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Twinned Crystals. II. α-1,2: 4,5-Tetrachlorobenzene

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The α-phase of 1,2:4,5-tetrachlorobenzene, stable below 188 ± 2 °K, is triclinic with $a=9{\cdot}60$, $b=10{\cdot}59$, $c=3{\cdot}76$ Å, $\alpha=95°$, $\beta=102\frac{1}{2}$, $\gamma=92\frac{1}{2}$, space group probably $P\bar{1}$ and with 2 molecules in the unit cell. The crystals are twinned with the (010) normal as twin axis (the albite law) and this is considered to be a consequence of the monoclinic to triclinic displacive phase transformation at 188 °K.

Introduction

The occurrence of a low-temperature phase transformation in 1,2:4,5-tetrachlorobenzene was first demonstrated by study of its nuclear quadrupole resonance spectrum, which changed from a quadruplet below 188 ± 2 °K to a doublet above (Monfils, 1955). Direct evidence of a crystallographic change was provided by comparison of Weissenberg photographs taken at 300 and 150 °K (Gafner & Herbstein, 1960) but detailed crystallographic parameters for the low-temperature (α) phase were not obtained. The 150 °K photographs were complicated in appearance, with many non-space-group absences and an apparent increase in the length of the *b* axis (erroneously given as the *a* axis in the 1960 paper) by a factor of about 7 compared with that in the room-temperature (β) phase. In this paper it is shown that these, and other, photographs can be interpreted in terms of a monoclinic β → triclinic α phase change, the triclinic phase always being twinned with the (010) normal as twin axis. Somewhat similar complicated photographs from 10-methyl-1,2-benzanthracene (Mason, 1958) have also been interpreted in terms of twinning (Herbstein, 1964). The results for these two crystals illustrate many of the points made by Buerger (1960, Chapter 5) in an introduction to this general field.

Experimental

Single crystals of the α phase were obtained by blowing cold dry nitrogen over single crystals of β phase sealed into glass capillaries. Use of capillaries was essential to prevent evaporation of the crystals during setting and shattering during transformation. Photographs using oscillation, Weissenberg and precession techniques, all with Cu *Kα* radiation, were taken at temperatures of about 150 °K. The relative orientation of the two phases (see later) was derived from corresponding photographs, taken without change of crystal setting, at 300 and 150 °K.

Comparison of photographs of the two phases showed that their cell dimensions and orientations are closely related; the axes of the triclinic cell have therefore been chosen to correspond to those of the β phase. The cell dimensions and morphology of the β phase (Dean, Pollak, Craven & Jeffrey, 1958; Gafner & Herbstein, 1960) are given in Table 1.

The *h*0*l* precession photograph of the α phase showed only minor changes from the corresponding β phase photograph but the 0*kl* precession and *hk*0 Weissenberg photographs were strikingly different (Figs. 1 and

Table 1. *Crystallographic data for triclinic and monoclinic* 1,2:4,5-*tetrachlorobenzene*

	Triclinic (α) at ~150°K	Monoclinic (β) at ~300°K
a	9·60 Å	9·73 Å
b	10·59	10·63
c	3·76	3·86
α	95°	90°
β	$102\frac{1}{2}$	103·5
γ	$92\frac{1}{2}$	90
V	371 Å³	388 Å³
Space group	$P1$ or $P\bar{1}$, probably the latter	$P2_1/a$
Number of molecules per cell	2	2
Molecular symmetry	1 (C_1)	$\bar{1}$ (C_i)
Morphology	Needles elongated along [001].	Needles elongated along [001] showing {110}

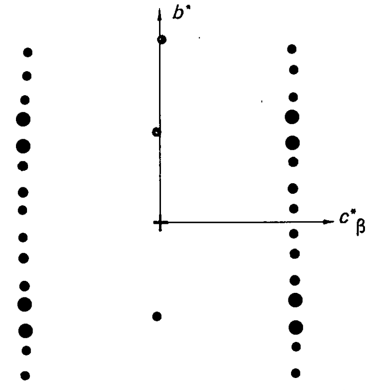

Fig. 1. Tracing of 0*kl* precession photograph of α phase at ~150°K. Irregularities in the tracing are due to poor spot shape on the original photograph. The positions of **b*** (common to both phases) and **c**$_\beta$* are marked. Rough indications of intensity are given by spot size.

2). Inspection of the $0kl$ precession photograph suggested, at first sight, that $b_\alpha \sim 7b_\beta$. A similar impression was obtained from the appearance of the festoons with constant h on the $hk0$ Weissenberg photograph. This photograph had two lines of apparent symmetry, 90° apart in ω. The separation of the spots along the festoons with constant h varied from festoon to festoon.

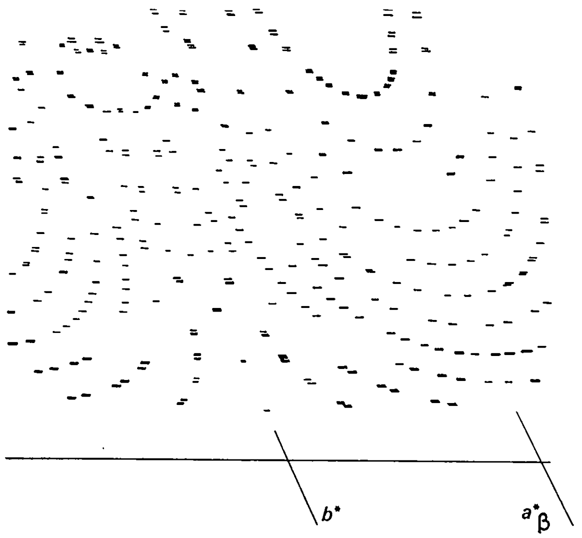

Fig. 2. Tracing of $hk0$ Weissenberg photograph of α phase at ~150°K. The positions of **b*** (common to both phases) and **a**$_\beta$* are marked. Rough indications of intensity are given by spot size.

The $hk0$ Weissenberg photograph could not be interpreted by inspection or with the aid of a Buerger template. The reciprocal lattice layer was therefore

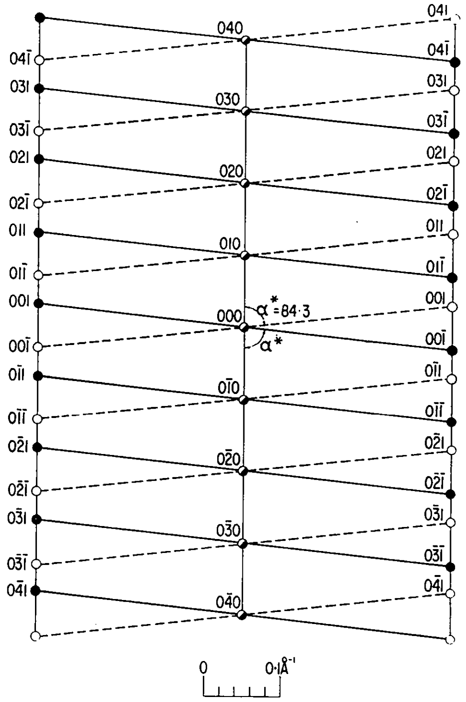

Fig. 4 Twinned zero-layer **b*** **c*** nets. Positions but not intensities of reflexions are shown. This figure should be compared with Fig. 1.

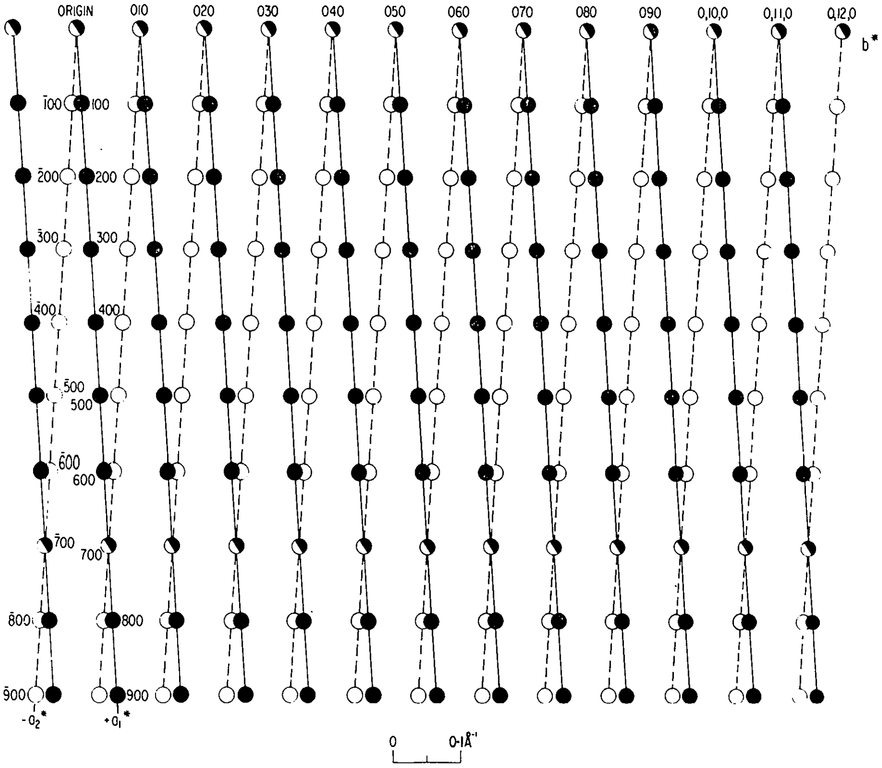

Fig. 3. Twinned zero-layer **a*** **b*** nets. Positions but not intensities of reflexions are shown.

plotted from measurements of ω and Υ (Buerger, 1942, pp. 225–7) for each reflexion on the photograph. All the reflexions could be explained in terms of two twinned non-orthogonal **a*****b*** nets, with **b*** axes parallel (Fig. 3). The 0*kl* precession photograph was explained on similar lines (Fig. 4), the *c* axes of the two individuals being here anti-parallel. Anti-parallel disposition of *c* axes for the two individuals is also required by Fig. 3, right-handed sets of axes being used for both individuals.

It can be seen that the small separations between some neighbouring reflexions along lines of constant *h* in reciprocal space are simply consequences of the mutual disposition of the reciprocal lattices of the two individuals of the twin and have nothing to do with the length of **b***. The apparent symmetry is also a result of the twinning, the *hk*0, 0*kl*, *h*0*l* reciprocal lattice layers of the individuals not having any symmetry other than a centre. The fact that the intensities as well as the positions of reflexions are symmetrical indicates approximate equality of volumes of the two individuals.

Crystallographic results

Measurements of direct and reciprocal cell parameters for the α phase were made as follows:

[001]: oscillation photograph about [001]
d_{100}, d_{010}, γ^*: *hk*0 Weissenberg photograph
d_{010}, d_{001}, α^*: 0*kl* precession photograph
d_{100}, d_{001}, β^*: *h*0*l* precession photograph

γ^* was also calculated from the measured values of d_{100}, d_{010} and the observation that the twinned *hk*0 reciprocal lattices overlapped at $h=7, 14\ldots$. The dimensions of the direct cell are summarized in Table 1.

If the α phase is centrosymmetric then the unit cell will contain 4 independent chlorine atoms, in agreement with the NQR quadruplet found below 188 °K (Monfils, 1955). It is therefore probable that the space group is $P\bar{1}$ (C_i) and not $P1$ (C_1). The systematic absences of the β phase have been weakened to pseudo-absences, with some weak reflexions occurring in place of previously forbidden spectra. Comparisons of cell dimensions and intensity distributions for the two phases indicate that the molecular arrangements must have much in common; however no attempt has been made to investigate this point in detail.

Orientation relationship between α and β phases

The oscillation and Weissenberg photographs about [001] show that the orientation relationship between an individual of the α phase and the β phase is:

$$[001]_\alpha \parallel [001]_\beta\,;\ (010)_\alpha \parallel (010)_\beta.$$

It is also found that $[100]_\alpha$ and $[100]_\beta$ are parallel within experimental error. This is not required by the orientation relationship given above, although compatible with it. The relationship between the unit cells of α and β phases is shown in Fig. 5.

Description of twinning

The 0*kl* precession and *hk*0 Weissenberg photographs of the α phase show that the **a*** and **c*** axes of the reciprocal lattices of the two individuals in twin orientation point in opposite directions while their **b*** axes are common (Figs. 3 and 4). This means that coincidence of the direct lattices of the two individuals will be obtained by 180° rotation about **b***, the normal to (010), the twin plane therefore being (010). The approximately equal volumes of the two components in all samples examined suggest that multiple twinning occurs, the individuals being rather small.

The important fact to be emphasized is that the twin plane is almost a symmetry plane of the structure. This type of twinning falls into Friedel's category of *twinning by pseudo-merohedry* (Cahn, 1954). The obliquity (Donnay & Donnay, 1959, see p. 105) is 6°.

The twin law is that familiar from studies of the feldspars as the albite law (see for example Bragg, 1937, p. 243). The relationship between the monoclinic and triclinic forms of the molecular crystal of 1,2:4,5-tetrachlorobenzene is similar to that between monoclinic orthoclase and triclinic albite. It is interesting to note how the geometrical similarity of unit-cell dimensions and symmetry gives rise to the same type of twinning in structures which are otherwise very different in character.

Relation between the phase transformation and twinning

Twinning of the α phase of 1,2:4,5-tetrachlorobenzene appears to be a direct consequence of the $\beta \rightarrow \alpha$ phase transformation. The phase transformation is displacive, the triclinic α phase being derived from the monoclinic β phase by a process of shear in such a way that **b** is no longer normal to **a** and **c** in the low-temperature phase. This shear can be accomplished in either of two ways, both shown in Fig. 5. The angular setting of the high-temperature form is midway between the two twin components of the low-temperature form. The function of the twinning is to minimize the

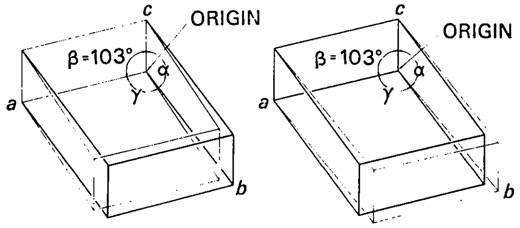

Fig. 5. Orientation relationship between β (thick lines) and α (thin lines) phases for both individuals of α phase. These diagrams are schematic and only roughly to scale; differences between the unit cells of the two phases have been exaggerated for clarity.

overall shape changes that occur in the macroscopic crystals on transformation from monoclinic to triclinic symmetry.

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Adaptation du Photosommateur au Calcul Photométrique Direct

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The photosummator has been adapted to quantitative work (moduli *and* phases). For this purpose it has been slightly modified, so that photometric measurements become possible when the direction of light in the apparatus is reversed. In the trial-and-error method, it is easy to perform three cycles in one day for a rather complex structure, *without having to note the atomic coordinates.*

Quant à la nature de ses ressources le photosommateur harmonique (v. Eller, 1955) constitue un outil bien adapté au travail des cristallographes si l'on songe qu'une expression qualitative des valeurs prises par les séries de Fourier suffit, en général, du moment que la géométrie des détails est rendue avec fidélité.

Il est pourtant des circonstances où l'on pouvait souhaiter soit davantage de rapidité, soit des indications plus quantitatives. En particulier, si le calcul optique des signes des facteurs de structure par la méthode de la phase auxiliaire (v. Eller, 1955, p. 181) à partir d'une hypothèse de répartition des atomes dans une maille centrosymétrique reste aisé, on ne peut plus en dire autant dans le cas des structures non centrées où il devient nécessaire de lier à chaque indice cristallographique une couronne de points photographiques correspondant à des phases espacées de 10 ccy et dont chacun requiert le passage sous le curseur de toutes les positions atomiques de la maille. Le procédé reste certes rentable tant que l'on ne dispose pas immédiatement d'une calculatrice électronique, mais il n'en laisse pas moins d'être fastidieux.

Nous avons donc recherché une adaptation du photosommateur au travail photométrique qui permette l'obtention de résultats directement numériques sans obliger à abandonner aucune des ressources photographiques habituelles.

Principe

On utilise le principe du retour inverse de la lumière.

Dans la fonction habituelle, photographique, du photosommateur, chaque point xy du plan de l'émulsion est prêt à enregistrer, modulé par la grille cosinusoïdale déphasée d'un angle ψ, un flux lumineux émis par la source linéaire. Ce flux est l'analogue de la contribution trigonométrique à xy, pour la phase ψ, du point hk visé sur le plateau par le curseur. (La photographie s'accommode, pour simuler l'amplitude de Fourier correspondante, d'un temps de pose spécifique de chaque hk à brillance constante de la fente lumineuse, mais rien n'empêcherait d'opérer à temps constant en spécifiant la brillance.)

Inversement, chaque point xy, émetteur de lumière au lieu d'être récepteur, enverrait, à travers la grille déphasée d'un angle ψ, sur une fente réceptrice au lieu d'être émettrice, un flux lumineux dont la valeur intégrale représenterait l'analogue de la contribution trigonométrique à hk visé par le curseur, pour la phase ψ, du point xy.

Plus généralement, toujours dans les mêmes conditions, un modèle lumineux complet de la fonction à analyser, disposé à l'emplacement de l'émulsion photosensible, enverrait sur la fente du photosommateur un flux qu'il suffirait de mesurer pour obtenir la valeur