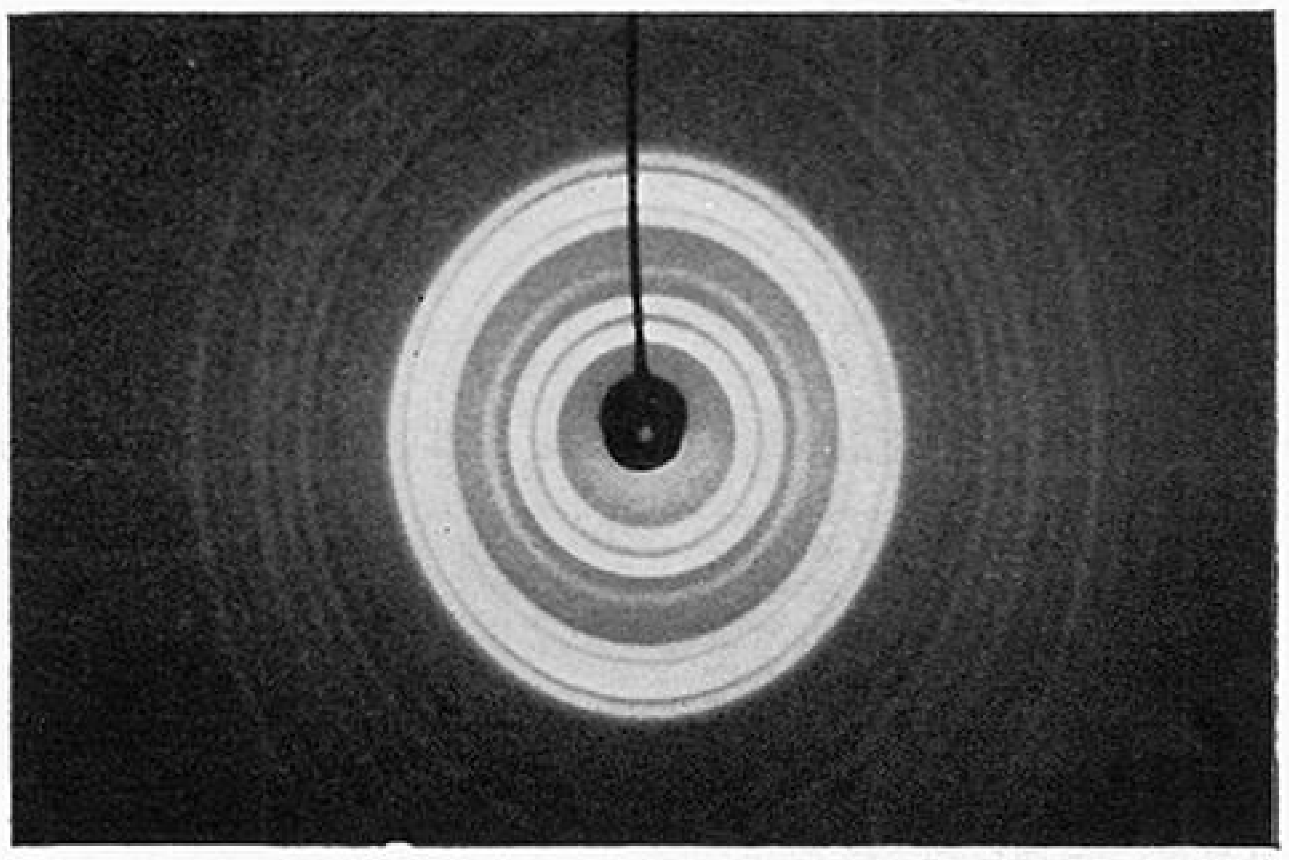
11 (*b*)



12 (*b*)



11 (*c*)



12 (*c*)

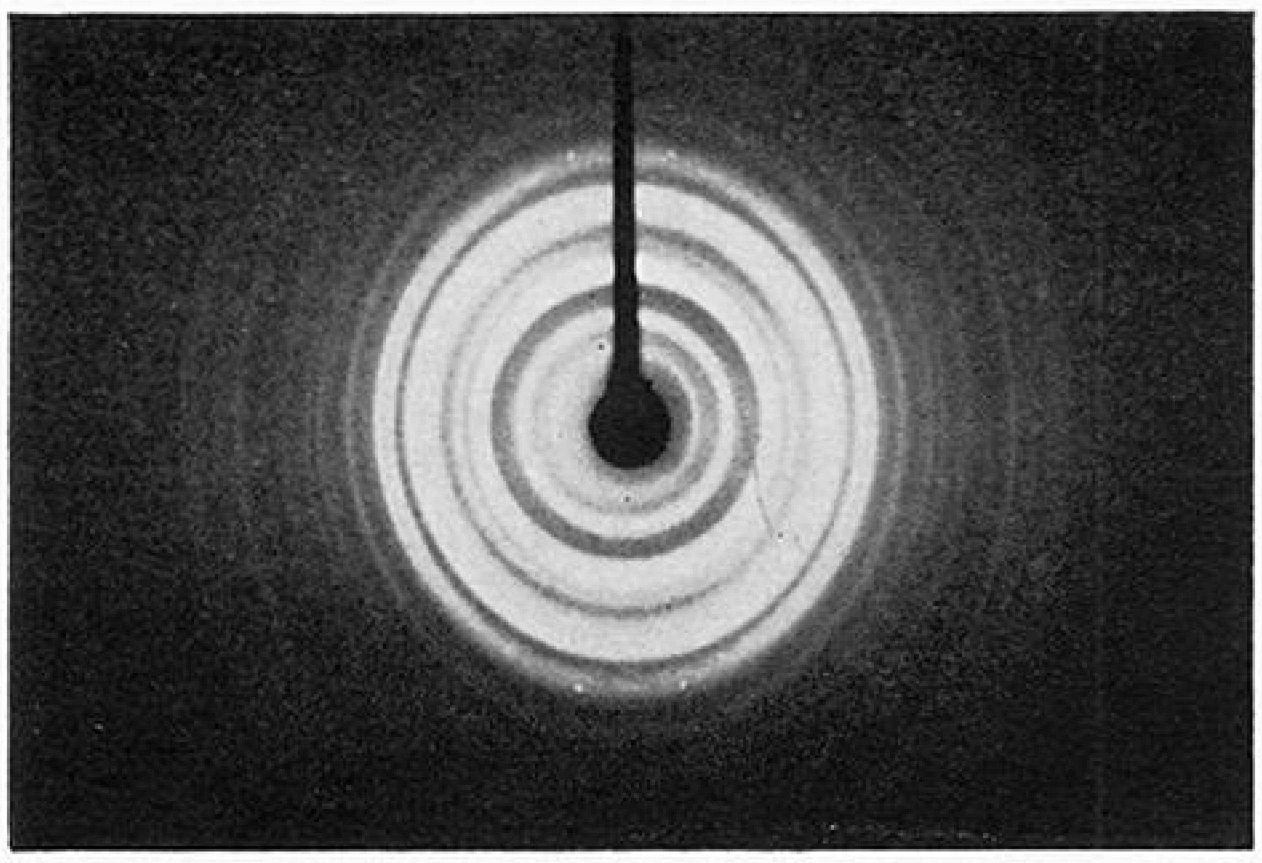


Figure 11. (*a*) Crystal of p.o.a. already decomposed at room temperature (~ 20 °C) by X-irradiation, then allowed to melt and recrystallized. The specimen, which was a grainy powder, contained some largish orientated crystals. It was rotated; Cu*K* radiation; 26 min exposure time. The resemblance is closer to 11(*b*) than to 11(*c*).

(*b*) Anthraquinone, for comparison.

(*c*) Anthrone, for comparison. The principal difference from 11(*b*) is in the presence of a moderately strong 201 line outside the two strong inner lines.

Figure 12. (*a*) Nearly converted crystal (heated for a total 3 h at 100 °C, with $1\frac{1}{2}$ h Cu*K* irradiation for setting and preliminary photographs). [010] rotation, Cu$K\alpha$, 30 min exposure, flat film. This pattern shows p.o.a. powder lines (compare 12(*c*)).

(*b*) The same; 'still' photograph in a setting similar to that of 1(*f* to *j*). This crystal shows very little twinning of *A*:*A* and none of p.o.a., but it does show much low-angle scattering and p.o.a. powder lines (compare 12(*c*)).

(*c*) P.o.a. powder pattern.

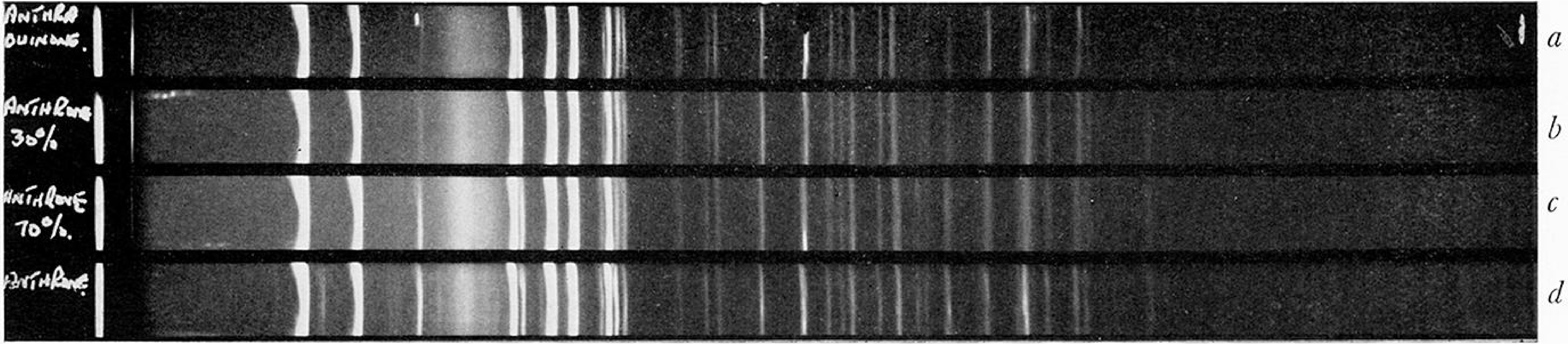


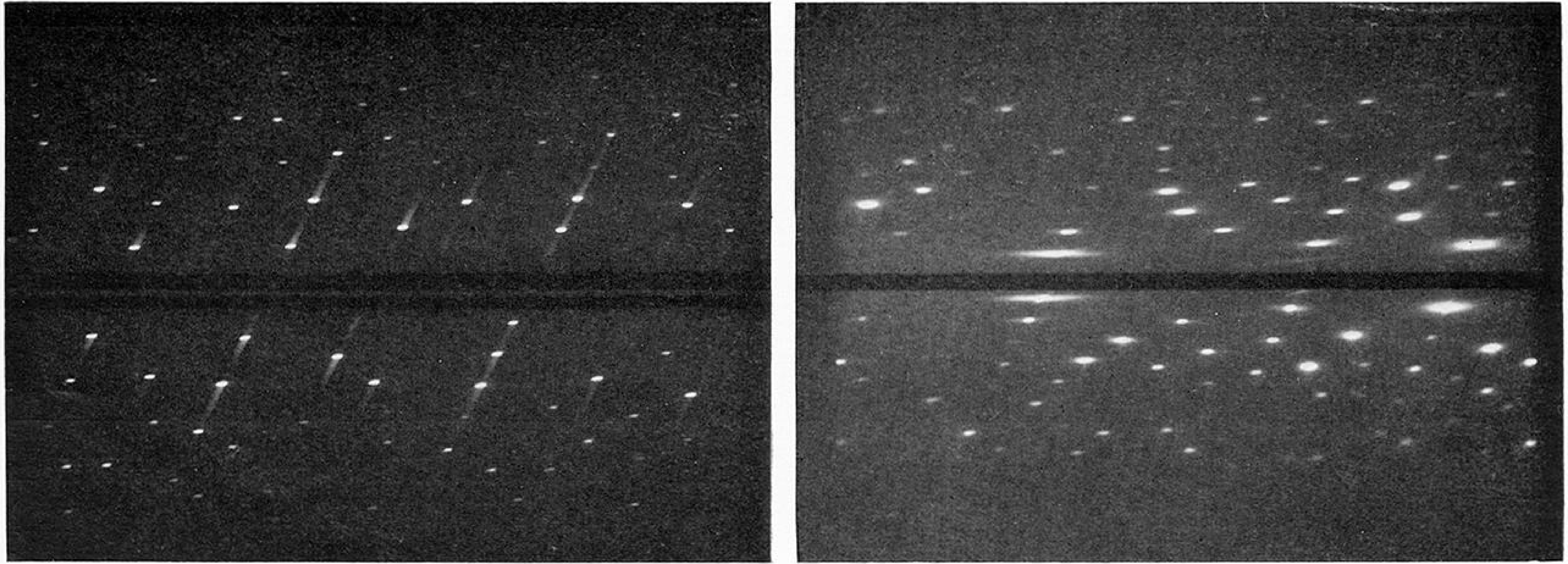
FIGURE 13. (*a*) Nonius powder pattern of anthraquinone, recrystallized from the melt.

(*b*) Nonius powder pattern of mixed anthraquinone: anthrone crystal (70 %, 30 %) recrystallized from melt.

(*c*) Nonius powder pattern of 30 %, 70 % mixed crystal.

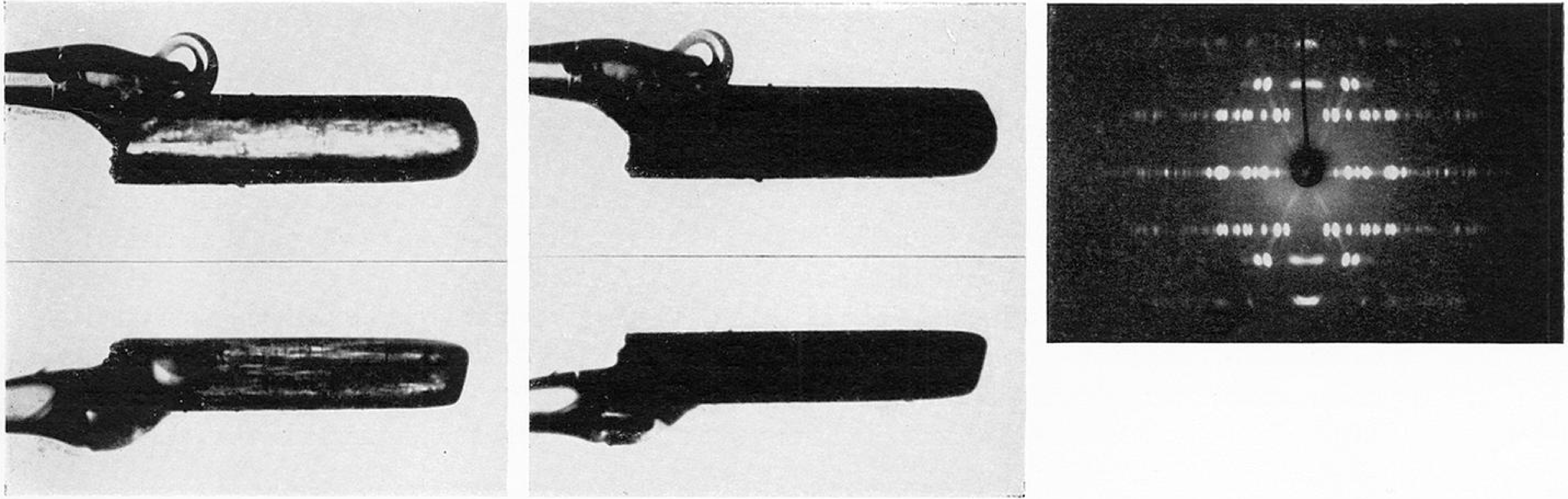
(*d*) Nonius powder pattern of anthrone. Note the variation of 201, the third line. (Some weak impurity lines are present.)

15 (*a*)



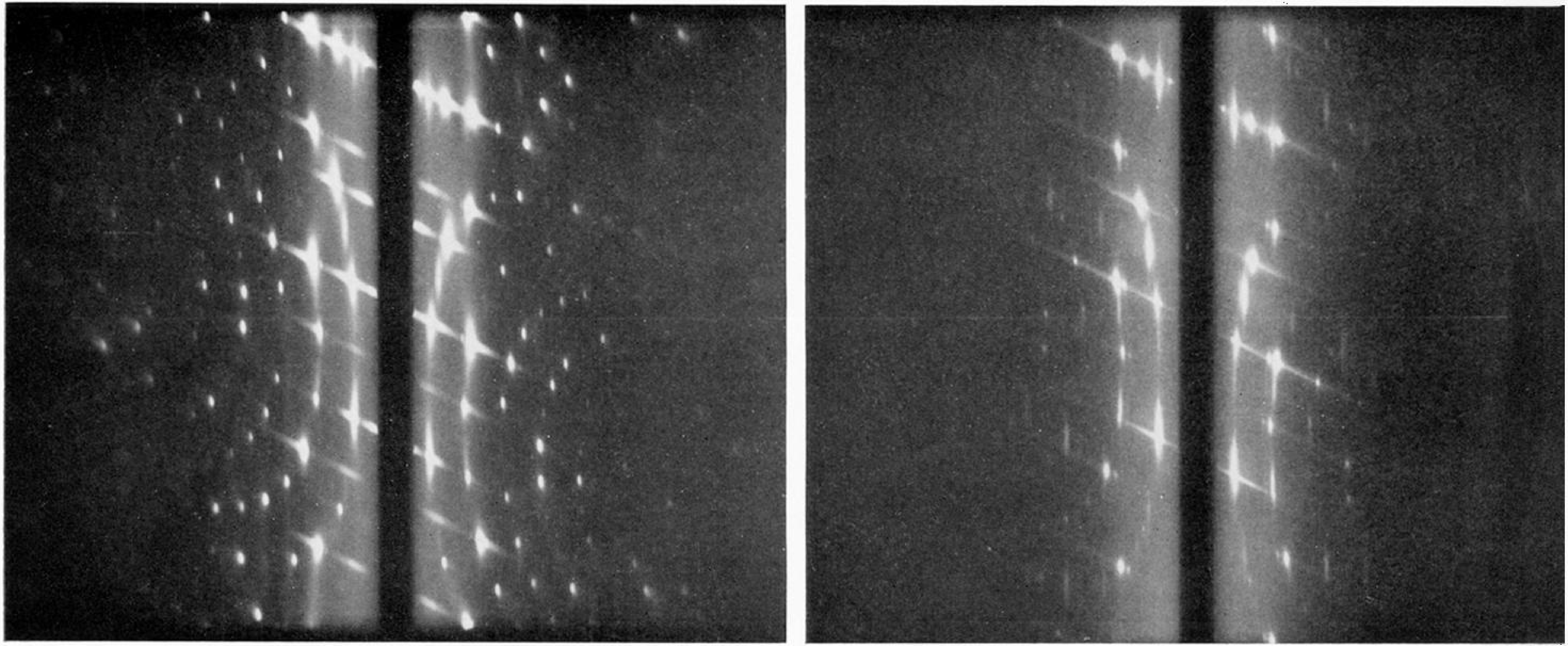
15 (*b*)

FIGURE 15. (*a*) Fresh p.o.a.: *h*0*l* Weissenberg photograph, Cu$K\alpha\beta$. Good crystal.
(*b*) *h*1*l* of another p.o.a. crystal, photograph strongly exposed.



16 (*a*) 16 (*b*) 16 (*c*)

FIGURE 16. (*a*) P.o.a. crystal before heating (magn. ×48.)
(*b*) Same after $13\frac{1}{2}$ h at 75 to 85 °C, now opaque but with no change of shape.
(*c*) X-ray photograph showing that the crystal was about half converted at this stage.



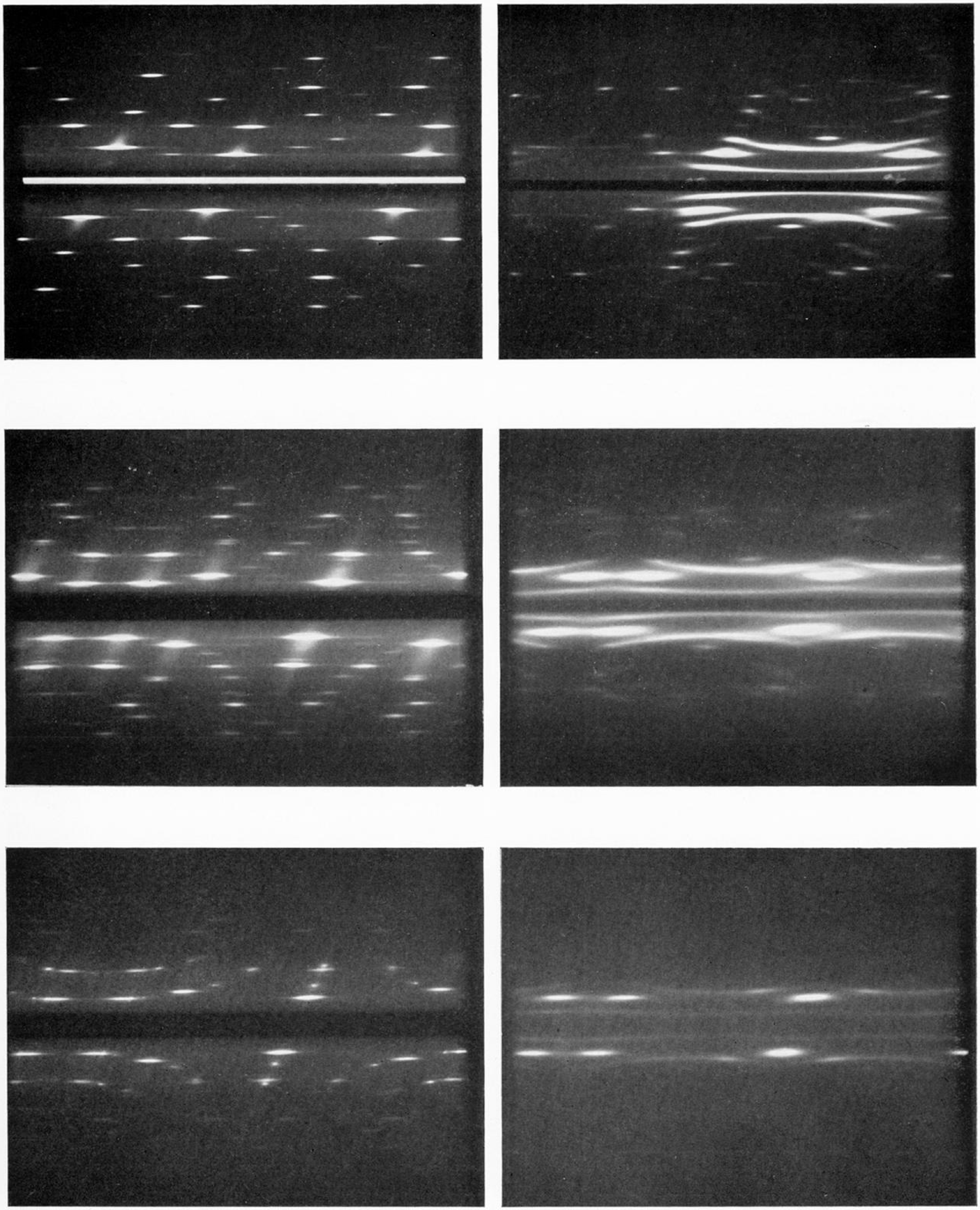
17 (*a*)

17 (*b*)

FIGURE 17. (*a*) $h0l$ Weissenberg photograph (Cu$K\alpha$, 45 h exposure time). Weak twinning across $A{:}A$ (001). The p.o.a. is single.

(*b*) A similar photograph of another crystal (Cu$K\alpha\beta$, $5\frac{1}{2}$ h exposure time) at a later intermediate stage, after 84·1 h irradiation by MoK, inside the lead cover of the X-ray tube window. (Compare 18(*b*), where the twinning is more nearly equal.)

(*c*) Interpretation of the main sets of reflexions on 17(*b*).



18 (*a*)

18 (*d*)

18 (*b*)

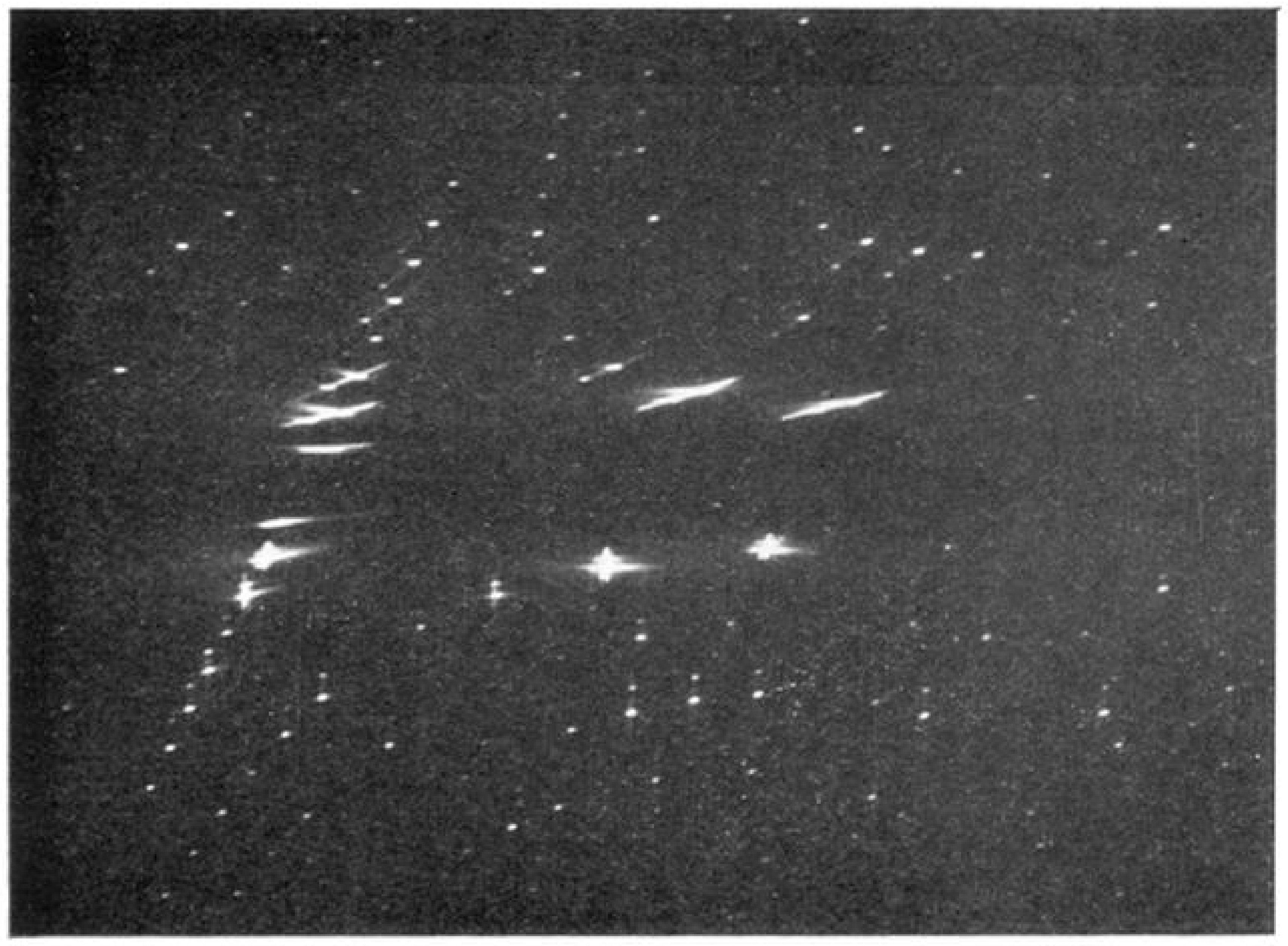
18 (*e*)

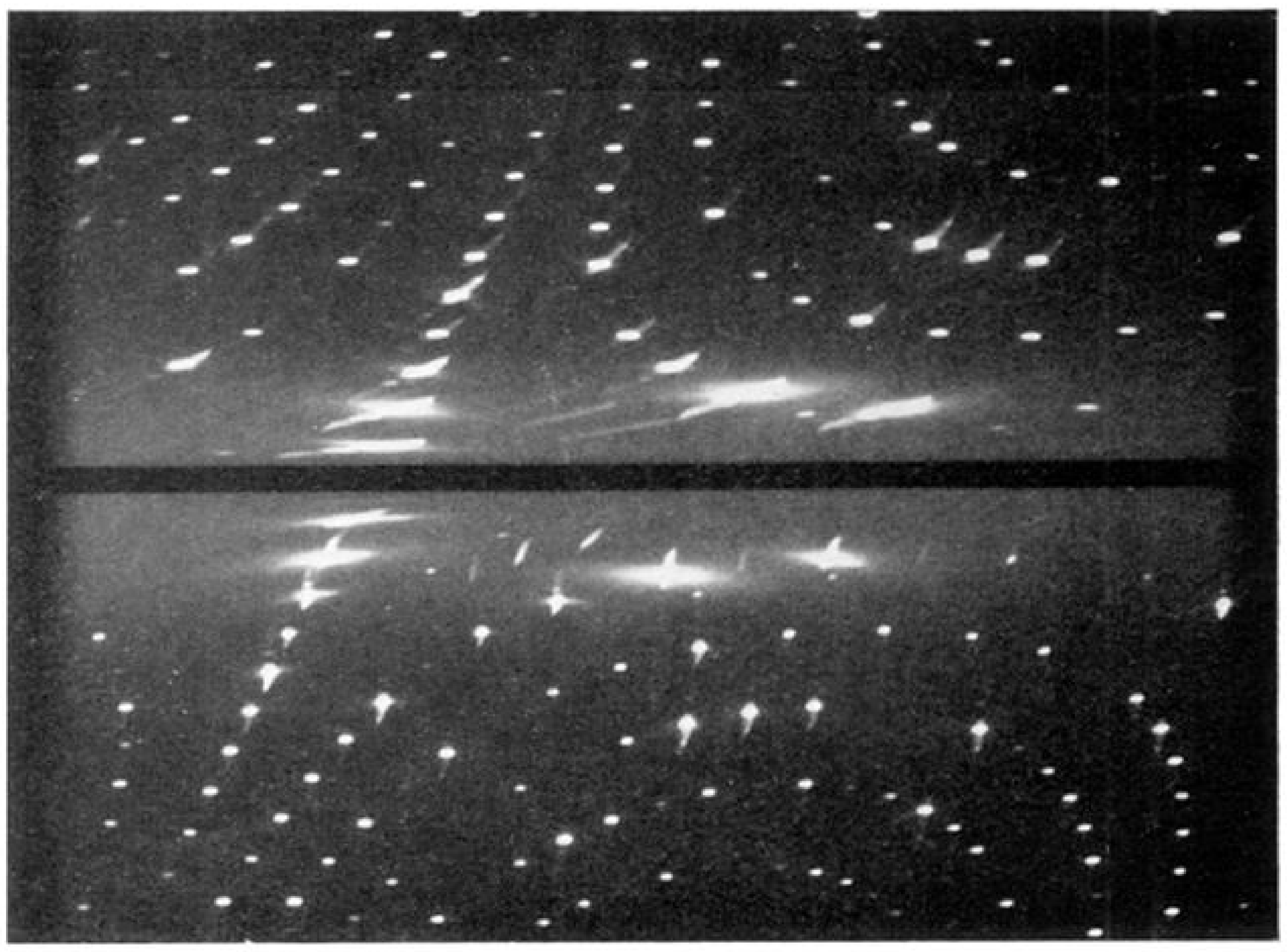
18 (*c*)

18 (*f*)

For legend see facing page.

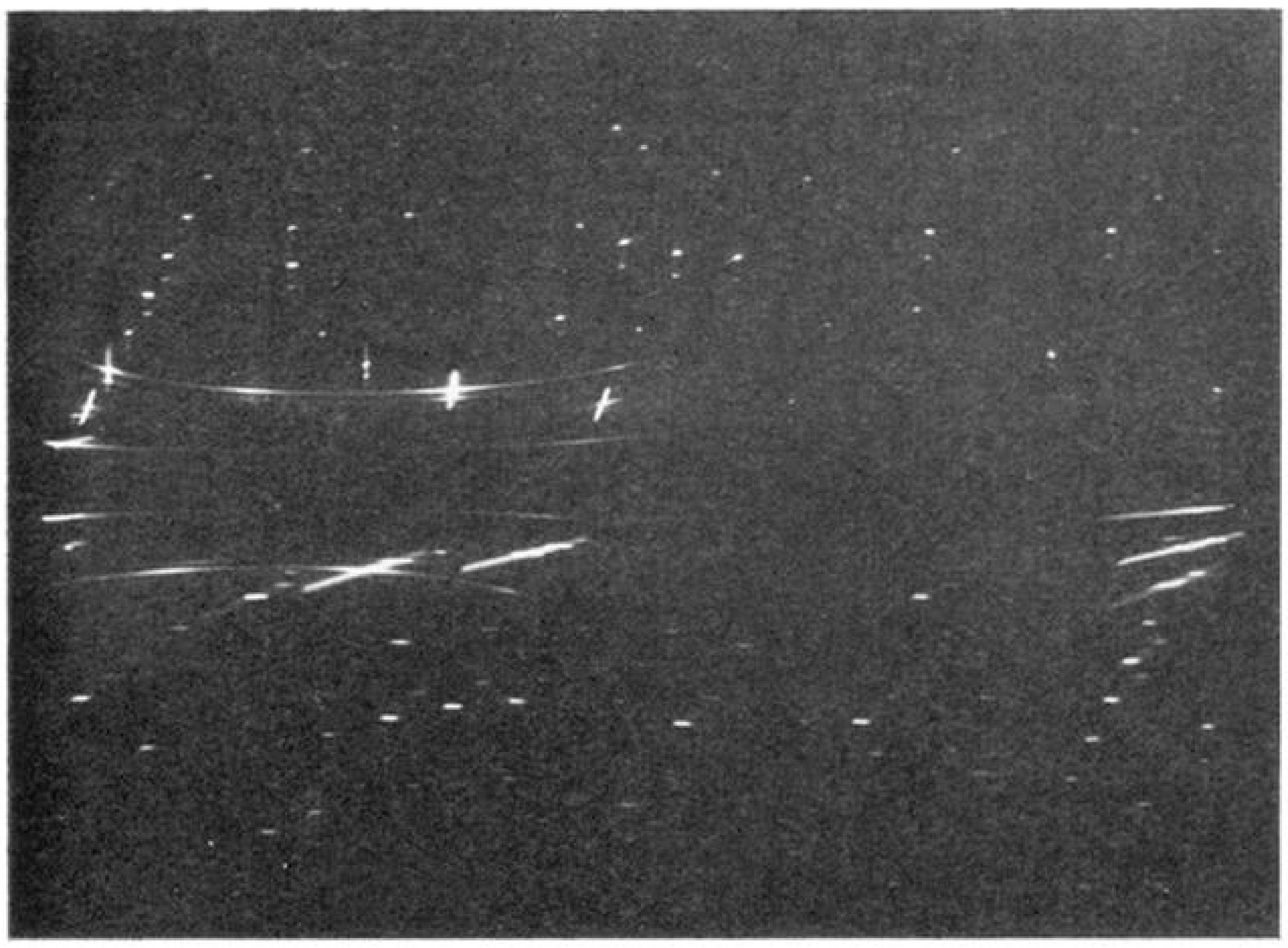
19 (*a*)





19 (*c*)

19 (*b*)



19 (*d*)

19 (*e*)

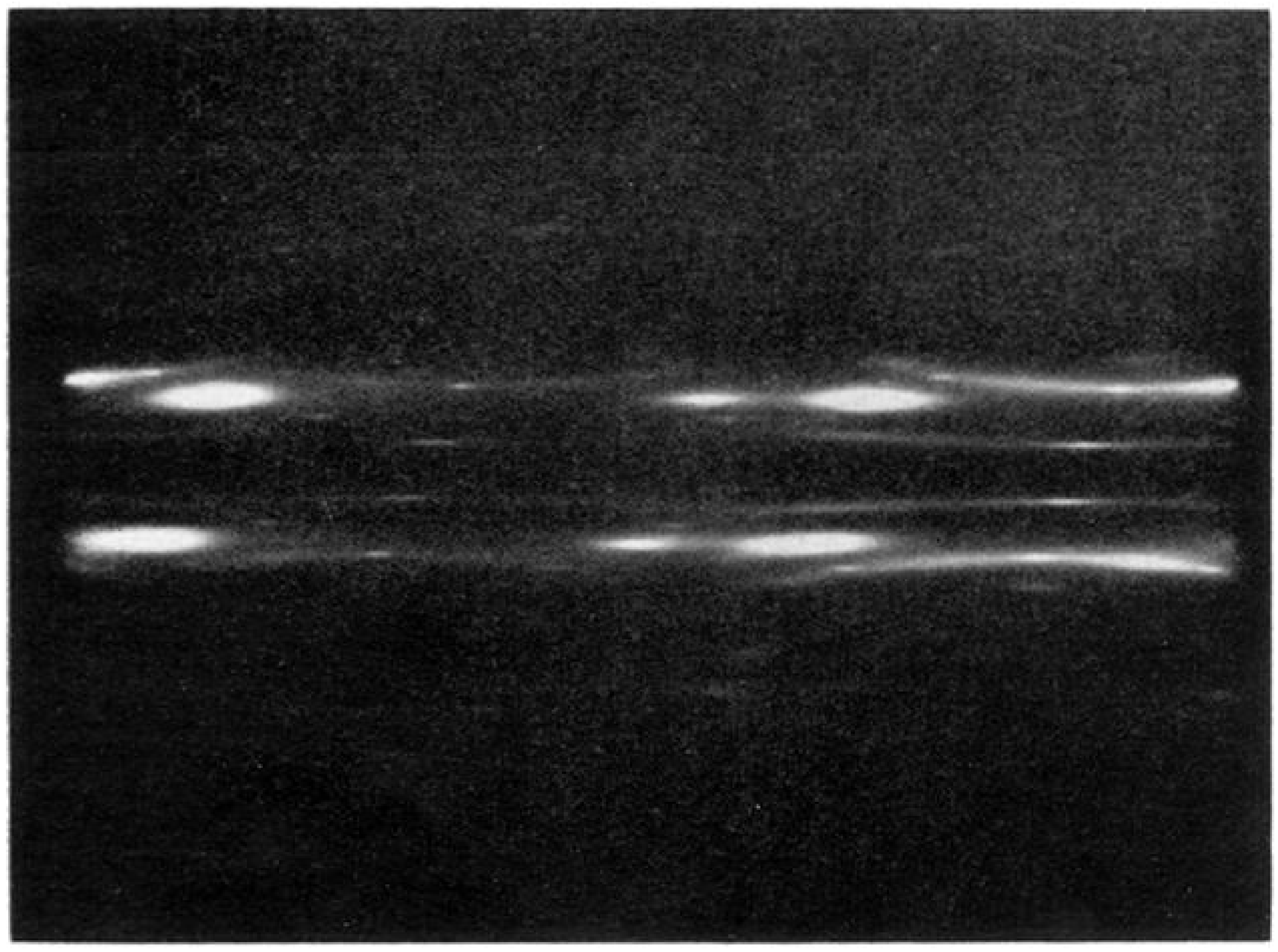


FIGURE 19. (*a*) *h*1*l* Weissenberg photograph of untwinned anthrone (Cu*K*, 7 h exposure time). The closely spaced reflexions all in a line are the *h*10. The strongest reflexions are the 011 and 111 (the latter being further from the central horizontal line).

(*b*) *h*1*l* of anthrone, recrystallized from hot acetic acid (Cu*K*, 6 h exposure time), unequally twinned across ($\bar{2}01$). The *h*10, 011, 111 of the main individual are still quite obvious. Note the sharp Cu$K\alpha$ streaking connecting 110 and $\underline{110}$ (underlining indicates twin reflexion) and 310, $\underline{111}$, 111, $\underline{310}$. Traces of the Cu$K\beta$ streak are also visible.

(*c*) *h*1*l* of anthraquinone (Cu*K*, 20 h exposure time), after heating for 6 min at 150 °C and allowing to cool. Although the 110, 210, 011, 111 (in particular) show that there is some distortion and strong thermal vibration, no twinning or streaks appear of the 19(*b*) type.

(*d*) *h*1*l* of 50:50 anthraquinone/anthrone mixed crystal from the melt (Cu*K*, 17 h) twinned about ($\bar{2}01$) but showing no streaks of the 19(*b*) type; rather distorted.

(*e*) *h*1*l* of a converted specimen (Cu*K*, 5 h; after 137 h Cu*K* irradiation) showing sharp, small super-lattice reflexions. Unequal twinning on both ($\bar{2}01$) and (001). Longer exposures did not bring up any more reflexions.

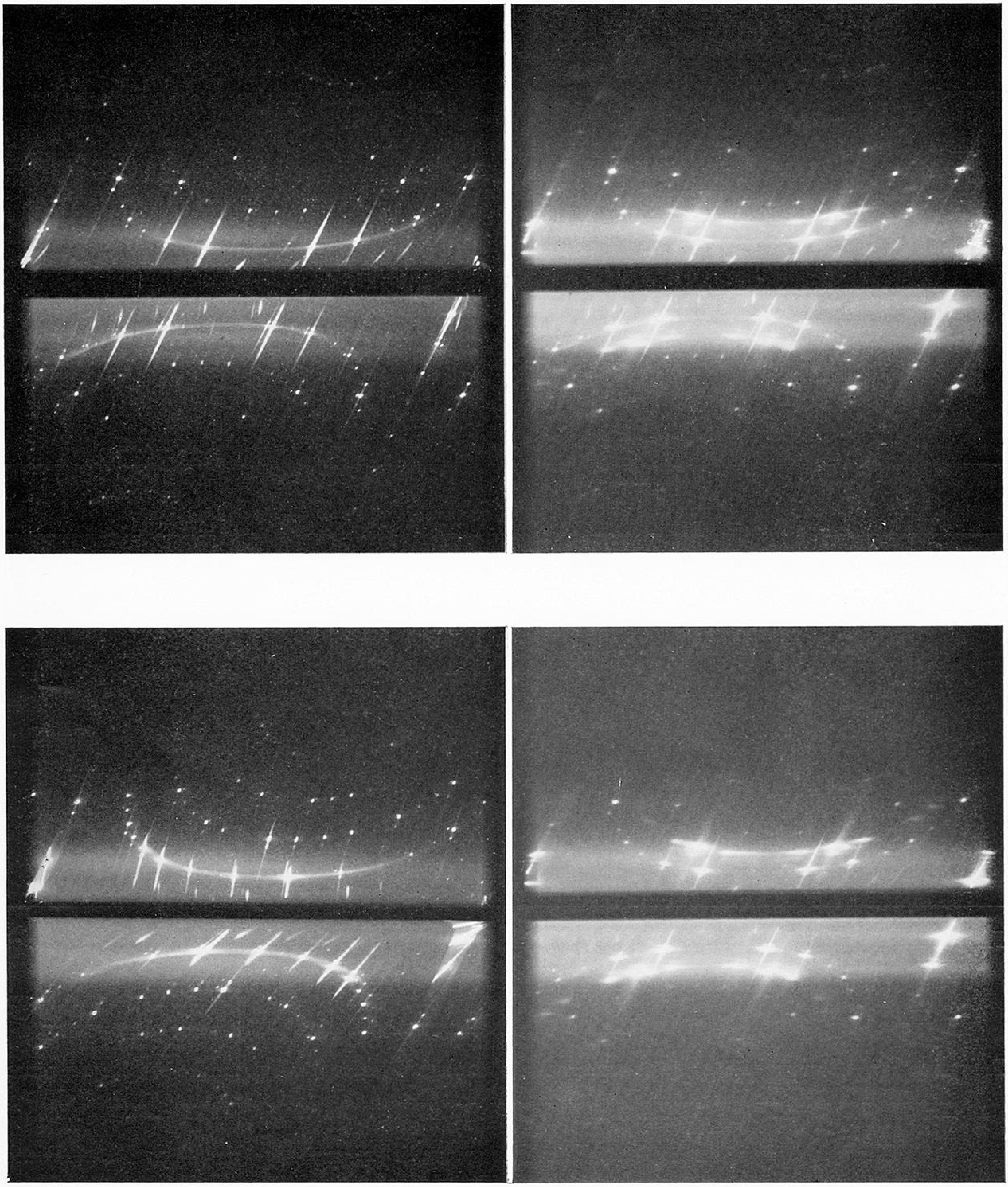


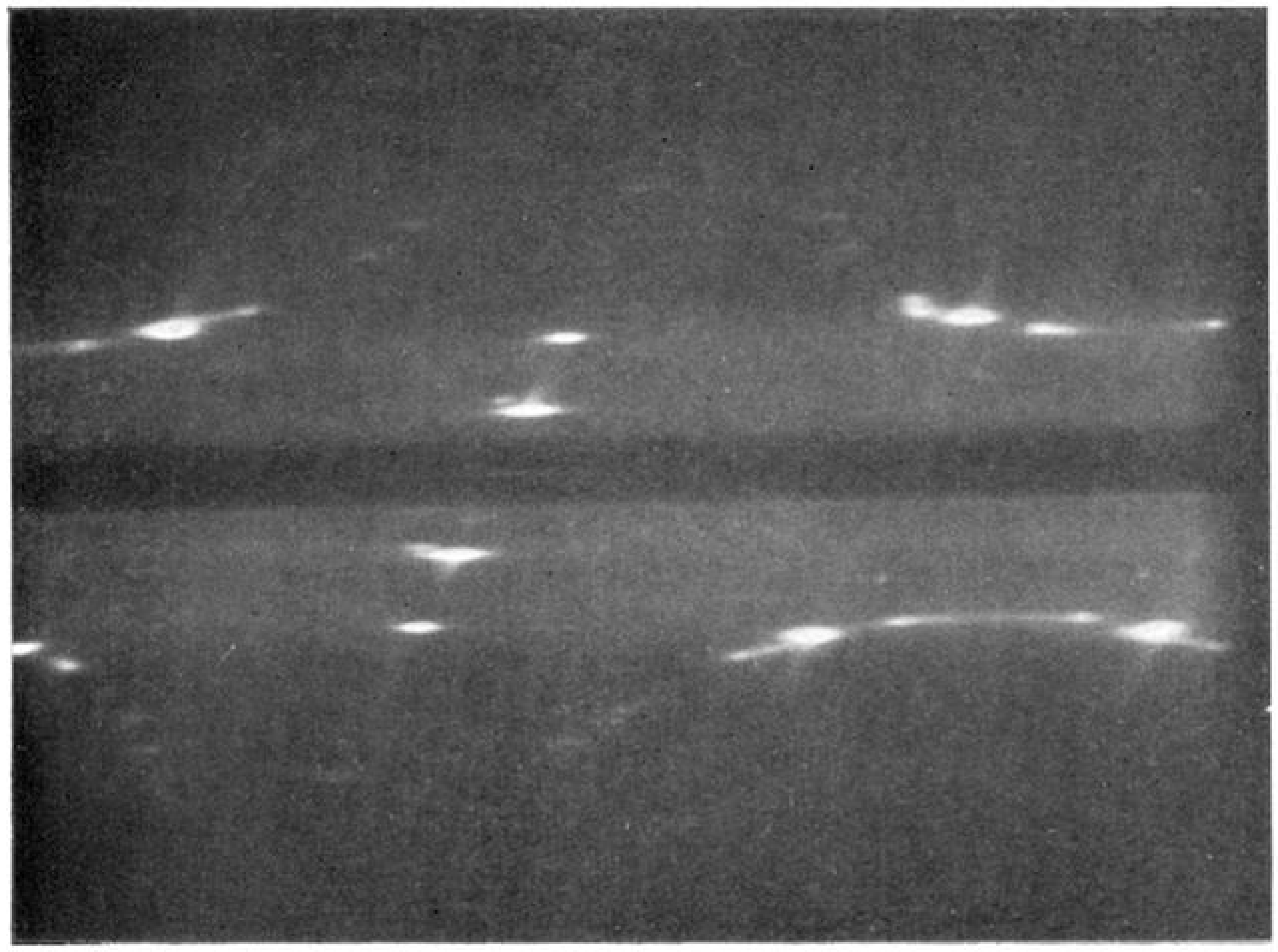
Figure 22. (*a*) *hk*0 Weissenberg photograph of almost fresh p.o.a. (2 to 8 h Cu*K* irradiation, that is, 6 h exposure time), showing sharp festoons out to $k = 5$.

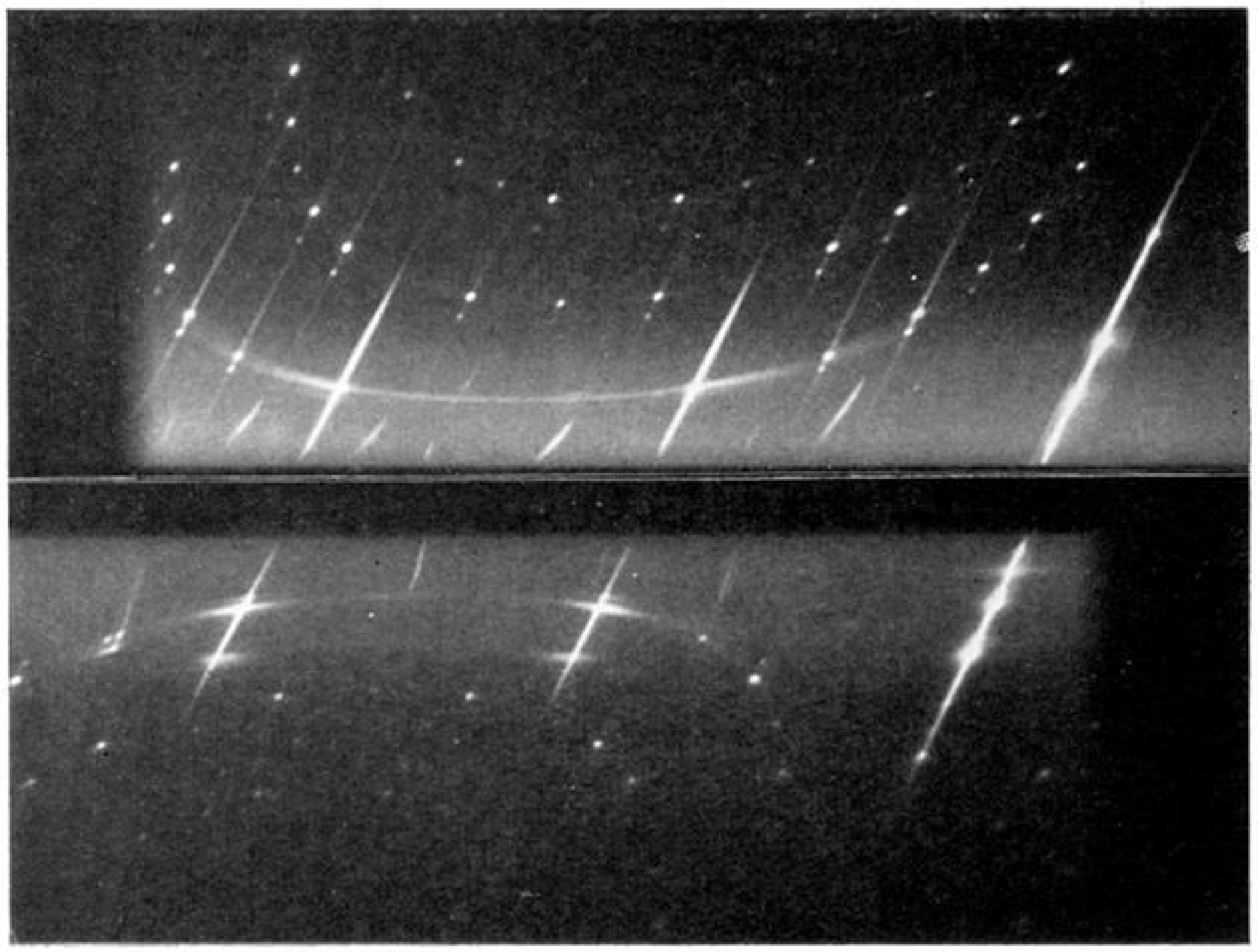
(*b*) *hk*1 of the same specimen after 8 to 14 h Cu*K* irradiation (that is, 6 h exposure time after a previous 8 h irradiation).

(*c*) *hk*0 of the same specimen after 14 to 20 h irradiation.

(*d*) *hk*0 of the same specimen after 50 to 56 h irradiation.

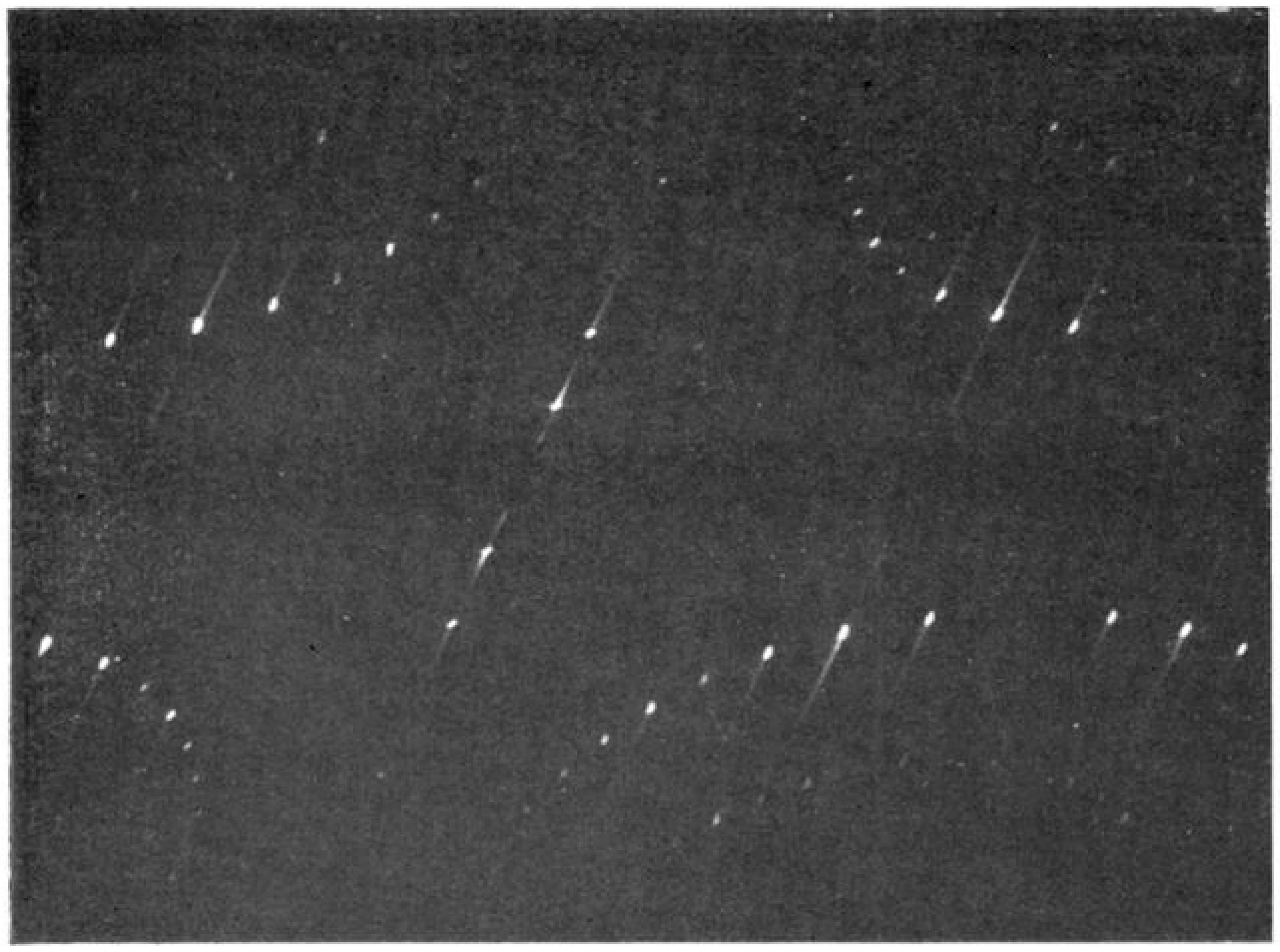
23 (*a*)

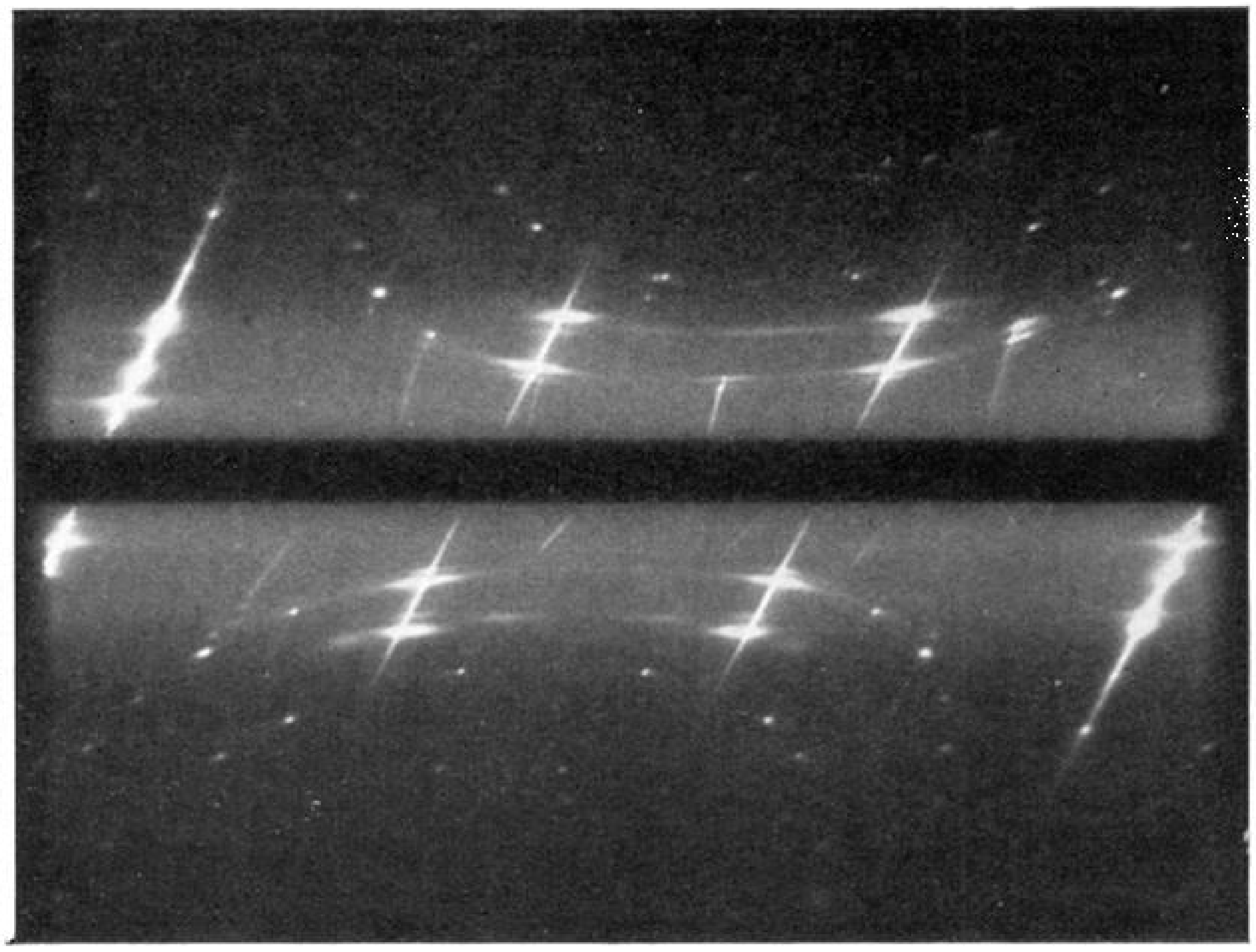




24 (*a*)

23 (*b*)





24 (*b*)

FIGURE 23. (*a*) *hk*0 of the same specimen as in figure 22 after 480 h irradiation, when only a trace of p.o.a. remains as very small, sharp 110 reflexions.

(*b*) *hk*0 of anthraquinone for comparison with figures 22(*d*) and 23(*a*). Note the presence on figures 22(*d*), 23(*a*) and 24(*b*) of *A*:*A h*10 reflexions where *h* is odd. These are quite strong.

FIGURE 24. (*a*) Composite 0*kl* Weissenberg photograph of almost fresh p.o.a. *above* (6 h exposure time, Cu$K\alpha\beta$), with the same after 40 h Cu*K* irradiation *below* (3 h exposure time, Cu$K\alpha\beta$). The sharp p.o.a. festoons are still visible after 40 h.

(*b*) The same after 49 to 55 h Cu*K* irradiation. As in the case of 18(*d*, *e*, *f*) and 19(*b*, *d*) the twinning across ($\bar{2}01$) produces apparent $01\frac{1}{2}$, $01\frac{3}{2}$ reflexions which are in fact $\underline{110}$, $\underline{310}$. They are weaker than the corresponding 110, 310 reflexions seen on figures 23(*a*, *b*). (This specimen was unfortunately lost before the final 0*kl* photograph, after full conversion, could be obtained.)