attendre par le chlore, mais par les groupements OH ou NH_2. Ceci peut s'observer sur la Fig. 6.

Tous les dérivés de la naphtoquinone-1,4 forment des empilements de molécules parallèles et distantes d'environ 3,5 Å. Les structures déjà étudiées permettent de ne distinguer qu'un nombre restreint d'empilements différents.

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Twinned Crystals. III. γ-*o*-Nitroaniline

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Crystallographic results are given for the β and γ phases of *o*-nitroaniline, the latter being the stable phase at 25 °C. The γ phase was reported by some earlier workers as orthorhombic and by others as twinned monoclinic. It is now confirmed as monoclinic, polysynthetically twinned on (100). The reasons for the earlier erroneous conclusions are discussed. Related examples from the literature are reviewed briefly; in some of these twinning has been detected while in others the diffraction patterns have been described in terms of complex unit cells which would appear to require reconsideration.

No twinned β-phase crystals were found.

Introduction

The essential first step in crystal-structure analysis is correct indexing of the diffraction patterns (Buerger, 1960, chapter 5). A wrong structure will be obtained if the initial indexing is wrong, *e.g.* the structure proposed for acetylcholine bromide (Sörum, 1959) has been shown to be wrong because twinning of the crystal used had not been detected (Dunitz, 1963). Thus further investigation of unusual diffraction patterns or crystals of uncertain or contradictory crystallography is desirable in order to build up a fund of experience that will help avoid such errors in future. In the first two papers of this series it was shown that the unusual diffraction patterns of 10-methyl-1,2-benzanthracene (Herbstein, 1964) and α-1,2:4,5-tetrachlorobenzene (Herbstein, 1965) could be explained in terms of twinning. A similar explanation is now advanced to account for the contradictory information given in the literature about the crystallography of *o*-nitroaniline, which gives diffraction patterns that are, at first sight, quite normal. It is also shown how these diffraction patterns from twinned monoclinic crystals could be plausibly but incorrectly interpreted in terms of an orthorhombic unit cell.

Previous work

Early goniometric work on *o*-nitroaniline (Jaeger, 1905; Groth, 1919, p. 180) indicated that the crystals were orthorhombic bipyramidal with axial ratios 0·6834:1:0·5792. Herrmann & Burak (1928) deduced from oscillation photographs about [100], [010], [001], [110], [101] and [011] that

$$a=29{\cdot}50,\ b=10{\cdot}11,\ c=8{\cdot}54\ \text{Å}.$$

These values have been converted to Å by multiplying by 1·00202 and the original *a* and *b* axes have been interchanged here (and in the rest of this paper) to facilitate comparison with other results. The space group was reported as V_h^{17} (D_{2h}^{17}–*Bbmm* with the present orientation), the non-centrosymmetric possibilities being omitted. The calculated density (for 16 molecules in the unit cell) was 1·45 g.cm^{-3}, in good agreement with the measured value of 1·442 g.cm^{-3} (Jaeger, 1905; Hartshorne, Walters & Williams, 1935).

The optical and goniometric studies of Dippy & Hartshorne (1930) (preliminary results) and Hartshorne & Stuart (1931) were made on carefully purified

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material and this enabled these workers to distinguish three phases by use of their melting points (α: 68·2°; β: 70·1$_5$°; γ: 71·2$_5$°). Monoclinic symmetry was assigned to all three phases from examination of their optical properties with a polarizing microscope and fine scale twinning of the γ phase was detected in the same way. Hartshorne & Stuart (1931) identified their γ-phase crystals with those examined by Jaeger (1905) and Herrmann & Burak (1928) and pointed out that their results did not entirely agree with those of the earlier workers.

Observation of definite melting points for β- and γ-phase crystals and no $\gamma \rightarrow \beta$ transformation suggests that these two phases are monotropically related, *i.e.* at atmospheric pressure the β phase is always metastable with respect to the γ phase.

Kitaigorodskii (1948) briefly reported that the crystals had the same cell dimensions as those given by Herrmann & Burak; although pseudo-orthorhombic, their actual symmetry was monoclinic, the probable space group being $B2_1/a\,(C_{2h}^5)$ (a and c axes interchanged here). No mention was made of twinning.

Experimental

Good crystals of the γ and β phases were obtained by recrystallization from ethanol–water mixtures. Mixtures containing about equal volumes of ethanol and water gave the γ phase (in agreement with Hartshorne & Stuart) while mixtures of greater water content gave β-phase crystals. No quantitative study was attempted of this interesting observation.

The γ-phase crystals were short orange needles showing straight extinction and marked pleochroism. The β-phase crystals (see below) were long thin orange laths showing straight extinction. Our melting point measurements on the two phases were not accurate enough to confirm the difference reported by Hartshorne & Stuart. It was noticed that β-phase crystals held in a stoppered bottle at ~25 °C for some months had become opaque and that needles had grown out of them. No changes were observed in γ-phase crystals under similar conditions. This evidence supports the conclusions of Hartshorne & Stuart that the γ-phase is stable with respect to the β-phase at 25 °C. Both phases have a relatively high vapour pressure and were therefore sealed into thin-walled glass capillaries before X-ray photography. All photographs were taken with Cu $K\alpha$ (nickel-filtered) radiation. Results for the γ phase are discussed immediately below, while those for the β phase are given at the end of the paper. The α phase has not been encountered in our work.

Crystallography of the γ-phase

An oscillation photograph about the needle axis had a mirror plane and a repeat distance of $8{\cdot}57 \pm 0{\cdot}03$ Å. The needle axis was thus identified as [001] in terms of the unit cell given by Herrmann & Burak. The $hk0$ and $hk1$ equi-inclination Weissenberg photographs both had symmetry planes 90° apart along the ω direction so that at this stage it seemed that the γ phase was orthorhombic.

Confirmation was sought from precession photographs of crystals set to rotate about [001].

Zero and first-level precession photographs ($\mu = 30°$) were taken with X-rays incident along an axis with 10·0 Å spacing (from a cone-axis photograph). Thus X-rays entered along [010] and the precession photographs were of the $h0l$ and $h1l$ layers. The reflexion *positions* on these photographs conformed to orthogonal nets with reciprocal spacings corresponding to Herrmann & Burak's values of a and c, but reflexion *intensities* showed small but definite deviations from *mm* symmetry. The true crystal symmetry was thus monoclinic and not orthorhombic and the orthogonal arrangement of reflexion positions was due to the twin relationship of two monoclinic **a*c*** nets, the volumes of the two individuals being nearly equal (Fig. 1). Similar photographs were taken of a number of crystals and these showed small differences in the extent to which they deviated from apparent orthorhombic symmetry. Evidently the relative volumes of the two individuals of a twin differ slightly from crystal to crystal; no untwinned γ-phase crystals were found.

The twinned **a*c*** nets of the $h0l$ precession photograph can be indexed in two ways, which give the same cell dimensions but different systematic absences:

(*a*) The reciprocal lattices of the two individuals superpose for l even [$(h0l)_1$ on $(h+l,\ 0,\ \bar{l})_2$, the subscripts indicating the individual from which the reflexion comes] but not for l odd. The systematic absence is $h0l$ absent for h odd [Fig. 1(*a*)].

(*b*) The reciprocal lattices of the two individuals superpose at all reciprocal lattice points. The systematic absence is $h0l$ absent for h odd, l even [Fig. 1(*b*)].

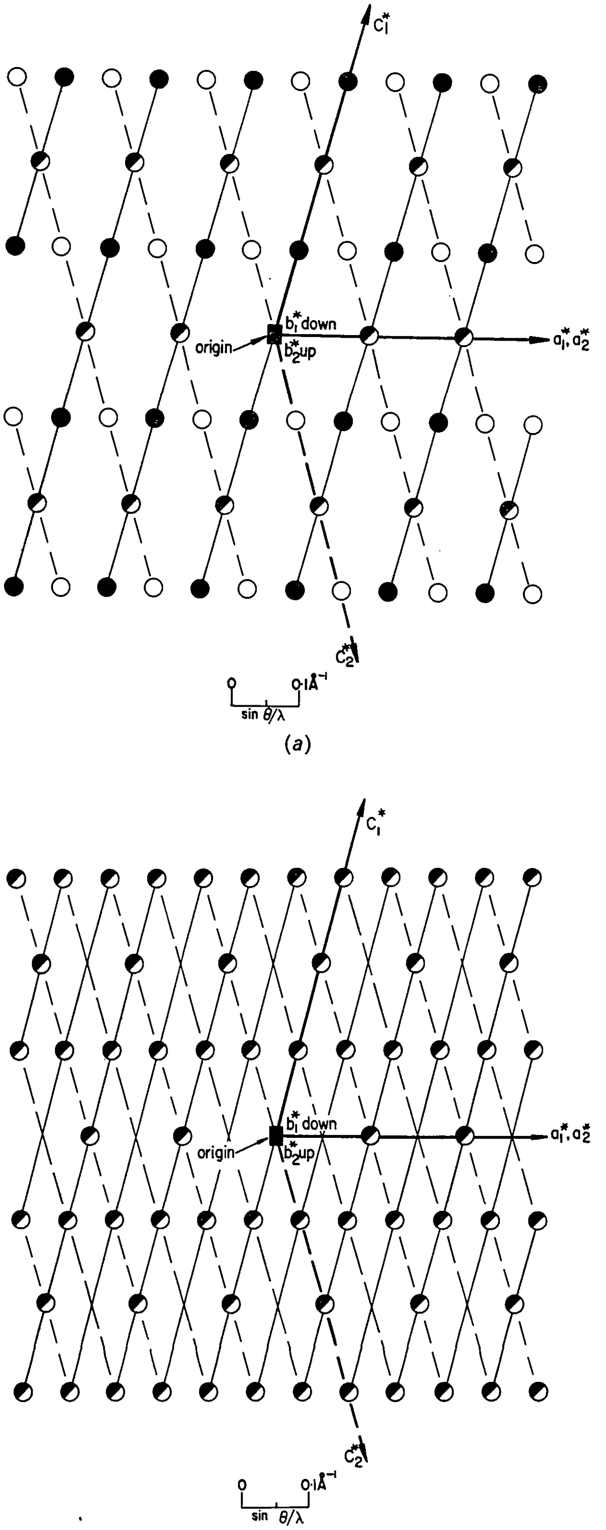
Thus the first method of indexing shows that there is an a glide plane present, whereas the systematic absence resulting from the second alternative does not correspond to any particular symmetry element. Both individuals contribute to all reflexions on the $h1l$ photograph which has no systematic absences.

The $0k0$ systematic absence was determined from another set of zero and first-layer precession photographs taken after increasing the dial-angle setting by 90° from that for the first set of precession photographs. These photographs of non-zonal sections through the reciprocal lattice show that $0k0$ is absent for k odd and confirm that $[010] = 10{\cdot}0 \pm 0{\cdot}05$ Å.

The crystallographic results deduced from the precession camera photographs are:

$$a = 15{\cdot}28 \pm 0{\cdot}03,\ b = 10{\cdot}0 \pm 0{\cdot}05,\ c = 8{\cdot}54 \pm 0{\cdot}03\ \text{Å};\quad \beta = 105\tfrac{1}{2} \pm 1°.$$

The space group is $P2_1/a$; with 8 molecules in the unit cell the calculated density is $1{\cdot}46 \pm 0{\cdot}01_5$ g.cm^{-3}, in good agreement with the measured value of 1·442 g.cm^{-3}.



(a)

(b)

Fig. 1. Twinned **a*****c*** nets deduced from $h0l$ precession photograph. Alternative ways of indexing are shown at (a) and (b). No attempt has been made to represent relative intensities of reflections.

Optical goniometric data were obtained for crystals rotated about [001]. The measured interfacial angles agreed well with those reported previously but the faces are here indexed in terms of the monoclinic cell deduced above. The (100), (210), (110) and (010) faces of a single individual were found. The two latter faces were not always present.

Comparison of the present X-ray diffraction results with those of Herrmann & Burak shows that [010] and [001] agree well, the present value of d_{100} is half the earlier value of [100], while β, the space group and number of molecules per unit cell differ. The present X-ray results agree well with Hartshorne & Stuart's conclusions regarding crystal symmetry, the presence of twinning and the orientation of the crystals (they pointed out that the b axis of the monoclinic crystals was the b axis of the pseudo-orthorhombic crystals). The primitive unit cell given above can be easily transformed into the unit cell centred on the B face that was preferred by Kitaigorodskii (1948).

Interpretation of oscillation and Weissenberg photographs of the γ-phase

The relative dispositions of the reciprocal lattices of two individuals twinned on (100) are sketched in Fig. 2(a). In a monoclinic crystal $I(hkl)=I(h\bar{k}l)$ and thus an oscillation photograph about [001] will have a plane of symmetry if the effective diffracting volumes of the two individuals are equal. In the first-layer Weissenberg photograph about [001] one finds exact coincidence of $(hk1)_1$ and $(h+1, \bar{k}, \bar{1})_2$ reflexions and this means [see Fig. 2(b)] that $|\mathbf{c}^*| \cos\beta^* = \frac{1}{2}|\mathbf{a}^*|$. The respective measured values are 0·0337 and 0·034 Å^{-1}. This coincidence of reflexions leads to simplification of the photographs because all reflexions are composite except for $h0l$ reflexions with l odd, where the space-group absence ($h0l$ absent for $h\neq 2n$) leads to disappearance of the contribution from either the first or the second individual.

The contributions of the two individuals to a first-layer Weissenberg photograph about [001] are shown in Fig. 2(b). One quadrant will be made up of $(hk1)_1 + (h\bar{k}\bar{1})_2$ and a second of $(\bar{h}\bar{k}\bar{1})_2 + (\bar{h}k1)_1$. If the effective diffracting volumes of the two individuals are the same, then these two quadrants will also present the same appearance although they are not related by the (monoclinic) symmetry of the crystal. The additional apparent symmetry of oscillation and Weissenberg photographs is thus due to the twinning; it is clear from Fig. 2(b) that reflexions occur along the true symmetry line of the $hk1$ Weissenberg photograph but not along the line of apparent symmetry. This situation occurs in the same or modified form (i.e. a paucity of reflexions instead of a complete absence) in diffraction patterns of similarly twinned monoclinic or triclinic crystals (cf. 10-methyl-1,2-benzanthracene (Herbstein, 1964) and α-1,2:4,5-tetrachlorobenzene (Herbstein, 1965)) and provides a useful starting point for the recognition of the existence of twinning and the subsequent interpretation of the diffraction patterns.

Relation of present and previous diffraction results for γ-phase

If the deviations from orthorhombic symmetry on the precession photographs are ignored, then analysis of these photographs leads to the same cell dimensions and space group as reported by Herrmann & Burak but with additional absences *h*00 absent for $h \neq 4n$, 00*l* absent for $l \neq 4n$ [these absences were not reported by Herrmann & Burak, who noted the occurrence of 600 (weak) and 002 (medium to weak)]. It seems that Herrmann & Burak understandably but erroneously ascribed the mirror-plane symmetry of their oscillation photographs to orthorhombic symmetry instead of to twinning.

Very similar volumes for the two individuals are quite feasible from a physical point of view, particular-

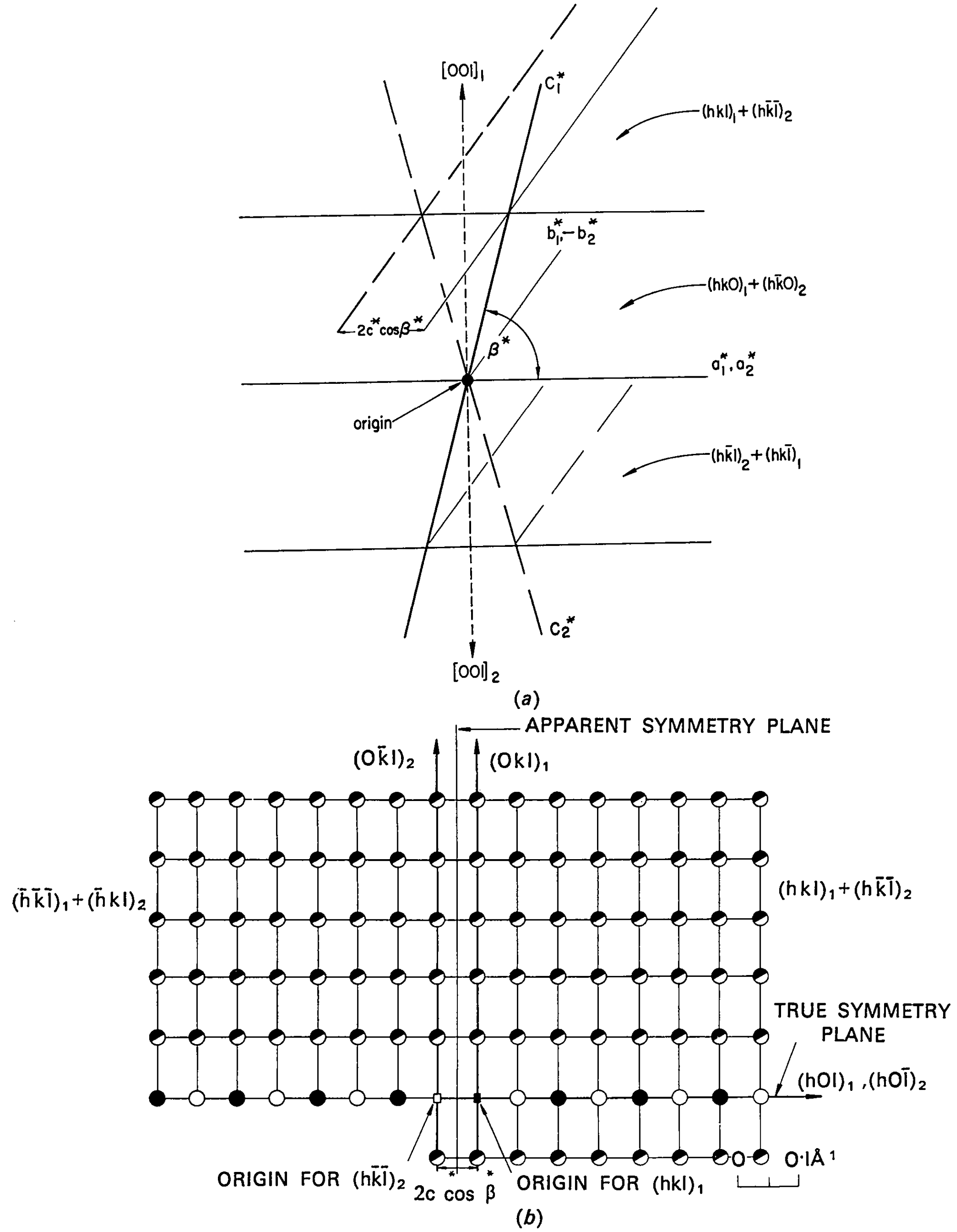


Fig. 2. (*a*) The relative disposition of the reciprocal lattices of two twinned individuals. This diagram is only approximately to scale. (*b*) Twinned **a*b*** nets deduced from the *hkl* Weissenberg photograph. No attempt has been made to represent relative intensities of reflections.

ly if fine-scale twinning occurs. In this event only the extra *h*00 and 00*l* absences would deter one from preferring one of the possible orthorhombic space groups to an interpretation of the diffraction patterns in terms of twinning. Buerger (1960, chapter 5) has pointed out that reports of certain space groups (*e.g. Pmmm*) may be wrong because twinned reciprocal lattices were indexed in terms of a single unit cell. The present results suggest that reports of space group *Bbmm* should also be viewed with caution, particularly if one cell edge is larger than usual. It would appear desirable to photograph a number of crystals before accepting one of these space groups as correct.

Description of twinning in γ-phase crystals

The relative disposition of the reciprocal axes is shown in Figs. 1 and 2(*a*) and that of the direct cells of the two individuals in Fig. 3. The twin plane is (100). The *hk*0 and *hk*1 Weissenberg photographs show that lattices can be chosen for the two individuals of the twin which will be parallel to each other within experimental error. Thus γ-*o*-nitroaniline is an example of twinning by merohedry in terms of Friedel's classification (Cahn, 1954). It is to be emphasized that Friedel's classification of twins is based on lattices and not on structure.

The reflexions on the *hk*0 Weissenberg photographs of γ-*o*-nitroaniline are sharp but those on the *hk*1 Weissenberg photographs are joined by weak diffuse streaks running parallel to **a***. A similar situation (but with much more marked streaking) has been observed with crystals of $Zn(N_2H_4)_2Cl_2$ which are twinned on (100) (Braibanti, Bigliardi, Lanfredi & Camellini, 1964) and has been explained as due to the occurrence of polysynthetic twinning parallel to (100) (Braibanti, Bigliardi & Lanfredi, 1964). The latter authors have also shown that the presence of diffuse scattering on *hk*1 photographs but its absence on *hk*0 photographs implies the irrationality of either or both of $a \cos \beta / c$ and the lattice displacement (Δ_c in their notation). It has already been shown that $a \cos \beta / c = 2$ for γ-*o*-nitroaniline so that Δ_c must be irrational. This cannot be tested because the crystal structure is not known. The weakness of the diffuse streaks suggests that the polysynthetic twin domains are relatively large.

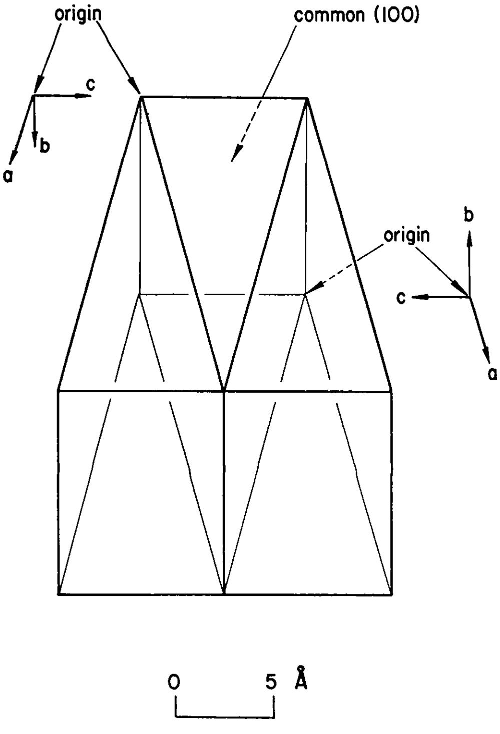


Fig. 3. The orientation relationship between the unit cells of two twinned individuals. The diagram is only approximately to scale.

Similar twinning in other crystals

No attempt has been made to survey the presumably large number of similar examples of twinning already reported, but comparison with some other crystals is worth while. The equimolar molecular compound of naphthalene and pyromellitic dianhydride (Boeyens & Herbstein, 1965) shows the same type of twinning but no ambiguity occurs because the individuals are usually clearly different in size. Partial coincidence of the reciprocal lattices of the two individuals occurs and the twinning is by reticular (or lattice) merohedry in terms of Friedel's classification. The twin plane is (100). The monoclinic crystals of 10-methyl-1,2-benzanthracene (10-methylbenz-*a*-anthracene) (Herbstein, 1964) are twinned on (001) and corresponding layers of the reciprocal lattices (*e.g.* the composite *h*0*l* layers shown in Fig. 1 of Herbstein (1964) and Fig. 1 of the present paper) have the same appearance, the bunching and spreading-apart of reflexions being particularly striking. Similar twinning on (100) in $Zn(N_2H_4)_2Cl_2$ has already been mentioned and is also found in the isostructural $Mn^{II}(N_2H_4)_2Cl_2$ (Ferrari, Braibanti & Bigliardi, 1962). The twinning in all these crystals is similar to that found in γ-*o*-nitroaniline but there are differences in detail.

The crystallography of tetracyclohexyldiphosphine disulphide $[(c\text{–}C_6H_{11})_2(S)P\text{–}P(S)(c\text{–}C_6H_{11})_2]$ (Issleib & Gründler, 1964) seems to be similar to that of *o*-nitroaniline. The compound crystallizes as needles (α phase) and plates (β phase). The α phase was reported as orthorhombic, with $a = 27{\cdot}5$, $b = 114{\cdot}5$, $c = 10{\cdot}1$ Å, no systematic absences. The β phase was reported as triclinic with $a = 19{\cdot}30$, $b = 18{\cdot}13$, $c = 15{\cdot}62$, $\alpha = \beta = \gamma = 90°$, space group probably $P\bar{1}$. It seems probable that the α-phase crystals are twinned and that reinterpretation of the diffraction patterns on this basis is required. Another crystal where reinterpretation of the diffraction patterns seems desirable is anhydrous nitric acid at an unspecified temperature below -42 °C. These crystals were reported as monoclinic, $\beta = 90°$, with 16 molecules in the unit cell. Non-space-group absences occurred and there were diffuse streaks in the direction of **a*** (Luzzati, 1951). In view of the present and previous results, it seems possible that the crystals were twinned in a way which was not considered during the original indexing of the diffraction patterns.

Some other crystals in which the apparent orthorhombic symmetry of the diffraction patterns is due to twinning have been discussed recently by Dunitz (1964). In these examples the selection rules governing the appearance of reflexions were not characteristic of any orthorhombic space group and discussion of possible molecular arrangements compatible with the selection rules was found to necessitate abandonment of the orthorhombic symmetry. These conclusions were confirmed by optical means or by discovery of truly single-crystal fragments which gave diffraction patterns of lower symmetry than orthorhombic.

Crystallography of the β phase

Suitable Weissenberg and precession photographs gave the following crystallographic results for the β phase:

$$a=13{\cdot}8\pm0{\cdot}05,\ b=3{\cdot}90\pm0{\cdot}04,\ c=23{\cdot}4\pm0{\cdot}05\ \text{Å};\quad \beta=94\tfrac{1}{2}\pm\tfrac{1}{2}^\circ.$$

The space group is $P2_1/c$. Additional absences are $h00$ absent (or very weak) for $h\neq2n$, $00l$ absent for $l\neq4n$. The density measured here, with the use of K_2HgI_4 solution saturated with *o*-nitroaniline as suspension medium, was 1·43 g.cm^{-3}. The calculated density corresponding to 8 molecules in the unit cell is 1·46 g.cm^{-3}. An earlier measured value of 1·28 g.cm^{-3} was obtained by Hartshorne, Walters & Williams (1935) using a modified form of the volumenometer of Garner & Ryder (1925). However, this value must be rejected because of its incompatibility with the present crystallographic results.

The measured interfacial angle agrees with that given by Hartshorne & Stuart (1931). In terms of the unit cell above the laths show (001) and $(10\bar{2})$ faces. No twinned crystals were found.

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