Acta Cryst. (1955). **8**, 487

The Crystal Structure of Phenyl-Propiolic Acid

By J. S. Rollett*

Department of Structural Chemistry, The University of Leeds, England

(*Received* 13 *January* 1955)

Phenyl-propiolic acid, $C_6H_5.C{\equiv}C.COOH$, forms orthorhombic crystals at room temperature with $a = 5{\cdot}11$, $b = 15{\cdot}02$, $c = 9{\cdot}96$ Å and space group *Pnnm*. These crystals are disordered, but at −110° C. there is a very similar, ordered, structure of symmetry $P2_1/n$. The structure of the room-temperature form was solved by trial and error, and two projections were refined by Fourier methods. The molecules form hydrogen-bonded, planar dimers.

Introduction

Various organic chemical syntheses have been accomplished recently in which acetylenic compounds are used as intermediates (cf. β-carotene (Karrer & Engster, 1950; Inhoffen, Bohlmann, Bartram, Rummert & Pommer, 1950; Inhoffen, Pommer & Bohlmann, 1950; Inhoffen, Bohlmann, Aldag, Bork & Leibner, 1951); vitamin *A* (Cornwall, 1948)). This subject is reviewed by Johnson (1949); Jones (1950), Rydon (1950) and Weedon (1951, 1952).

Jones, Whiting, Armitage, Cook & Entwistle (1951), Bohlmann (1951) and Schlubach & Franzen (1951) have described the characteristic features of the absorption spectra of acetylenic and poly-acetylenic compounds. By means of these spectra a number of plant and fungus products have themselves been identified as acetylene derivatives by Stavholt & Sörenson (1950*a*, *b*), Anchel, Polatnick & Kavanagh (1950), and Kavanagh, Hervey & Robbins (1949). Of these natural products, some of the fungus materials possess antibiotic activity (nemotin, nemotinic acid, nemotin *A* and agrocybin).

Calculations have been made by Dunitz & Orgel (1952) for molecules in which ethylenic groups are conjugated to either end of an acetylenic link. These indicate that the configuration in which the ethylenic groups are coplanar is more stable than that in which they are at right angles by about 1 kcal./mole. This conclusion is supported by the planar form of the molecule of diphenyl acetylene (Robertson & Woodward, 1938). If a carboxyl group is taken to be similar in conjugating power to an ethylenic link, then the planar form of acetylene dicarboxylic acid in its dihydrate (Dunitz & Robertson, 1947*a*) confirms this. The data from these two structures have now been supplemented by results for anhydrous phenyl-propiolic acid, $C_6H_5C{\equiv}C.COOH$, which is known to be not ionized in the crystal structure.

Experimental

The crystals used were prepared by slow evaporation of solutions in water at room temperature. The specimens so obtained were needles up to 4 mm. in length and 0·1–0·2 mm. thick, elongated parallel to the *a* axis, with well developed {011} faces and irregular terminations. The crystallographic date are:

Crystal system: orthorhombic.
$a = 5{\cdot}113 \pm 0{\cdot}010$, $b = 15{\cdot}022 \pm 0{\cdot}015$, $c = 9{\cdot}963 \pm 0{\cdot}015$ Å.
Space group: *Pnnm*.
Absent spectra:
(0*kl*) with $(k+l)$ odd,
(*h*0*l*) with $(h+l)$ odd.
Molecules per unit cell: 4.
Density (calc.): $1{\cdot}26_8$ g.cm.$^{-3}$.
Density (obs.): $1{\cdot}27_6$ g.cm.$^{-3}$.
Absorption coefficient for Cu *Kα* radiation: 8·6 cm.$^{-1}$.
Refractive indices for white light:
$\alpha = 1{\cdot}615 \pm 0{\cdot}005$; $\|$**c**,
$\beta = 1{\cdot}730 \pm 0{\cdot}005$; $\|$**b**,
$\gamma = 1{\cdot}750 \pm 0{\cdot}005$; $\|$**a**.

The value of **a** was determined from a rotation photograph and those for **b** and **c** from Straumanis photographs about **a**. Refractive indices were measured by immersion in matching liquids in a rotation apparatus of the type described by Hartshorne & Stuart (1950).

The (0*kl*) and (*hk*0) structure factors were determined by visual estimation of zero-layer **a**- and **c**-axis Weissenberg photographs, using the Leeds Weissenberg goniometer (Beard, Cox & Sutton, 1951) with Ilfex Industrial G film, and comparing the intensities with an intensity scale made under the same conditions. The measurements covered a range of 14,000:1 for (0*kl*) and 1,300:1 for (*hk*0), 85 independent *F* values being determined for the former and 44 for the latter. The intensity values were corrected for polarization and Lorentz factors, and approximate scale and temperature factors were derived by application of Wilson's (1942) method to the (0*kl*) struc-

---

* Present address: Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, U.S.A.

ture factors. These values were later refined by plotting $\log \Sigma|F_o| \div \Sigma|F_c|$ against $\sin^2 \theta/\lambda^2$, summing over groups of planes in limited ranges of spacing. The temperature factor given by Wilson's method was not found to be significantly in error, but the scale factor was multiplied by 0·883.

The absorption errors were kept small by the use of crystals of linear dimensions normal to the rotation axis not greater than 0·1 mm., and errors due to variations of spot shape and size should be negligible. The random errors of estimation have been assessed from the reproducibility of the ratios between intensity values obtained from different films and so it was possible to estimate the accuracy of the F values quite independently of the analysis that followed. The standard deviations due to all errors save extinction effects were $0{\cdot}048 \times F$ and $0{\cdot}073 \times F$ for (0*kl*) and (*hk*0) respectively. These values were useful criteria of the significance of various levels of agreement between F_o and F_c obtained in the subsequent structure analysis.

Determination of the approximate structure

The negative optic sign indicates that the greatest dimensions of the molecules are oriented in or near to the plane normal to the **c** axis. On the other hand the maximum birefringence of 0·135 is rather small for a perfect layer structure and this is also improbable because (002), (008) and (0,0,10) are strong reflexions, but (004) and (006) are weak. These facts are consistent with a structure of planar molecules in which the plane of each molecule is parallel to the **c** axis and its maximum length is in the **ab** plane, which is then a mirror plane in the space group *Pnnm* only if the carboxyl oxygens are equivalent. The strength of reflexion from (130), at 45° to the **b** axis, suggests that the molecules are nearly parallel to planes of this form. This orientation and the **a**-axis length of 5·1 Å lead to a separation of 3·5 Å between the planes of successive molecules in the **a** direction, and there is just sufficient space for the molecules without any atom approaching within 1·25 Å of the diad axes which lie parallel to **c** at intervals of half a unit cell.

The atomic positions given by these considerations were consistent with the features of the (0*kl*) Patterson synthesis. The (0*kl*) structure factors were computed for a trial structure and gave a disagreement index, $R = \Sigma||F_o|-|F_c|| \div \Sigma|F_o|$ of 0·27.

Refinement of parameters

The refinement was carried out in two stages. In the first stage *Pnnm* symmetry and isotropic thermal vibration were assumed. For both **a** and **c** projections further refinement was found to be impossible when the disagreement indices were approximately 0·18. In the second stage reasons were sought for the significant difference between the R values of 0·18 and the total errors of the F_o of the order of 0·05 to 0·07. It was found to be possible to improve the agreement by abandoning the assumptions given above.

The **a** projection was refined first. Since the plane of the molecule is at 45° to **a**, several of the atoms are separated by distances of the order of 0·8 Å in this projection. It was realised that the high temperature factor ($\exp[-6{\cdot}2 \sin^2 \theta/\lambda^2]$) would lead to poor resolution of these atoms. For this reason the first Fourier synthesis was computed with terms derived by dividing 50 values of F_o by this temperature factor. This synthesis is shown in Fig. 1(*a*) and may be compared with Fig. 1(*b*), which shows a synthesis computed from 83 terms with unmodified F_o values.

The background areas of the sharpened synthesis are not nearly so flat, but the heights of the peaks are more constant and they are more clearly resolved than those of the unsharpened synthesis. Atomic positions were determined from the maxima of both, and a preliminary survey showed that those from the sharpened synthesis gave better structure-factor agreement, although subsequent comparison with coordinates corrected for series errors showed no significant difference between the systematic errors of the two (r.m.s. values

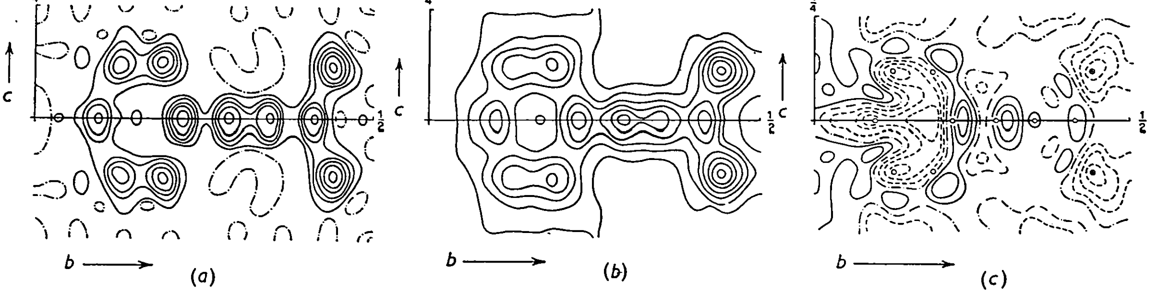


Fig. 1. (*a*) Electron-density projection on the plane normal to **a**, obtained using $F_o/\exp[-6{\cdot}2 \sin^2 \theta/\lambda^2]$ as terms. The contour interval is 2 e.Å^{-2}, zero-level chain dotted, negative contours broken.

(*b*) Electron-density projection on the plane normal to **a**, using F_o as terms. The contour interval is 1 e.Å^{-2} and the lowest contour is at 1 e.Å^{-2}.

(*c*) (F_o-F_c) synthesis of the projection on the plane normal to **a**. The contour interval is 0·2 e.Å^{-2}, zero-level chain dotted, negative contours broken. ○: one carbon atom; ⊙: one oxygen atom.

of 0·051 Å for the sharpened and 0·045 Å for the unsharpened synthesis).

A complete set of structure factors was computed from the positions given by the maxima of the sharpened synthesis, giving the value $R = 0{\cdot}260$ on 85 terms and no sign changes. These structure factors were corrected for the contributions of hydrogen atoms in assumed positions and used for an unsharpened $(F_o - F_c)$ synthesis (Fig. 1(*c*)), which was subtracted from the F_o synthesis at the atomic positions so that the series errors could be determined. The new atomic positions gave $R = 0{\cdot}197$, and if the contributions of hydrogen atoms in assumed positions were included $R = 0{\cdot}186$. If (002), which was probably strongly affected by extinction, was omitted from the set corrected for hydrogen contributions, $R = 0{\cdot}179$. There were still no sign changes, so that further refinement was impossible without a change of assumptions.

A trial structure for the **c** projection in which the molecules lay in {130} was successful. It was followed by a Fourier synthesis (Fig. 2) to check the precise molecular orientation. This, and an $(F_o - F_c)$ synthesis (Fig. 3), gave no indication that the plane of the molecule should be altered, but showed a shift of two of the atoms of the benzene ring in this plane. The final value of R was 0·180.

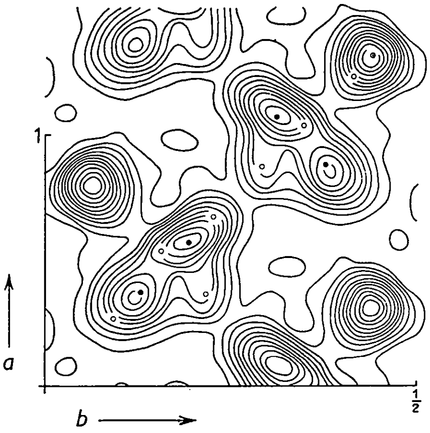


Fig. 2. Electron-density projection on the plane normal to **c**. The contour interval is 1 e.Å^{-2}, and the lowest contour is at 1 e.Å^{-2}. ○: one carbon atom; ●: two carbon atoms; ⊙: two oxygen atoms.

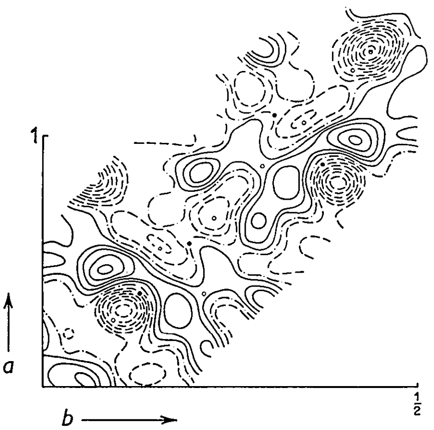


Fig. 3. $(F_o - F_c)$ synthesis of the projection on the plane normal to **c** assuming isotropic vibration. The contour interval is 0·2 e.Å^{-2}, zero-level chain dotted, negative contours broken. ○: one carbon atom; ●: two carbon atoms; ⊙: two oxygen atoms.

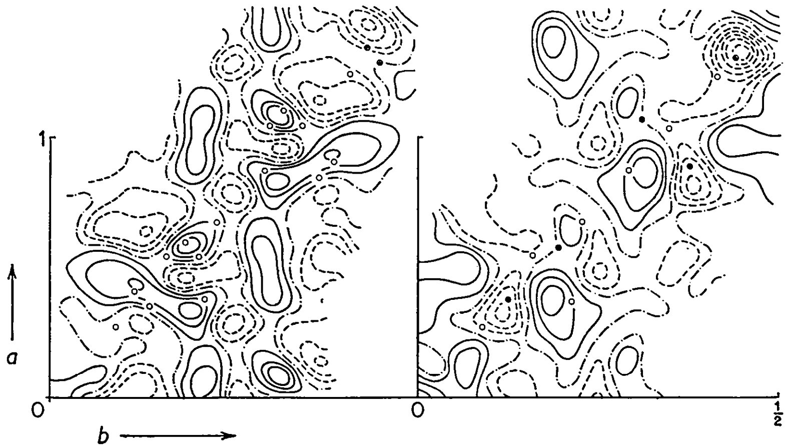
This level of agreement between F_o and F_c, in both projections, is about that at which many structure analyses are considered complete. It should be noted, however, that inclusion of the hydrogen contributions in the $F(0kl)$ made a very small improvement. Moreover, for $(0kl)$ with $l < 6$, $R = 0{\cdot}135$; but for $l > 5$, $R = 0{\cdot}335$. This suggests that the z coordinates are in error. If *Pnnm* symmetry is truly satisfied only three independent atoms have $z \neq 0$, and it is possible to see that no combination of parameters near to those found will give satisfactory F values for certain planes. This suggests that the structure is pseudo-symmetrical and this is in agreement with structural evidence on the asymmetry of the carboxyl group which would be bisected by a mirror plane normal to the O–O line if the space group were *Pnnm*. It is well established, however, that in the unionized carboxyl group the C–O distances are not equal and have the values 1·19 Å and 1·29 Å (α-anhydrous oxalic acid (Cox, Dougill & Jeffrey, 1952); oxalic acid dihydrate (Ahmed & Cruickshank, 1953); *N*-acetylglycine (Carpenter & Donohue, 1950)). For these reasons, tests were made of various arrangements of lower symmetry which approximated to that found in the *Pnnm* refinement.

The carboxyl group of each molecule lies next to that of another in the same plane, so that the oxygen atoms are separated by 2·6 Å. It is evident that hydrogen-bonded dimers are formed. These are found in the crystal structures of a number of other monocarboxylic acids (e.g. *p*-chlorobenzoic acid (Toussaint, 1951); salicylic acid (Cochran, 1953); lauric acid (Vand, Morley & Lomer, 1951); iso-palmitic acid (Stenhagen, Vand & Sim, 1952); trans β-ionylidene crotonic acid (MacGillavry, Kreuger & Eichhorn, 1951); formic acid gas (Allen & Sutton, 1950)), and are centro-symmetrical. Consequently, the symmetry should be $P2_1/n$ rather than $Pnn2$. The diffraction pattern, however, has definite orthorhombic symmetry. Two possibilities arise: (1) There is a randomly disordered arrangement of dimers in orientations related to one another by the mirror plane of the *Pnnm* pseudo-symmetry, so that this symmetry is statistically satisfied. (2) The crystals examined are polycrystalline twins on the pseudo-mirror plane, containing equal quantities of material in the two orientations.

Both possibilities were tested by structure-factor computation. It was assumed that the oxygen coordinates were correct, and the displacements of the carbon atoms from the positions for the pseudo-structure were calculated from the curvatures $(\partial^2\varrho/\partial z^2)$

Table 1. *Final atomic coordinates*

	x/a	y/b	z/c	x (Å)	y (Å)	z (Å)	$\sigma(y)$
C_1	0·669	0·2229	0·0000	3·42	3·348	0·000	0·023
C_2	0·572	0·1906	0·1217	2·92	2·863	1·212	—
C_3	0·367	0·1223	0·1217	1·88	1·837	1·212	—
C_4	0·282	0·0941	0·0000	1·44	1·413	0·000	—
C_5	0·367	0·1223	−0·1217	1·88	1·837	−1·212	—
C_6	0·572	0·1906	−0·1217	2·92	2·863	−1·212	—
C_7	0·871	0·2903	0·0000	4·45	4·361	0·000	0·031
C_8	0·039	0·3463	0·0000	0·20	5·202	0·000	0·036
C_9	0·234	0·4113	0·0000	1·20	6·179	0·000	0·016
O_1	0·318	0·4394	0·1105	1·63	6·601	1·101	—
O_2	0·318	0·4394	−0·1105	1·63	6·601	−1·101	—



(a) (b)

Fig. 4. $(F_o - F_c)$ syntheses of the projection on the plane normal to **c** (*a*) assuming that the molecule is tilted 10° from a plane parallel to **c**, (*b*) assuming anisotropic vibration. The contour interval is 0·2 e.Å^{-2}, zero-level chain dotted, negative contours broken. ○: one carbon atom; ●: two carbon atoms; ⊕: one oxygen atom; ⊙: two oxygen atoms.

on the $(F_o - F_c)$ synthesis (Fig. 1(*c*)). The contribution of one orientation to $F(0kl)$ is equal to that of the other to $F(0\bar{k}l)$. For the disordered crystal both orientations will scatter in phase, so that

$$F\{0kl\} = \tfrac{1}{2}(F(0kl) + F(0\bar{k}l))\,.$$

For a polycrystalline twin there will be no phase relation between the two orientations, so that

$$F^2\{0kl\} = \tfrac{1}{2}(F^2(0kl) + F^2(0\bar{k}l))\,.$$

Both assumptions led to improved agreement, the values of R being 0·164 and 0·159 for models based on disorder and on twinning respectively. This improvement confirmed the hypothesis of an asymmetric carboxyl group, but decisive evidence was still lacking. It was finally obtained from a zero-layer **a**-axis Weissenberg photograph taken at −110° C. Before cooling, and after warming again to room temperature, the crystal used gave the usual diffraction pattern, but at low temperature it split into two portions of unequal size, slightly disoriented relative to each other and having no n glide plane normal to **a**. The $(0kl)$ reflexions with $(k+l)$ odd have low intensity except when l is large, and when this is so there are large changes in the intensities of $(0kl)$ with $(k+l)$ even.

This evidence demonstrates that at room temperature the crystal structure is disordered and that between +15° C. and −110° C. there is a transition to an ordered structure of $P2_1/n$ symmetry, the monoclinic symmetry axis being close to or coincident with the orthorhombic **b** axis. Furthermore, the mean z coordinates are significantly different at the two temperatures.

The refinements required to improve the R value for the **c** projection were deduced from $(F_o - F_c)$ syntheses. On that obtained at the end of the first stage of refinement (Fig. 3) there were positive curvatures at all atoms in the direction normal to the greatest length of the molecule. This suggested two hypotheses: (1) That the benzene ring and carboxyl group are tilted out of the plane parallel to **c**, so that *Pnnm* symmetry is no longer satisfied. (2) That the thermal motion of the molecule is anisotropic, with the greatest vibration normal to its length.

Structure factors for a molecule tilted 10° out of the plane parallel to **c** were computed. The structure factors for the molecule in this plane were corrected for anisotropic vibration by the use of

$$\Delta F = -4 \sum_j \Delta f_j \sin 2\pi hx_j \sin 2\pi ky_j, \quad (h+k) \text{ even},$$

$$\Delta F = +4 \sum_j \Delta f_j \cos 2\pi hx_j \cos 2\pi ky_j, \quad (h+k) \text{ odd},$$

where

ΔF is the correction to the structure factor,

Δf_j is half the difference between the scattering factor of symmetry equivalent atoms of type j for $(hk0)$:

$$\Delta f_j = \bar{f}_j \sinh\,[hk.a^*b^*(q_1-q_2)]\,,$$

$\bar{f}_j$ is the mean scattering factor for atoms of type j,

q_1 and q_2 are the thermal vibration parameters of one atom of type j for its principal vibration directions.

This form for Δf_j could be used because the principal vibration directions are at 45° to the crystallographic axes. More general expressions will be published elsewhere (cf. Rollett & Davies, 1955).

Both sets of structure factors gave better agreement ($R = 0{\cdot}127$ for the tilted model and $R = 0{\cdot}134$ for the anisotropically vibrating model). The correct assumption of anisotropic vibration was distinguished by an (F_o-F_c) synthesis which could be interpreted. The syntheses are shown in Fig. 4(*a*) (10° tilt) and Fig. 4(*b*) (anisotropy). Fig. 4(*a*) shows features which are difficult to explain except by assuming thermal anisotropy. In particular, there are still positive curvatures at the acetylenic carbon atoms. Fig. 4(*b*) is much more satisfactory, the principal feature being a deep trough at the position of the oxygen atoms. This was taken to indicate an error in the ratio between the assumed scattering powers of carbon and oxygen, so that the values given by James & Brindley (1932) were replaced by those due to McWeeny (1951), he antisotropy of the McWeeny oxygen model being added to the thermal anisotropy. The resulting value

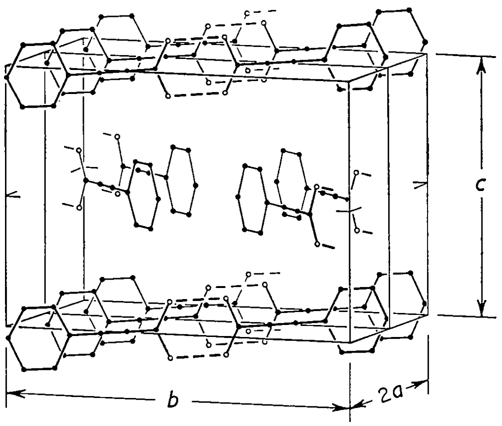


Fig. 5. Diagram of two unit cells of the crystal structure showing the 'stacking' of hydrogen-bonded dimers in columns parallel to **a**.

Table 2. *Bond-length values*

Bond	Length (Å)	Standard deviation (Å)
C_1–C_7	1·447	0·055
C_7–C_8	1·202	0·067
C_8–C_9	1·396	0·049
O_1–O_2	2·60	0·04

Table 3. *Observed and calculated structure factors*

F_c are for the pseudo-structure and are corrected for the contributions of hydrogen atoms in assumed positions. F'_c are for a disordered structure and are not corrected for the contributions of hydrogen atoms.

hkl	F_o	F_c	F'_c
020	14·2	−11·3	−14·9
040	32·2	−34·1	−35·4
060	24·6	−27·6	−24·8
080	21·6	−23·4	−23·7
0,10,0	6·6	+ 5·5	+ 2·5
0,12,0	5·1	− 6·4	− 5·8
0,14,0	5·2	+ 3·7	+ 5·1
011	17·3	−12·4	−24·9
031	34·4	−38·6	−36·8
051	8·7	+ 7·4	+10·4
071	11·7	+12·6	+15·6
091	20·1	+22·8	+22·2
0,11,1	1·8	+ 1·6	+ 3·4
0,13,1	6·4	− 8·6	− 7·2
0,15,1	1·5	− 1·8	− 1·2
0,17,1	2·5	+ 1·5	+ 1·1
002	72·8	+90·7	+96·2
022	12·1	− 9·4	−15·5
042	8·2	− 7·3	− 9·1
062	15·0	−14·6	−15·7
082	6·0	− 6·3	− 5·3
0,10,2	5·4	+ 3·6	+ 4·7
0,14,2	3·8	+ 3·6	+ 3·6
0,16,2	4·7	− 4·1	− 4·2
013	10·3	−11·1	− 6·6
033	43·4	+45·6	+41·8
053	12·1	− 8·8	−10·5
073	12·8	−12·9	−14·6
093	2·6	− 5·8	− 4·1
0,11,3	4·2	− 6·0	− 3·1
0,13,3	3·1	+ 4·3	+ 4·2
0,15,3	2·8	− 2·1	− 2·5
0,17,3	2·8	+ 1·5	+ 1·8
004	17·3	−18·0	−21·3
024	20·6	−21·5	−20·0
044	8·0	+ 5·3	+ 6·3
064	7·1	− 3·5	− 2·9
084	11·4	+11·2	+12·3
0,10,4	6·0	+ 5·9	+ 6·9
0,12,4	5·0	+ 7·3	+ 6·8
0,14,4	3·0	+ 2·8	+ 1·7
0,16,4	8·2	− 9·1	− 9·1
015	5·6	+ 4·7	+ 5·6
035	30·2	+28·9	+28·8
055	8·1	− 8·2	− 9·4
075	12·9	−14·4	−14·2
095	4·7	− 6·6	− 4·2
0,11,5	5·2	− 5·8	− 3·7
0,13,5	2·7	+ 4·1	+ 3·8
0,15,5	1·4	− 1·1	− 1·2
0,17,5	2·3	+ 1·6	+ 2·0
006	12·5	+13·2	+13·1
026	14·1	−11·7	−12·1
046	1·4	− 2·7	− 2·3
066	3·0	− 2·4	− 1·6
086	2·9	+ 3·2	+ 3·3
0,10,6	4·2	+ 5·2	+ 5·1

Table 3 (*cont.*)

hkl	F_o	F_c	F'_c
0,12,6	1·4	+ 1·7	+ 1·4
0,14,6	3·5	+ 1·5	+ 1·4
0,16,6	3·0	− 3·8	− 3·3
017	3·1	+ 0·6	− 4·1
057	3·8	0·0	+ 1·0
077	1·5	− 2·0	+ 0·1
097	2·8	+ 6·6	+ 3·9
0,11,7	1·9	− 1·0	0·0
0,13,7	2·3	− 2·8	− 2·3
008	25·2	+30·5	+28·3
028	4·6	− 2·5	− 3·0
048	3·3	− 5·8	− 4·2
068	2·8	− 3·9	− 3·2
088	4·9	− 3·9	+ 2·5
0,10,8	1·5	+ 2·7	+ 1·7
0,14,8	2·0	+ 0·9	+ 1·4
019	5·2	− 1·6	− 4·1
039	4·1	− 5·0	− 4·1
059	3·8	+ 1·4	+ 2·2
079	2·5	+ 2·4	+ 2·5
099	3·2	+ 4·8	+ 2·6
0,13,9	1·5	− 2·4	− 1·8
0,0,10	9·8	+11·0	+ 8·0
0,6,10	2·2	− 2·8	− 2·4
0,8,10	1·9	− 1·8	− 1·6
0,1,11	2·4	− 2·1	− 2·1
0,3,11	1·7	+ 2·3	+ 1·6
110	31·7	−30·6	
120	15·9	+17·8	
130	68·9	+82·4	
140	23·4	+23·0	
150	26·1	−25·1	
160	43·2	+46·8	
170	4·0	− 5·5	
190	12·4	−12·7	
1,10,0	14·0	−16·1	
1,12,0	7·5	− 7·5	
200	27·9	−29·6	
210	7·5	+ 6·8	
220	30·2	−36·2	
230	44·6	+47·7	
250	9·2	+10·0	
260	29·0	+30·0	
270	12·0	−13·4	
280	5·8	+ 7·3	
2,13,0	6·5	− 7·6	
310	8·1	− 7·6	
320	3·4	− 2·6	
330	12·7	−13·2	
340	18·3	−17·0	
350	6·0	+ 3·4	
390	14·1	+13·2	
3,10,0	6·4	− 7·7	
3,12,0	3·8	+ 3·5	
400	6·6	− 5·8	
410	9·5	− 9·5	
420	9·2	+ 6·6	
430	7·0	− 8·3	
470	9·0	+ 6·1	
490	4·1	+ 3·6	
4,11,0	3·5	+ 2·4	
520	4·8	+ 3·9	
540	5·0	− 5·2	
610	3·8	− 2·5	

of R was 0·105 for all planes except (130), suspected of showing a large extinction effect. This is still not so low as the R value given by $\sigma(F_o)$ but there are indications that part of the discrepancy could be caused by librations of the molecule. Because of the small number of observations available, extra parameters for libration were not used.

The refinement process was discontinued at this stage since the orientation of the molecules, their configuration and the nature of the intermolecular linkages were firmly established.

The appearance of the crystal structure is shown in Fig. 5. The final coordinates and the bond-length values which are considered reliable are given in Tables 1 and 2, together with their standard deviations (where these have been determined). The observed structure factors, the calculated structure factors for the pseudo-structure and those for the disordered structure are given in Table 3.

The accuracy of the analysis

The disorder described in the last section gives rise to Fourier syntheses for the **a** projection on which each peak represents two atoms separated by a distance of the order of 0·1 Å. Where any given atomic coordinate is not the same for both atoms by symmetry, the accuracy with which it may be determined for either atom is reduced greatly. For atoms off the centre line of the molecule this applies to both y and z coordinates, but for those on the centre line the two y coordinates are equal and these coordinates can be determined with the same accuracy as if the peaks represented single atoms.

In the **c** projection there are 22 positional parameters and only 44 independent observations. Moreover, no atom is resolved in the Fourier synthesis. The positions derived from this projection are consequently somewhat imprecise, but it is possible to determine the angles between the plane of the molecule and the faces of the unit cell with good accuracy. Since the triple bond and the adjacent single bonds are on the centre line of the molecule and nearly perpendicular to **c**, their lengths can be determined from the y coordinates of the atoms and the molecular orientation if it is assumed that the molecule is accurately planar. This procedure has been adopted and the standard deviations of the coordinates have been derived, using the equations given by Cruickshank & Rollett (1953). The resulting values are given in Table 1.

Discussion of the structure

The molecule of phenyl-propiolic acid has been shown to be planar within the limits of error of the analysis. This supports the evidence from the structures of diphenyl-acetylene (Robertson & Woodward, 1938) and acetylene-dicarboxylic acid dihydrate (Dunitz & Robertson, 1947*a*) that this configuration of planar groups containing multiple bonds, conjugated with a triple bond, corresponds to minimum energy. The experimental results are in agreement with the calculations of Dunitz & Orgel (1952) for systems of this type.

Interest attaches to the values obtained for bond lengths in carboxyl groups in various environments. In the structures of the two acetylenic acids previously examined by Dunitz & Robertson (1947*a*, *b*) it was found that the two C–O bond lengths were practically equal, but the results of these analyses were not significantly different from those for the carboxyl groups in α-anhydrous oxalic acid (Cox, Dougill & Jeffrey, 1952), oxalic acid dihydrate (Ahmed & Cruickshank, 1953) and *N*-acetyl glycine (Carpenter & Donohue, 1950). Moreover, there is a possibility that the two acetylenic dicarboxylic acids are ionized in their hydrate crystal structures. Phenyl-propiolic acid is certainly not ionized in its crystalline form, and the disorder found in its crystal structure is clear evidence of the asymmetry of the carboxyl group. Unfortunately, this disorder has prevented the precise determination of the C–O distances by this analysis, but the relatively good agreement obtained with a model having dimensions equal to those found for α-anhydrous oxalic acid suggests that the lengths in phenyl-propiolic acid are nearer to 1·19 Å and 1·29 Å rather than to equal values of 1·25 Å.

The dimensions of the acetylenic side chain and the phenyl group agree with lengths for similar bonds obtained from other structure analyses within the limits of experimental error.

The molecules form hydrogen-bonded dimers. The length of the hydrogen bonds is 2·60 Å, and although the standard deviation of this length is not known with certainty it is probably about 0·04 Å. There is a possibly significant difference between this length and that of 2·71 Å in α-anhydrous oxalic acid for a similar link, and this is consistent with the fact that in the phenyl-propiolic acid structure the expected direction of the O–H link is very close to that of the line joining the two oxygen atoms.

The order–disorder transition occurring at low temperature is of interest in that the time average z coordinates of the atoms are temperature dependent. This suggests that at room temperature the molecules oscillate between the two configurations of minimum potential energy.

Except for the hydrogen-bonded pairs of oxygen atoms, the shortest distances between atoms in different molecules are 3·53 Å between the *o*-carbon atom of the benzene ring and a carboxyl oxygen, 3·59 Å between *p*-carbon atoms of benzene rings, 3·60 Å between the substituted carbon atom of the ring and the carbon of the carboxyl group, and 3·61 Å between the α-acetylenic carbon and the carboxyl carbon. The dimers are closely packed in columns parallel to **a** with their centres on the lines $y = \frac{1}{2}$, $z = 0$, and $y = 0$, $z = \frac{1}{2}$. The closest contacts between different columns are the C–O distance of 3·53 Å and the *p*-carbon to *p*-carbon distance of 3·59 Å. All other contacts between columns are distances of 3·81 Å or more.

All the distances given above are for the pseudo-structure. For the disordered structure, however, some of the separations between benzene-ring atoms and others could be reduced by about 0·1 Å where adjacent molecules are not in corresponding orientations.

The writer wishes to acknowledge a Further Education and Training grant from the British Ministry of Education. He would also like to thank Prof. E. G. Cox for his encouragement of this work.

References

AHMED, F. R. & CRUICKSHANK, D. W. J. (1953). *Acta Cryst.* **6**, 385.

ALLEN, P. W. & SUTTON, L. E. (1950). *Acta Cryst.* **3**, 46.

ANCHEL, M., POLATNICK, J. & KAVANAGH, F. (1950). *Arch. Biochem.* **25**, 208.

BEARD, D. S., COX, E. G. & SUTTON, G. J. (1951). *J. Sci. Instrum.* **28**, 246.

BOHLMANN, F. (1951). *Ber. dtsch. Chem. Ges.* **84**, 785.

CARPENTER, G. B. & DONOHUE, J. (1950). *J. Amer. Chem. Soc.* **72**, 2315.

COCHRAN, W. (1953). *Acta Cryst.* **6**, 260.

CORNWALL, B. C. (1948). *Chem. Abstr.* **42**, 5174.

COX, E. G., DOUGILL, M. W. & JEFFREY, G. A. (1952). *J. Chem. Soc.* p. 4854.

CRUICKSHANK, D. W. J. & ROLLETT, J. S. (1953). *Acta Cryst.* **6**, 705.

DUNITZ, J. D. & ORGEL, L. E. (1952). *J. Chem. Phys.* **20**, 1328.

DUNITZ, J. D. & ROBERTSON, J. M. (1947*a*). *J. Chem. Soc.* p. 148.

DUNITZ, J. D. & ROBERTSON, J. M. (1947*b*). *J.Chem.Soc.* p. 1145.

HARTSHORNE, N. H. & STUART, A. (1950). *Crystals and the Polarizing Microscope.* London: Arnold.

INHOFFEN, H. H., BOHLMANN, F., ALDAG, H. J., BORK, S. & LEIBNER, G. (1951). *Liebigs Ann.* **573**, 1.

INHOFFEN, H. H., BOHLMANN, F., BARTRAM, K., RUMMERT, G. & POMMER, H. (1950). *Liebigs Ann.* **570**, 54.

INHOFFEN, H. H., POMMER, H. & BOHLMANN, F. (1950). *Liebigs Ann.* **569**, 237.

JAMES, R. W. & BRINDLEY, G. W. (1932). *Phil. Mag.* (7), **12**, 81.

JOHNSON, A. W. (1949). *Rep. Progr. Chem.* **46**, 168.

JONES, E. R. H. (1950). *J. Chem. Soc.* p. 754. (Tilden Lecture.)

JONES, E. R. H., WHITING, M. C., ARMITAGE, J. B., COOK, C. L. & ENTWISTLE, N. (1951). *Nature, Lond.* **168**, 900.

KARRER, P. & ENGSTER, C. H. (1950). *Helv. chim. Acta*, **33**, 1172.

KAVANAGH, F., HERVEY, A. & ROBBINS, W. J. (1949). *Proc. Nat. Acad. Sci., Wash.* **36**, 1, 102.

MACGILLAVRY, C. H., KREUGER, A. & EICHHORN, E. L. (1951). *Proc. K. Ned. Akad. Wet.* B, **54**, 449.

MCWEENY, R. (1951). *Acta Cryst.* **4**, 413.

ROBERTSON, J. M. & WOODWARD, I. (1938). *Proc. Roy. Soc.* A, **164**, 436.

ROLLETT, J. S. & DAVIES, D. R. (1955). *Acta Cryst.* **8**, 125.

RYDON, H. N. (1950). *Rep. Progr. Chem.* **47**, 166.

SCHLUBACH, H. H. & FRANZEN, V. (1951). *Liebigs Ann.* **572**, 116.

STAVHOLT, S. K. & SÖRENSON, N. A. (1950*a*). *Acta chem. Scand.* **4**, 1567.
STAVHOLT, S. K. & SÖRENSON, N. A. (1950*b*). *Acta chem. Scand.* **4**, 1575.
STENHAGEN, E., VAND, V. & SIM, A. (1952). *Acta Cryst.* **5**, 695.
TOUSSAINT, J. (1951). *Acta Cryst.* **4**, 71.
VAND, V., MORLEY, W. M. & LOMER, T. R. (1951). *Acta Cryst.* **4**, 324.
WEEDON, B. C. L. (1951). *Rep. Progr. Chem.* **48**, 156.
WEEDON, B. C. L. (1952). *Rep. Progr. Chem.* **49**, 137.
WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.

Acta Cryst. (1955). **8**, 494

Compounds of Uranium with the Transition Metals of the Second and Third Long Periods

BY T. J. HEAL AND G. I. WILLIAMS

Physics Laboratory, Fulmer Research Institute, Stoke Poges, Bucks., England

(*Received* 7 *March* 1955)

In the course of an investigation of the occurrence and structure of compounds UX_2, where X is Ru, Rh, Pd, Re, Os, Ir or Pt, the existence has been established of the compounds UOs_2 and UIr_2 (*C*15 structure), UPd_3 (*D*O24 structure), URu_3 (*L*12 structure) and UPt_3 (*D*O19 structure).

1. Introduction

In the course of investigations of the occurrence and structure of compounds UX_2, where X is Ru, Rh, Pd, Re, Os, Ir or Pt, the existence of a number of compounds has been established. They are UOs_2 and UIr_2 with the *C*15 structure (Strukturbericht, 1931*c*), UPd_3 with the *D*O24 structure (Strukturbericht, 1943), URu_3 with the *L*12 structure (Strukturbericht, 1931*b*) and UPt_3 with the *D*O19 structure (Strukturbericht, 1940).

2. Preparation of the alloys

All alloys were prepared as 10 g. buttons by arc melting on a water-cooled copper hearth in an atmosphere of purified argon. They were repeatedly remelted to homogenize the ingots. The X elements were of very high purity, approaching that of spectroscopic standards. The uranium was also of high purity; it contained some oxide but was aluminium-free. Heat treatments were carried out on lump specimens in alumina sheaths in evacuated silica tubes. No heat treatments of powdered alloys were necessary, the amount of cold work obtained during powdering being negligible.

3. UX_2 alloys

(i) UOs_2

This alloy crystallizes in a face-centred cubic lattice and is isostructural with $MgCu_2$, the *C*15 structure type. Only Debye–Scherrer powder patterns were necessary to determine the structure. Chemical analysis of the powder used gave 33·5 atomic% uranium. The patterns from the 'as cast' and the heat treated alloy (2 weeks at 900° C.) were identical. The lattice parameter was determined using Co radiation and the Nelson–Riley (1945) extrapolation as

$$a = 7{\cdot}4974 \pm 0{\cdot}0005 \text{ kX.* at } 24^\circ \text{ C.},$$

which gave the X-ray density as 19·42 $g.cm.^{-3}$.

The *C*15 structure has space group O_h^7–$Fd3m$ and the atomic sites are as given in *International Tables* (1952, No. 227), i.e. equivalent positions $0, 0, 0;\ 0, \frac{1}{2}, \frac{1}{2};\ \frac{1}{2}, 0, \frac{1}{2};\ \frac{1}{2}, \frac{1}{2}, 0$ with

$$8 \text{ U at } (a)\ 0, 0, 0;\ \tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4};$$
$$\text{and } 16 \text{ Os at } (d)\ \tfrac{5}{8}, \tfrac{5}{8}, \tfrac{5}{8};\ \tfrac{5}{8}, \tfrac{7}{8}, \tfrac{7}{8};\ \tfrac{7}{8}, \tfrac{5}{8}, \tfrac{7}{8};\ \tfrac{7}{8}, \tfrac{7}{8}, \tfrac{5}{8}.$$

Observed and calculated intensities are given in Table 1.

Since the structure is parameterless, visual intensity estimates have been compared with calculated intensities from which the absorption and temperature factors have been omitted. The observed and calculated values of I are seen to be in good agreement for diffractions occurring at similar θ values. Interatomic distances of near neighbours are given in Table 2.

(ii) UIr_2

The Debye–Scherrer patterns of the UIr_2 alloy were identical with those of UOs_2, apart from weak additional lines identified as iridium lines. Analysis of the powder used gave a uranium content of 31·2 atomic%. Assuming the uranium to be combined as UIr_2, 6·4% free iridium would be present; a finding

---

* Wavelengths of X-radiations used:

Cu $K\alpha_1$	1·537395	kX.
Co $K\alpha_1$	1·78529	kX.
Cr $K\alpha_1$	1·28503	kX.