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Unit-cell dimensions and space group of some polyphenyls.*

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Terphenyl mixtures are used as coolants in some types of nuclear reactor. Quater-, quinqua- and hexa-phenyls result from the decomposition of these terphenyls during reactor operation, and some knowledge of their structural properties is of interest. Therefore, in connection with a previous investigation concerning the X-ray diffraction patterns of a great number of polyphenyls (Toussaint & Vos, 1966), a crystallographic study has been made on some quater- and quinqua-phenyls and p-hexaphenyl.

Rotation, zero and first layer Weissenberg photographs were taken in each case on at least two crystallographic axes, with Cu $K\alpha$ radiation. The temperature at which the photographs were taken was 22°C. The chemical formulae of the polyphenyls investigated are given in Fig. 1. The crystallographic data for all the compounds are presented in Table 1, together with some brief notes on the appearance of the crystals. Space groups were determined by systematic absences.

Starting with biphenyl, the linear polyphenyls p-terphenyl (Hertel & Römer, 1933*a*; Pickett, 1933) and p-quaterphenyl (Hertel & Römer, 1933*b*) are found to be isostructural in the a–b section with β almost constant. This shows that the long axes are directed almost or even precisely along **c**. The increase of about 4·2 Å in the **c** direction is the length of one C–C bond plus the diameter of one phenyl-ring. Furthermore the same space group and number of molecules in the unit cell was found for these first three members.

The results for p-quinqua- and p-hexa-phenyl investigated in our study show that up to the hexa-phenyl these linear polyphenyls differ merely in the extension of the molecules along the c axis. Since only a very small quantity of p-quin-

Table 2. *Comparison of observed and calculated* $\sin^2\theta$ *values for p-quinquaphenyl*

hkl	$\sin^2\theta$ observed	$\sin^2\theta$ calculated
001	0·0012	0·0012
002	0·0049	0·0049
101	0·0108	0·0108
010	0·0197	0·0197
110	0·0282	0·0288
111	0·0304	0·0304
200	0·0368	0·0370
211	0·0589	0·0588
212	0·0610	0·0631

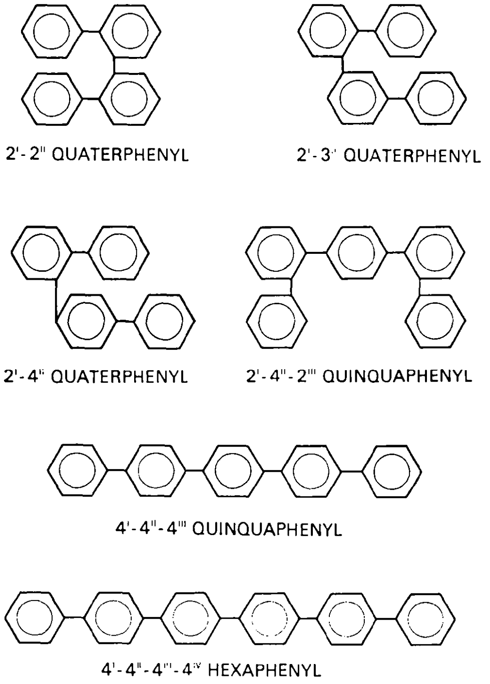

Fig. 1. Chemical formulae of the investigated polyphenyls.

Table 1. *Crystallographic data for some polyphenyls*

	2′–2″ φ_4	2′–3″ φ_4	2′–4″ φ_4	2′–4″–2‴ φ_5	4′–4″–4‴ φ_5	4′–4″–4‴–4⁗ φ_6
Crystal system	Tetragonal	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
a (Å)	11·72 ± 0·02	12·00 ± 0·02	9·68 ± 0·03	11·89 ± 0·02	8·040 ± 0·005	8·09 ± 0·02
b (Å)	—	7·70 ± 0·02	10·16 ± 0·05	9·10 ± 0·02	5·485 ± 0·005	5·60 ± 0·01
c (Å)	31·2 ± 0·1	11·07 ± 0·02	22·25 ± 0·15	10·57 ± 0·02	21·99 ± 0·01	26·24 ± 0·15
α (°)	—	—	—	91·5 ± 0·4	—	—
β (°)	—	121·2 ± 0·2	127·2 ± 0·2	106·5 ± 0·4	92·0 ± 0·2	91·8 ± 0·2
γ (°)	—	—	—	102·0 ± 0·4	—	—
U (Å^3)	4286	875	1743	1073	970	1189
Z	10	2	4	2	2	2
M	306·41	306·41	306·41	382·51	382·51	458·68
D_{calc}, (g.cm^{-3})	1·187 ± 0·005	1·163 ± 0·005	1·167 ± 0·005	1·183 ± 0·005	1·309 ± 0·005	1·280 ± 0·005
Space group	$P4/nmm$	$P2_1/c$	$P2_1/c$	$P1$ or $P\bar{1}$	$P2_1/a$	$P2_1/a$
Appearance	Bipyramidal crystals	Small bars with [010] along longitudinal axis	Needles along [100]	Twinned needles along [001]	Leaflike crystals	Needle-shaped crystals along [010]

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* Work performed as part of the ORGEL program.

Table 3. *Comparison of the crystal data of the p-polyphenyls*

	a (Å)	b (Å)	c (Å)	β (°)	Z	Space group	DC
Biphenyl	8·04	5·51	9·39	94·5	2	$P2_1/a$	4·20
p-Terphenyl	8·08	5·60	13·59	91·9	2	$P2_1/a$	4·22
p-Quadriphenyl	8·05	5·55	17·81	95·8	2	$P2_1/a$	4·18
p-Quinquephenyl	8·04	5·485	21·99	92·0	2	$P2_1/a$	4·24
p-Hexaphenyl	8·09	5·60	26·23	91·8	2	$P2_1/a$	

quaphenyl was available of which no good single crystals could be isolated, no single-crystal work was carried out. But with the above considerations about the homologous isomorphism of the *p*-polyphenyls and the result for the *p*-hexaphenyl, the available powder pattern could easily be indexed. After this a refinement was carried out, computing $\sin^2\theta$ values to find the best agreement between observed and calculated $\sin^2\theta$ values. The final agreement obtained for the most important reflexions is given in Table 2.

A final comparison between the linear polyphenyls so far investigated is presented in Table 3.

The author is indebted to Dr C. Stam and Mr A. Kreuger (both of the Laboratory of Crystallography, University of Amsterdam), the former for his constant advice and the latter for his expert help in handling the crystals and taking the X-ray photographs; also to Dr F. Geiss of the Organic Chemical Division of Euratom, Ispra, for providing the samples and to Dr G. Vos for the interest that he has shown in this work.

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The existence of a chromium-molybdenum *A*15 structure.

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In the course of an investigation of Cr–Mo alloys under way in this laboratory an *A*15 or β-W structure (*Strukturbericht*, 1937) was found, which is probably a chromium-molybdenum suboxide. The Cr–Mo alloy was made by argon-arc melting of a mixture of chromium blocks and molybdenum wire. An X-ray diffraction pattern with Cr $K\alpha$ radiation of the button showed only the presence of the b.c.c. primary solid solution with a lattice constant of $a_\alpha = 2{\cdot}94$ Å (corresponding to ~ 18 at.% Mo). The alloy was then homogenized by heating in an evacuated (pressure about 0·1 mmHg) sealed silica tube for 65 hr at 1230°C and slowly cooled. The X-ray pattern (Fig. 1) showed, in addition to the b.c.c. reflexions of the solid solution, strong extra lines, which could be indexed on a cubic cell with lattice constant $a_\beta = 4{\cdot}65$ Å. The ratio between the lattice constants of both phases ($a_\beta/a_\alpha = 1{\cdot}58$) is, within the accuracy attained, practically the same as the ratio between β-W ($a = 5{\cdot}036$ Å) and b.c.c. W ($a_\alpha = 3{\cdot}158$ Å), which is $a_\beta/a_\alpha = 1{\cdot}59$. The indices of the reflexions of the new phase correspond to those of β-W, whereas the relative intensities are approximately the same (Burgers & van Liempt, 1931).

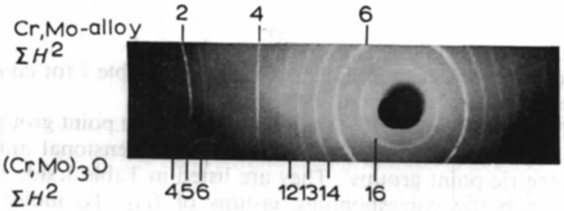

Fig. 1. Straumanis pattern, with Cr $K\alpha$ radiation, of Mo–Cr alloy and (Mo, Cr)$_3$O phase. Camera diameter 57·3 mm.

According to Hägg & Schönberg (1954) β-W is not a tungsten modification, but a metallic oxide with the probable ideal formula W_3O. They assumed that the 6 W atoms and the 2 O atoms are distributed at random over the 8 (*a*) and (*c*) positions of the *A*15 cell. Schönberg (1954*a*) also prepared a chromium oxide with the β-W structure, having the probable formula Cr_3O and with a lattice constant of $a_\beta = 4{\cdot}544$ Å. From intensity calculations of the X-ray pattern the conclusion was drawn that this structure was ordered with 6 Cr atoms situated on the 6(*c*) sites and 2 O atoms on the 2(*a*) sites of the *A*15 cell. Also for the Cr structure the ratio of the lattice constants a_β/a_α appears to be 1·58. Therefore we suggest that the phase found is a Cr, Mo oxide with the formula (Cr, Mo)$_3$O, having an *A*15 crystal structure. Of the weak 110 and 220 reflexions which must be present in the case of an ordered structure, only a very weak 110 reflexion was detectable. Thus it could not be decided if this structure was ordered. The possibility that the relative amounts of Cr and Mo can vary in the (Cr, Mo)$_3$O phase is indicated by a diffraction pattern from a Cr, Mo alloy (~ 46 at.% Mo) that was heated under the same conditions as above. Besides the b.c.c. reflexions of the solid solution (lattice constant $a_\alpha = 3{\cdot}02$ Å) also the 222, 320, 321 and 400 reflexions, which are strong for the β-W structure, were present. The lattice constant of the assumed *A*15 cell was $a_\beta = 4{\cdot}77$ Å, and also in this case the ratio $a_\beta/a_\alpha = 1{\cdot}58$, as for W_3O with respect to W, and Cr_3O with respect to Cr.