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The Crystal Structures of the Monoclinic and Orthorhombic Forms of Zinc(II) n-Butylphenylphosphinate Polymer

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The crystal structures of the monoclinic and orthorhombic forms of zinc(II) n-butylphenylphosphinate polymer, $\{Zn[(n\text{-}C_4H_9)(C_6H_5)PO_2]_2\}_n$, are described. The cell dimensions for the monoclinic form are: $a=10{\cdot}16$, $b=14{\cdot}08$, $c=32{\cdot}59$ Å, $\beta=96{\cdot}8°$; and for the orthorhombic form are: $a=10{\cdot}18$, $b=14{\cdot}10$, $c=32{\cdot}43$ Å. The space group for the monoclinic form is $P2_1/c$ and for the orthorhombic form is $P2_12_12_1$ with eight formula units per cell. The crystal structure of the monoclinic form has been determined from three-dimensional X-ray diffraction data while that of the orthorhombic form has been based on two-dimensional data. The structures consist of polymeric chains in which single and triple phosphinate groups alternate between tetrahedral zinc atoms. Disorder is present in the organic side chains because of a random occurrence of n-butyl and phenyl groups.

Introduction

There has been considerable interest recently in the synthesis and properties of coordination polymers. Interpretation of the results of these works, however, has been somewhat hampered by the lack of any detailed knowledge of the molecular structure of these compounds.

In an attempt to give the structural reasons for the variations in properties in substituted phosphinate polymers, we have undertaken the structural investigation of a number of coordination polymers containing phosphinate bridging groups between tetrahedral metal atoms (Giordano, Randaccio & Ripamonti, 1967*a*; Giancotti, Giordano, Randaccio & Ripamonti, 1968; Gemiti, Giancotti & Ripamonti, 1968). We have now completed an X-ray analysis of the monoclinic and orthorhombic forms of zinc(II) n-butylphenylphosphinate polymer, $\{Zn[(n\text{-}C_4H_9)(C_6H_5)PO_2]_2\}_n$. A preliminary account of the structure of the monoclinic form has been published (Giordano, Randaccio & Ripamonti, 1967*b*).

Experimental

Several crystalline forms of zinc(II) n-butylphenylphosphinate can be obtained (Giancotti & Ripamonti, to be published). Single crystals suitable for an X-ray diffraction study were prepared by the reaction of stoichiometric amounts of n-butylphenylphosphinic acid (3·44 g) and zinc acetate dihydrate (1·9 g) in benzene (250 ml). This solution was refluxed for 5 hr, then ethanol (60 ml) was added. Crystals prismatic in habit were obtained by slow evaporation of this solution. A large number of crystals were examined, most of which were monoclinic. Eventually, orthorhombic crystals were found.

The cell dimensions were obtained from precession photographs taken with Cu $K\alpha$ radiation. They are: monoclinic, $a=10{\cdot}16\pm0{\cdot}02$, $b=14{\cdot}08\pm0{\cdot}02$, $c=32{\cdot}59\pm0{\cdot}04$ Å, $\beta=96{\cdot}8°\pm0{\cdot}2°$; orthorhombic, $a=10{\cdot}18\pm0{\cdot}02$, $b=14{\cdot}10\pm0{\cdot}02$, $c=32{\cdot}43\pm0{\cdot}04$ Å. The systematic absences of reflexions $h0l$ with l odd and $0k0$ with k odd identified the space group $P2_1/c$ for the monoclinic form, while the systematic absences of $h00$ with h odd, $0k0$ with k odd and $00l$ with l odd identified the space group $P2_12_12_1$ for the orthorhombic form. The density of the monoclinic crystals measured by flotation was found to be 1·32 g.cm^{-3}. Too few well formed orthorhombic crystals were available for a determination of density. The calculated densities, assuming eight formula units, $Zn[(C_4H_9)(C_6H_5)PO_2]_2$, in the monoclinic and orthorhombic cells are 1·32 and 1·31 g.cm^{-3}, respectively.

A monoclinic crystal of dimensions 0·3 × 0·1 × 0·1 mm was used for collecting intensity data. Intensities were estimated visually from multiple film equi-inclination Weissenberg photographs (Cu $K\alpha$) of layers 0 to 9 about **a**. $h0l$ and $hk0$ precession photographs (Mo $K\alpha$) were recorded to provide cross-correlation terms. The full sphere of data for copper radiation could not be obtained since the diffraction patterns faded at $\theta\sim55°$. 2212 non-zero reflexions were observed and scaled with the aid of cross-correlation terms. The usual Lorentz and polarization factors were applied together with spot-elongation corrections for the upper layers. No corrections were made for absorption or for anomalous dispersion.

The cell dimensions and intensity distribution of the rotation photographs around **a** indicated that the monoclinic and orthorhombic forms are closely related. Furthermore the intensities of $0kl$ reflexions of the two forms were the same within the experimental errors. Therefore, it was not considered worth while to record three-dimensional data for the orthorhombic form and the analysis of this form was based on the intensities of the reflexions visually estimated from $h0l$ precession photographs (Mo $K\alpha$). The data were corrected for Lorentz and polarization factors.

All calculations were performed on an IBM 7040 computer equipped with a 32K memory. The least-squares program was that of Albano, Domenicano & Vaciago (1966), which minimizes the function $\Sigma\, w(|F_o|-|F_c|)^2/\,\Sigma\, w|F_o|^2$, where F_o and F_c are the observed and calculated structure factors, respectively, and w is the weighting factor. The weighting scheme $w=[a+b|F_o|+c|F_o|^2]^{-1}$, with $a=10{\cdot}0$, $b=1{\cdot}0$, $c=0{\cdot}005$, was used. Programs of Domenicano & Vaciago (unpublished) were used for data processing, Fourier functions and distances and angles. The best molecular planes formed by sets of specified atoms and the perpendicular distances of these and other atoms from these planes were calculated by a least-squares method with a program of our own design (unpublished).

Atomic scattering factors were taken as the values reported in *International Tables for X-ray Crystallography* (1962) for neutral Zn, P, O and C.

Structure determination

Monoclinic form

The intensity distribution along the layer lines of the rotation photographs taken about **a** indicated that molecular chains with a backbone structure similar to that established for $\{Zn[(n\text{-}C_4H_9)_2PO_2]_2\}_n$ (Giordano, Randaccio & Ripamonti, 1967*a*) and $\{Zn[(n\text{-}C_4H_9)_2PO_2(n\text{-}C_6H_{13})_2PO_2]\}_n$ (Giancotti, Giordano, Randaccio & Ripamonti, 1968) are parallel to **a**. A three-dimensional Patterson map verified the chain-like structure with zinc atoms bridged by alternate single and triple phosphinate groups. The chains repeat identically after two zinc atoms and therefore are located in general fourfold positions. Two alternative arrangements (I and II) were possible on the basis of the approximate positions of the zinc and phosphorus atoms found by interpretation of the Patterson map. For case I the zinc atoms of the same chain projected on (010) at $y=0{\cdot}25$ and $z=0{\cdot}09$ and for case II they were shifted of 0·25 along **c**. Thus the chains less displaced along *c* could be related by either a centre of symmetry or a screw-axis.

Fourier syntheses, using phases calculated from the zinc and phosphorus atoms, revealed the oxygen and carbon atoms attached to the phosphorus atoms for both cases. For case I the electron density map revealed in addition a n-butyl and a phenyl group whose C(5) and C(6) are the first carbon atoms respectively. A sketch of the backbone structure is shown in Fig. 1. After inclusion of the located carbon atoms in the structure factors ($R=0{\cdot}39$ and 0·41 for cases I and II respectively) no clear indication of the positions of the remaining carbon atoms could be obtained in the subsequent Fourier syntheses. This suggested a random occurrence of the two different organic side groups along the chain in agreement with the similarity of the X-ray powder spectra of the monoclinic form of $\{Zn[(n\text{-}C_4H_9)\,(C_6H_5)PO_2]_2\}_n$ and of the mixed ligand species $\{Zn[(n\text{-}C_4H_9)_2PO_2]_{2-2x}[(C_6H_5)_2PO_2]_{2x}\}_n$ richer in diphenylphosphinate groups (Giancotti & Ripamonti, 1969). The latter compounds can be formulated as random copolymers, which show isomorphous replacement of the two kinds of phosphinate groups within the crystal lattice of the related homopolymers. A similar phenomenon was observed for the mixed ligand species $\{Be[(n\text{-}C_4H_9)_2PO_2]_{2-2x}\text{-}[(C_6H_5)_2PO_2]_{2x}\}_n$ (Gemiti, Giancotti & Ripamonti, 1968). Since the monoclinic form of $\{Zn[(n\text{-}C_4H_9)\text{-}(C_6H_5)PO_2]_2\}_n$ was found to have the same basic crystal structure as the γ-form of $\{Zn[(C_6H_5)_2PO_2]_2\}_n$ it appears likely that the crystal packing is essentially determined by the phenyl side groups and that half-butyl and half-phenyl groups should be located on the same substituent site. Therefore, a random occurrence of the two different side groups was assumed and the coordinates of the carbon atoms were determined taking into account the best possible crystal packing. Standard bond lengths and angles and a zigzag planar conformation of the n-butyl groups were assumed. Three cycles of block-diagonal least-squares refinement, allowing the positional parameters and isotropic temperature factors of zinc, phosphorus and oxygen atoms to vary, reduced R to 0·25 and 0·37 for case I and II respectively. Furthermore, for case II some bond angles and lengths of the main chain were not acceptable, therefore, the refinement was continued only for case I.

A three-dimensional Fourier synthesis of electron density and a difference synthesis, including the atoms of the main chain and the carbon atoms attached to the phosphorus atoms, were computed. The regions of the electron density maps between adjacent main chains

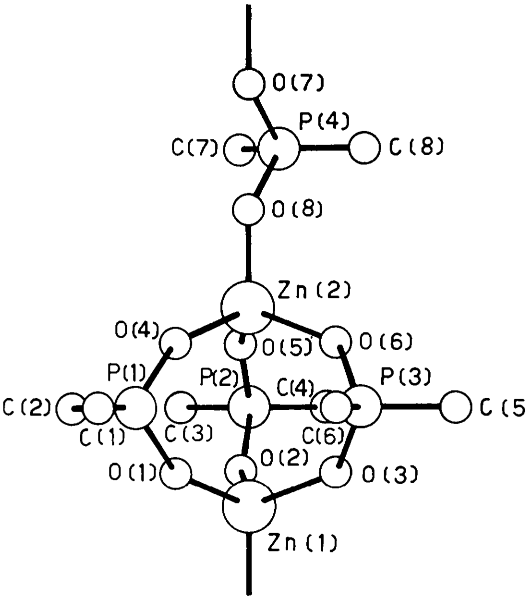

Fig. 1. Sketch of the backbone structure of zinc(II) n-butylphenylphosphinate polymer and numbering scheme for the atoms. Only the first carbon atoms of the organic side groups are shown.

were examined for peaks due to carbon atoms. The location of the n-butyl and phenyl groups revealed in the first Fourier synthesis was confirmed. Furthermore well resolved peaks were observed in the regions corresponding to the carbon atoms of the phenyl side groups in *para* positions to the phosphorus atoms. However, only broad regions of electron density of about 2 e.Å^{-3} could be noted where the remaining carbon atoms were expected. The packing of the phenyl side groups was consequently re-examined and the model shown in Fig. 2 was obtained. Very efficient contacts are experienced by the phenyl group at the substituent site (6) and a similar close packing was found for the phenyl group at (8). Replacement of phenyl groups with n-butyl groups in zigzag conformation provided short van der Waals contacts, except for the replacement of the side group at the substituent site (5). These packing considerations and the prominent features of the electron density distribution led us to assume that the n-butyl groups were employed mostly to fill the empty space existing in the crystal lattice. Therefore the n-butyl groups, with the exception only of that at the substituent site (5), were considered completely disordered and a further refinement was attempted, including the carbon atoms of the phenyl groups at the calculated positions of the model in Fig. 2 and of the n-butyl group in (5). An occupancy factor of 0·5 was given to all carbon atoms except to those attached to the phosphorus atoms.

Five cycles of block-diagonal least-squares refinement of the coordinates and isotropic temperature factors reduced the R value to 0·18. While the thermal parameters for the *para* ring carbon atoms and for the carbon atoms of the phenyl groups at the substituent sites (6) and (8) and of the n-butyl group at (5) were quite normal, unusually large amplitudes of thermal motion were obtained for the other carbon atoms. This suggested an orientational disorder of the phenyl groups due to loose packing in the corresponding regions of the structure. In fact, if one assumes a random occurrence of n-butyl and phenyl groups, it seems unlikely that each phenyl group is fixed in a definite orientation irrespective of other neighbouring groups. At this stage a further electron density difference map with the atoms of the main chain, the carbon atoms directly bonded to the phosphorus atoms and those of the side groups bonded to C(5), C(6) and C(8) subtracted out, was calculated using the results of the last refinement. Broad peaks of the electron density, found in the expected regions for the missing carbon atoms, supported a random occupancy at the substituent sites. In addition they indicated that the n-butyl groups could not be considered free to choose any possible orientation irrespective of their nearest neighbours. However, while it was possible to interpret the electron density with the first three carbon atoms of each n-butyl group, there was no evidence for the location of the fourth carbon atoms. Therefore, the missing side groups were oriented in such a way as to obtain the best interpretation of the electron density difference map. The carbon atoms at the ends of the n-butyl chains were ignored. In order to take into account the

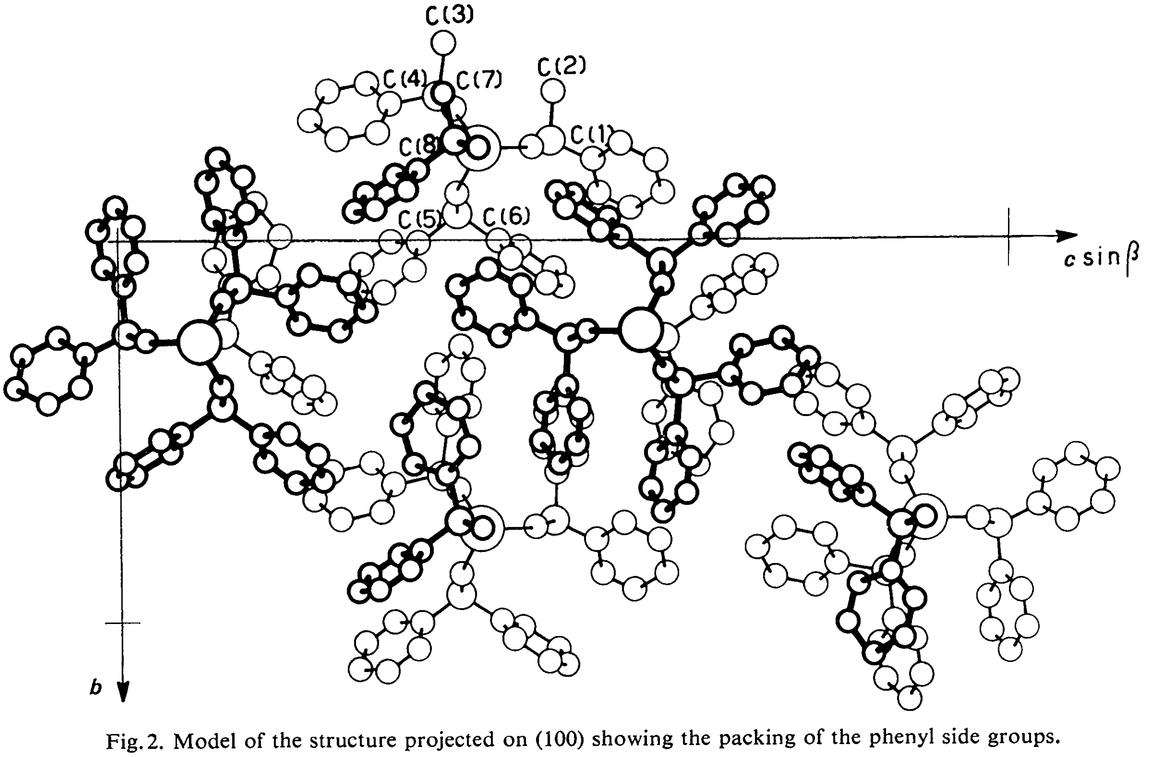

Fig. 2. Model of the structure projected on (100) showing the packing of the phenyl side groups.

Table 1. *Observed and calculated structure factors* (*monoclinic form*)

H	K	L	FO	FC
1	0	0	43.3	35.5
2	0	0	326.0	-302.4
3	0	0	110.6	138.3
5	0	0	117.1	110.4
6	0	0	26.2	-26.4
7	0	0	21.3	-8.7
8	0	0	12.7	-11.0
10	0	0	40.2	35.5
11	0	0	25.2	-20.0
0	0	2	260.3	256.9
1	0	2	207.4	190.0
1	0	-2	148.0	-217.1
2	0	2	76.9	62.7
2	0	-2	154.3	-180.1
3	0	2	195.5	238.5
3	0	-2	74.6	-77.9
4	0	2	19.6	-23.5
4	0	-2	16.3	-19.2
5	0	2	75.7	92.3
6	0	2	95.4	124.8
6	0	-2	155.0	-182.8
7	0	2	29.2	27.4
8	0	2	49.8	47.5
8	0	-2	24.8	37.3
10	0	2	29.7	28.1
10	0	-2	23.9	-33.4
11	0	-2	38.3	-40.7
0	0	4	257.0	-308.3
1	0	4	56.0	32.8
1	0	-4	110.6	-50.8
2	0	4	68.6	-84.8
2	0	-4	72.1	95.2
8	0	-24	25.0	-27.3
11	0	-24	21.0	-19.8
0	0	26	17.7	10.2
1	0	26	27.3	22.0
1	0	-26	22.2	-19.1
2	0	26	28.3	-31.9
5	0	-26	42.0	-43.6
8	0	-26	30.5	-33.7
0	0	28	30.7	-27.2
1	0	-28	14.6	-13.0
2	0	-28	31.7	-31.4
3	0	-28	22.5	-26.4
4	0	-28	18.4	13.2
5	0	-28	34.4	-31.6
0	0	30	28.2	-27.1
3	0	-32	23.7	29.0
6	0	34	24.2	17.1
1	1	0	129.8	164.3
2	1	0	57.0	66.6
3	1	0	116.6	112.5
4	1	0	18.7	12.0
5	1	0	71.6	65.9
6	1	0	122.5	135.3
7	1	0	21.5	-21.1
8	1	0	29.8	27.6
9	1	0	22.3	13.7
10	1	0	34.3	33.2
11	1	0	27.1	24.1
0	1	1	29.8	-33.5
1	1	1	7.9	-20.4
1	1	-1	7.9	9.8
2	1	1	43.7	16.4

Table 1 (*cont.*)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	9	2	69.7	-77.5	3	9	-7	26.7	-30.8	0	9	14	37.9	-40.5	3	10	-5	22.8	24.9	2	11	-1	32.2	38.2
1	9	2	18.1	10.1	4	9	7	43.4	53.9	1	9	-14	20.3	20.4	0	10	6	38.4	41.9	3	11	1	25.6	27.7
2	9	2	25.6	-32.2	5	9	-7	29.1	24.2	2	9	-14	14.2	22.1	2	10	6	21.6	24.8	0	11	2	39.5	52.[illegible]
2	9	-2	19.5	17.8	0	9	8	36.6	40.1	5	9	-14	40.3	47.0	2	10	-6	16.0	18.7	1	11	2	16.9	-25.[illegible]
3	9	2	26.3	-26.6	2	9	8	34.4	42.3	0	9	15	23.5	21.0	3	10	6	25.0	33.6	1	11	-2	16.0	-15.4
3	9	-2	66.1	57.4	2	9	-8	25.5	-23.7	1	9	-15	16.4	11.5	5	10	-6	26.7	17.7	1	11	-3	16.0	-13.7
5	9	-2	18.2	20.5	3	9	8	30.4	35.7	0	9	16	15.8	-24.3	0	10	7	24.9	-37.7	2	11	-3	16.7	16.5
1	9	3	17.7	-11.2	3	9	-8	31.1	-29.1	1	9	16	21.6	-24.8	1	10	7	19.4	15.1	3	11	3	21.7	24.5
1	9	-3	19.9	20.7	5	9	8	29.8	12.2	1	9	-16	14.2	-12.7	1	10	-7	22.4	27.1	3	11	-3	23.7	-29.7
2	9	3	42.2	44.9	5	9	-8	29.2	-23.8	0	9	17	35.6	36.2	2	10	7	24.4	-23.0	0	11	4	31.6	36.[illegible]
3	9	3	29.2	-28.4	0	9	9	16.1	-22.7	5	9	-17	27.0	26.3	2	10	-7	27.9	30.4	0	11	5	35.4	-44.0
3	9	-3	70.5	67.3	1	9	9	24.0	26.3	1	9	18	15.6	-22.0	3	10	7	19.3	-15.2	2	11	-5	16.7	-20.5
4	9	3	27.9	-31.8	1	9	-9	19.5	-15.9	1	9	-18	14.5	-20.9	3	10	-7	21.0	22.4	3	11	-5	23.7	-27.1
4	9	-3	31.5	39.0	2	9	9	28.4	-32.9	5	9	-18	27.0	-22.5	4	10	-7	24.7	-26.9	5	11	-5	30.2	-27.1
0	9	4	51.4	-58.1	2	9	-9	24.3	-25.6	0	10	0	72.3	-84.4	5	10	-7	26.8	30.0	1	11	6	15.3	11.7
1	9	4	17.2	16.7	3	9	9	22.7	-25.4	3	10	0	36.6	-39.0	2	10	-8	25.4	25.0	0	11	7	33.6	-35.4
1	9	-4	12.5	12.7	3	9	-9	38.4	-38.9	2	10	1	49.0	57.3	3	10	8	19.1	14.2	2	11	-7	20.6	-16.3
2	9	4	15.0	-11.7	4	9	-9	37.1	45.1	3	10	1	18.5	-21.2	3	10	-8	23.1	-33.4	3	11	7	19.6	-22.1
2	9	-4	28.7	28.5	5	9	9	35.4	34.6	3	10	-1	71.7	-76.7	0	10	9	44.1	-49.6	0	11	8	22.3	-29.2
3	9	4	65.0	-64.4	6	9	-9	32.9	-35.5	4	10	1	26.9	-30.9	2	10	-9	14.3	20.8	5	11	-8	23.4	18.4
5	9	-4	25.7	21.3	1	9	10	15.1	7.5	4	10	-1	15.5	-13.6	3	10	9	23.6	-29.4	1	11	9	14.5	-7.9
0	9	5	53.9	62.2	2	9	10	13.8	22.2	0	10	2	29.4	-35.8	3	10	-9	19.0	-17.1	3	11	-9	19.6	15.7
1	9	5	14.3	-7.2	2	9	-10	35.0	-30.1	1	10	2	12.3	-9.6	5	10	-9	37.9	41.4	1	11	10	11.0	-15.6
1	9	-5	20.1	9.5	3	9	10	18.7	21.5	3	10	2	39.4	-47.3	0	10	10	36.1	-43.3	2	11	-10	17.0	16.4
2	9	5	34.9	35.8	3	9	-10	35.4	31.8	3	10	-2	20.7	21.7	3	10	-11	25.4	-36.9	0	11	11	26.6	25.[illegible]
2	9	-5	44.4	43.3	5	9	-10	32.3	-32.5	6	10	-2	28.0	30.7	0	10	12	15.8	-17.6	1	11	11	11.1	5.7
3	9	5	39.6	45.0	0	9	11	41.1	-42.8	0	10	3	32.4	38.7	1	10	12	12.1	-6.4	2	11	-11	14.8	17.1
3	9	-5	45.7	49.2	1	9	-11	15.2	-15.5	2	10	3	28.5	27.3	0	10	13	33.7	37.2	3	11	-11	[illegible]	20.[illegible]
4	9	5	18.5	20.8	2	9	-11	33.5	-34.2	2	10	-3	54.0	-61.0	3	10	-13	23.8	-26.5	0	11	12	18.2	28.5
4	9	-5	27.8	-28.2	3	9	11	16.4	-29.3	3	10	3	28.0	35.4	5	10	-13	19.1	-27.5	2	11	-12	14.9	22.6
5	9	5	29.3	12.7	3	9	-11	18.5	8.3	3	10	-3	35.9	-43.3	1	10	14	16.5	-13.0	2	11	-13	21.1	18.6
6	9	5	33.0	-30.0	4	9	11	15.8	-19.9	4	10	-3	29.0	31.2	1	10	-14	14.4	9.7	0	12	0	22.7	28.7
0	9	6	20.9	20.9	4	9	-11	36.2	40.3	0	10	4	33.2	43.1	2	10	-14	22.4	-22.0	1	12	0	15.6	-5.2
1	9	-6	18.5	14.1	5	9	-11	45.9	-54.1	1	10	4	19.6	-16.0	0	10	15	24.3	27.7	0	12	1	24.3	-26.[illegible]
2	9	-6	22.5	10.4	0	9	12	33.8	-42.1	2	10	4	16.0	16.6	1	10	15	15.6	18.4	1	12	2	15.6	-8.6
3	9	6	18.0	-16.0	1	9	12	40.9	36.3	3	10	-4	48.9	48.7	1	10	-15	13.5	18.1	1	12	-2	23.4	9.9
3	9	-6	78.2	-75.4	1	9	-12	25.9	28.9	4	10	4	22.1	-6.1	5	10	-16	23.2	30.2	0	12	3	36.6	-42.3
5	9	6	41.7	-21.4	3	9	-12	24.7	17.0	5	10	4	35.5	-6.1	1	10	17	15.8	11.8	1	12	4	19.2	14.7
6	9	-6	27.6	-21.5	0	9	13	18.6	-15.0	0	10	5	20.9	24.2	2	10	-17	19.2	-7.9	1	12	-5	23.5	-25.9
0	9	7	40.7	45.4	1	9	13	20.3	-21.4	1	10	5	19.8	18.4	1	11	0	13.0	-12.6	0	12	7	21.7	22.1
2	9	7	20.4	-19.9	1	9	-13	11.6	14.6	2	10	5	16.1	-14.0	0	11	1	23.3	28.1	0	12	9	20.1	18.9
2	9	-7	23.8	19.4	3	9	-13	31.2	35.1	2	10	-5	19.5	-22.0	1	11	1	20.6	15.6	0	12	10	18.3	19.3
3	9	7	30.1	25.5	5	9	-13	26.8	-35.2															

possible orientational disorder, each group was considered free to choose one of two possible orientations. When these carbon atoms with an overall isotropic temperature factor of 10 Å^2 were included in the structure factor calculation, the R value slightly increased to 0·19. However, a marked improvement of the agreement between observed and calculated structure factors for some reflexions with low Bragg angle was noted. With regard to the small contribution of the disordered organic part of the crystal to the diffracted radiation, this organic part was taken as constant in the subsequent refining process. A block-diagonal least-squares refinement with anisotropic thermal parameters for the zinc, phosphorus and oxygen atoms and isotropic thermal parameters for the carbon atoms revealed in the Fourier syntheses was continued until no parameter changed by more than half of its standard deviation. The R value for observed reflexions was 0·14. The high thermal parameters obtained for some carbon atoms indicated that their positions could not be taken seriously. Furthermore, no improvement in the location of the carbon atoms held fixed during the last refinement could be obtained from examination of a difference-Fourier synthesis (all atoms except carbon atoms of the side groups held fixed subtracted out). Further attempts at refinement might lead to a better fit, but the difficulties encountered in resolving the structure of the side groups convinced us that the structure is refined as far as is justified for the present experimental data.

Table 1 lists the observed and calculated structure factors. The final atomic coordinates and temperature factors together with their estimated standard deviations are given in Tables 2, 3 and 4. The angles of rotation around the P–C bonds of the side groups held fixed in the least-squares refinement are given in Table 5.

Table 2. *Fractional atomic coordinates (monoclinic form)*

Standard deviations are given in parentheses. The coordinates and their standard deviations have both been multiplied by 10^4. The numbering of the carbon atoms is referred to that of the atoms attached to the phosphorus atoms and the symbols Bu and Ph indicate n-butyl and phenyl groups.

	x	*y*	*z*
Zn(1)	260 (3)	−2346 (3)	4123 (1)
Zn(2)	4027 (3)	−2366 (3)	4115 (1)
P(1)	2446 (8)	−2617 (6)	4905 (2)
P(2)	1947 (8)	−3830 (6)	3642 (3)
P(3)	2049 (7)	−661 (6)	3861 (2)
P(4)	7057 (7)	−2535 (6)	3847 (3)
O(1)	1097 (17)	−2393 (14)	4692 (6)
O(2)	730 (16)	−3446 (13)	3823 (6)
O(3)	799 (18)	−1224 (13)	3858 (6)
O(4)	3619 (18)	−2384 (15)	4679 (6)
O(5)	3256 (16)	−3471 (13)	3828 (7)
O(6)	3280 (19)	−1217 (13)	3830 (6)
O(7)	8372 (18)	−2298 (17)	4093 (6)
O(8)	5841 (18)	−2400 (15)	4072 (6)
C(1)	2657 (41)	−1952 (28)	5412 (12)
C(2)	2537 (40)	−3865 (28)	5001 (12)
C(3)	1984 (37)	−5263 (27)	3804 (11)
C(4)	1865 (53)	−3511 (40)	3121 (16)
C(5)	1871 (32)	196 (23)	3396 (10)
C(6)	2283 (25)	94 (18)	4314 (8)
C(7)	7054 (53)	−3824 (40)	3687 (17)
C(8)	6870 (34)	−1775 (24)	3394 (10)
C(5Bu1)	3478 (67)	626 (47)	3359 (21)
C(5Bu2)	3754 (163)	1200 (128)	3035 (50)

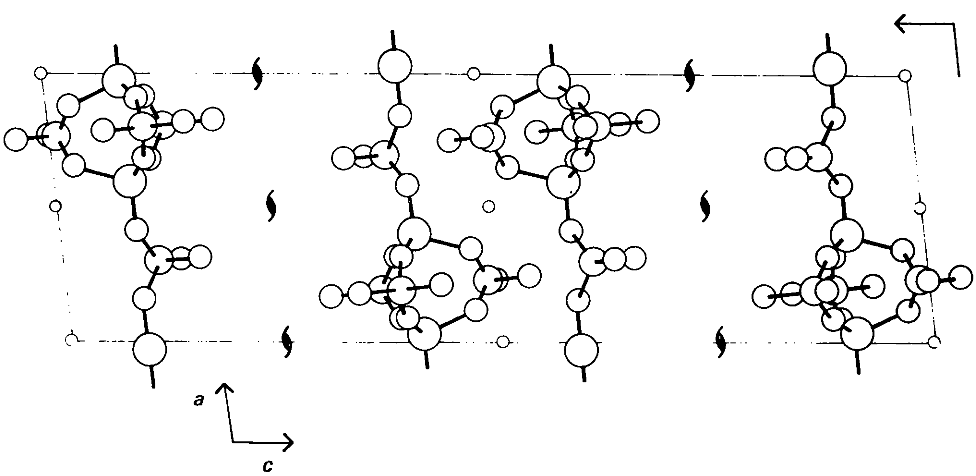

Fig. 3. Projection on (010) for the monoclinic form. Only the first carbon atoms of the organic side groups are shown.

Table 2 (*cont.*)

	x	y	z
C(5Bu3)	4242 (89)	1869 (64)	2879 (26)
C(6Ph1)	3514 (36)	405 (26)	4473 (11)
C(6Ph2)	3584 (49)	959 (34)	4822 (15)
C(6Ph3)	2556 (37)	1315 (27)	4986 (11)
C(6Ph4)	1384 (45)	977 (32)	4861 (14)
C(6Ph5)	1145 (41)	336 (30)	4499 (13)
C(8Ph1)	5721 (65)	−1547 (46)	3202 (20)
C(8Ph2)	5495 (81)	−898 (56)	2813 (25)
C(8Ph3)	6502 (71)	−600 (49)	2650 (22)
C(8Ph4)	7606 (98)	−879 (71)	2770 (32)
C(8Ph5)	7974 (71)	−1592 (52)	3158 (22)
C(1Ph3)	3019 (98)	−1077 (73)	6192 (31)
C(2Ph3)	2492 (73)	−5628 (52)	5134 (22)
C(3Ph3)	2022 (64)	−7011 (46)	4023 (19)
C(4Ph3)	978 (99)	−3073 (71)	2297 (29)
C(5Ph3)	2753 (207)	1541 (163)	2942 (65)
C(7Ph3)	6516 (86)	−5747 (61)	3522 (27)

Orthorhombic form

Since the intensities of the $0kl$ reflexions for the monoclinic and orthorhombic forms were the same within experimental errors (see *Experimental*), the projections of the two structures along the axis **a** were assumed to be coincident, with the origin for the orthorhombic form shifted $\frac{1}{4}$ along **b**. The x coordinates were easily determined from the Patterson projection onto (010). Structure factor calculations with the contribution of the zinc, phosphorus and oxygen atoms, with an overall temperature factor of 5 Å^2, and of the first carbon atoms of the side groups with an overall temperature factor of 8 Å^2, gave an R value of 0·23 for 53 $h0l$ observed reflexions. Table 6 lists the fractional atomic coordinates. The observed and calculated structure factors are given in Table 7.

Table 3. *Anisotropic thermal parameters (monoclinic form)*

The temperature factor expression used was

$$\exp\left[-(b_{11}h^2+b_{12}hk+b_{13}hl+b_{22}k^2+b_{23}kl+b_{33}l^2)\right].$$

The b_{ij} values and their estimated standard deviations (in parentheses) have both been multiplied by 10^4.

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Zn(1)	79 (1)	0 (6)	23 (2)	89 (2)	−7 (2)	18 (1)
Zn(2)	75 (1)	−2 (5)	20 (2)	80 (2)	0 (2)	19 (1)
P(1)	128 (2)	−12 (14)	23 (5)	99 (6)	3 (4)	15 (1)
P(2)	120 (6)	−23 (14)	33 (6)	93 (6)	−24 (5)	24 (1)
P(3)	109 (8)	5 (12)	18 (5)	69 (5)	4 (4)	15 (1)
P(4)	118 (8)	−22 (13)	25 (13)	75 (5)	−135 (5)	18 (1)
O(1)	113 (19)	61 (33)	19 (12)	134 (16)	24 (11)	21 (2)
O(2)	100 (17)	49 (27)	67 (11)	91 (12)	−15 (10)	27 (3)
O(3)	127 (22)	−53 (32)	6 (14)	93 (12)	−5 (10)	19 (2)
O(4)	129 (21)	−32 (34)	18 (12)	138 (16)	15 (11)	18 (2)
O(5)	62 (17)	−57 (28)	19 (14)	88 (13)	−21 (12)	37 (4)
O(6)	209 (27)	−35 (33)	45 (15)	76 (12)	6 (10)	22 (3)
O(7)	102 (20)	33 (37)	20 (13)	174 (19)	−20 (13)	23 (3)
O(8)	114 (19)	12 (40)	31 (13)	130 (16)	−18 (12)	26 (3)

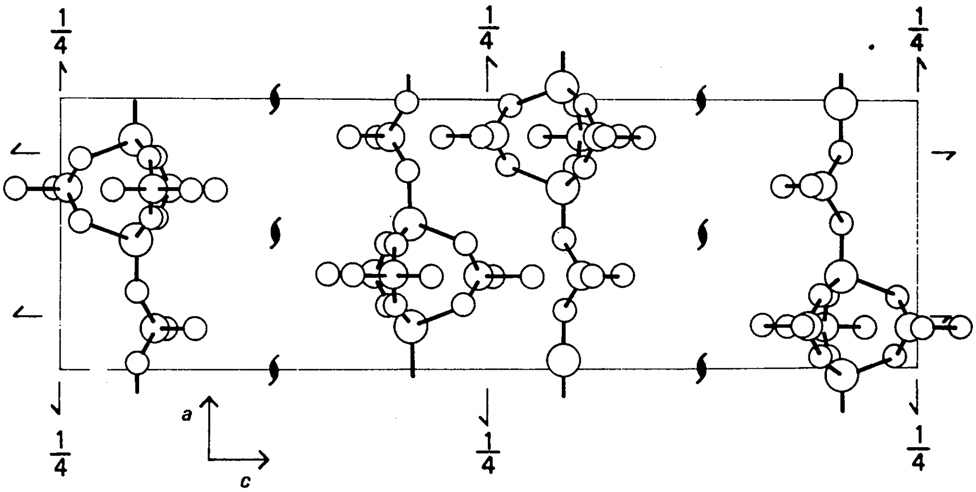

Fig. 4. Projection on (010) for the orthorhombic form. Only the first carbon atoms of the organic side groups are shown.

Table 4. *Isotropic temperature factors for carbon atoms* (*monoclinic form*)

The Debye–Waller factor is $\exp[-(B\sin^2\theta/\lambda^2)]$. Standard deviations × 10 are given in parentheses.

	B		B		B
C(1)	11·2 (11)	C(5Bu2)	32·4 (68)	C(8Ph3)	9·1 (19)
C(2)	10·9 (11)	C(5Bu3)	12·8 (25)	C(8Ph4)	14·6 (30)
C(3)	10·2 (10)	C(6Ph1)	2·2 (8)	C(8Ph5)	9·6 (19)
C(4)	16·5 (17)	C(6Ph2)	5·2 (12)	C(1Ph3)	14·4 (32)
C(5)	8·5 (8)	C(6Ph3)	2·5 (8)	C(2Ph3)	10·0 (20)
C(6)	5·4 (6)	C(6Ph4)	4·4 (10)	C(3Ph3)	8·2 (17)
C(7)	16·9 (17)	C(6Ph5)	3·4 (10)	C(4Ph3)	14·7 (29)
C(8)	8·8 (9)	C(8Ph1)	8·3 (16)	C(5Ph3)	36·5 (88)
C(5Bu1)	9·3 (17)	C(8Ph2)	11·3 (23)	C(7Ph3)	12·3 (25)

Table 5. *Orientations and occupancy factors of the side groups held fixed during the least-squares refinement* (*monoclinic form*)

The side groups were referred to the calculated positions of the carbon atoms attached to the phosphorus atoms, assuming the plane through the phosphorus and carbon atoms perpendicular to the axis **a** of the crystal system and hence almost perpendicular to the plane through the phosphorus and oxygen atoms.

P–C bond lengths of 1·80 Å and C–P–C bond angles of 110° were used. ψ is the angle of rotation about the P–C bond measured anti-clockwise from the plane defined by the axes u_1 and u_2 of a reference orthogonal system **u** with origin at the phosphorus atom; u_2 is directed along the P–C vector, u_3 along the axis **a** of the crystal system and u_1 is so chosen as to make the system right-handed. The second carbon atom of the n-butyl chain has positive component along u_1 when $\psi=0$.

Carbon atoms directly bonded to P	Side groups	Occupancy factors	ψ (°)
C(1)	Ph I	0·25	−40
	Ph II	0·25	40
	Bu I	0·25	170
	Bu II	0·25	190
C(2)	Ph I	0·25	60
	Ph II	0·25	70
	Bu I	0·25	55
	Bu II	0·25	235
C(3)	Ph I	0·25	80
	Ph II	0·25	60
	Bu I	0·25	−90
	Bu II	0·25	90
C(4)	Ph I	0·25	40
	Ph II	0·25	−40
	Bu I	0·25	165
	Bu II	0·25	185
C(5)	Ph I	0·25	55
	Ph II	0·25	75
C(6)	Bu I	0·25	80
	Bu II	0·25	270
C(7)	Ph I	0·25	30
	Ph II	0·25	20
	Bu	0·50	30
C(8)	Bu I	0·25	80
	Bu II	0·25	270

Discussion

The structures of the monoclinic and orthorhombic forms of $\{\mathrm{Zn}[(n\text{-}C_4H_9)(C_6H_5)PO_2]_2\}_n$ viewed down **b** are shown in Figs. 3 and 4. The most important aspect of these structures is the fact that they are built up of polymeric chains containing three-atom bridging groups between tetrahedral metal atoms with a backbone structure similar to that found in zinc(II) and cobalt(II) di-n-alkylphosphinate polymers (Giordano, Randaccio & Ripamonti, 1967*a*; Giancotti, Giordano, Randaccio & Ripamonti, 1968). Since the monoclinic form has the same basic crystal structure as the γ form of zinc(II) and cobalt(II) diphenylphosphinate (Giancotti & Ripamonti, 1969), it can be concluded that the backbone structure with alternate single and triple bridging phosphinate groups between tetrahedral metal atoms is also common to the infusible and insoluble diphenyl derivative.

Table 6. *Fractional atomic coordinates* (*orthorhombic form*)

The coordinates are multiplied by 10^3

	x	y	z
Zn(1)	158	515	412
Zn(2)	532	513	412
P(1)	345	488	491
P(2)	345	367	364
P(3)	345	684	386
P(4)	845	497	385
O(1)	222	511	469
O(2)	222	405	382
O(3)	222	628	386
O(4)	468	512	468
O(5)	468	403	383
O(6)	468	628	383
O(7)	968	520	409
O(8)	722	510	407
C(1)	345	555	541
C(2)	345	364	500
C(3)	345	224	380
C(4)	345	398	312
C(5)	345	770	340
C(6)	345	759	431
C(7)	845	368	369
C(8)	845	573	340

The bond lengths and angles, calculated from the atomic coordinates determined for the monoclinic form, are listed in Table 8. The eight Zn–O bond lengths and the twelve O–Zn–O angles at the two crystallographically non-equivalent zinc atoms average 1·92 Å and 109·5° with spreads of ±0·05 Å and ±3·8° respectively. The mean P–O length and O–P–O angle are 1·50 Å and 116·5° with spreads of 0·03 Å and 1·0° respectively. These results compare well with the expected values for these types of bonding. The Zn–O–P angles at the oxygen atoms of the triple-bridged unit lie in the range 132·3°–139·8° with an average value of 136·7° significantly smaller than the two Zn–O–P angles at the oxygen atoms of the single bridge which are 147·0° and 154·9°.

Neglecting the organic side substituents, the cage structure formed by the triple bridging phosphinate groups has nearly a C_{3h} symmetry with the threefold axis passing through the chain of metal atoms. The mean plane through P(1), P(2), P(3) and the middle point, Zn(0), of the two nearest zinc atoms has the following equation referred to the crystallographic axes:

$$10\cdot160x-0\cdot051y-3\cdot980z=0\cdot468\ .$$

Table 7. *Observed and calculated structure factors (orthorhombic form)*

H	K	L	|FO|	|FC|	H	K	L	|FO|	|FC|	H	K	L	|FO|	|FC|
0	0	2	249.6	291.2	2	0	0	160.5	78.0	3	0	9	67.1	100.1
0	0	4	235.6	400.0	2	0	1	220.3	136.2	3	0	13	85.8	93.9
0	0	6	119.2	191.5	2	0	3	83.0	71.4	4	0	6	50.2	63.7
0	0	8	189.3	200.3	2	0	5	92.2	77.8	4	0	7	50.1	60.2
0	0	10	220.4	244.4	2	0	6	76.8	74.1	4	0	8	51.0	35.3
0	0	12	77.2	44.7	2	0	7	217.4	222.0	5	0	2	123.0	111.1
0	0	14	71.5	67.8	2	0	8	60.0	67.5	5	0	4	83.9	77.4
0	0	16	67.2	55.5	2	0	9	75.4	64.4	5	0	8	125.1	105.7
1	0	1	50.5	91.3	2	0	11	86.7	118.4	5	0	10	117.7	100.5
1	0	2	132.2	187.1	2	0	13	80.9	91.6	5	0	14	103.2	109.5
1	0	3	103.1	99.2	2	0	15	72.1	77.3	5	0	16	99.6	95.0
1	0	4	73.0	55.9	2	0	17	121.0	131.2	6	0	0	140.6	181.9
1	0	6	45.1	52.1	3	0	1	93.7	69.8	6	0	1	84.1	68.0
1	0	7	73.3	29.7	3	0	2	55.6	29.6	6	0	2	63.1	55.3
1	0	9	45.6	28.7	3	0	3	198.8	170.9	6	0	4	74.1	83.3
1	0	10	55.1	63.6	3	0	4	48.4	34.4	6	0	5	62.9	37.1
1	0	11	57.7	48.2	3	0	5	82.8	74.4	6	0	6	69.0	38.3
1	0	12	64.4	40.4	3	0	7	96.1	105.5					

The perpendicular distances out of this plane are P(1) 0·028, P(2) 0·029, P(3) 0·030, Zn(0) −0·087 Å. The P(1)–P(2), P(1)–P(3) and P(2)–P(3) distances and P(1)–P(2)–P(3), P(1)–P(3)–P(2) and P(2)–P(1)–P(3) angles are 4·43, 4·36, 4·52 Å, 58·4°, 59·9° and 61·8° respectively. The increase of the identity period along the chain axis from 9·90 Å in di-n-alkylphosphinates (Giordano, Randaccio & Ripamonti, 1967*a*; Giancotti, Giordano, Randaccio & Ripamonti, 1968) to 10·16 Å in n-butylphenylphosphinate is related to a different conformation of the triple-bridged unit. In di-n-alkylphosphinates the top triplet of oxygen atoms is rotated with respect to the bottom triplet and the symmetry of the cage structure is D_3. The interactions between the organic substituents can be responsible for the different conformation of the triple-bridged unit when a phenyl group replaces an n-alkyl group bonded to the phosphorus atom. Thus, the backbone structure is more ordered in the n-butyl phenyl derivative for which one has to remove the possibility of a disordered distribution of the two enantiomorphous triple-bridged units found in the crystal structures of zinc(II) di-n-alkylphosphinates thus far determined.

However, the precision of the present structure is reduced by the disorder of the organic side groups because of the random occurrence of the n-butyl and phenyl groups at the substituent sites. The statistical disordering of the organic side groups is supported by the similarity between the X-ray powder pattern of the monoclinic crystals and that of the crystalline modification of mixed ligand species, $\{Zn[(n\text{-}C_4H_9)_2PO_2]_{2-2x}[(C_6H_5)_2PO_2]_{2x}\}_n$, isomorphous with the γ form of the diphenyl derivative (Giancotti &

Table 8. *Bond lengths and angles*

The average estimated standard deviations are:
Zn–O 0·02 Å; P–O 0·02 Å; P–C 0·04 Å;
O–Zn–O 0·8°; Zn–O–P 1·2°; O–P–O 1·2°; C–P–O 1·5°; C–P–C 1·8°.

Zn(1)–O(1)	1·95 Å	O(1)–Zn(1)–O(2)	110·5°	O(3)—P(3)–O(6)	116·1°
Zn(1)–O(2)	1·92	O(1)–Zn(1)–O(3)	110·0	O(3)—P(3)–C(5)	109·0
Zn(1)–O(3)	1·91	O(1)–Zn(1)–O(7)	111·9	O(3)—P(3)–C(6)	110·2
Zn(1)–O(7)	1·91	O(2)–Zn(1)–O(3)	109·6	O(6)—P(3)–C(5)	106·1
Zn(2)–O(4)	1·93	O(2)–Zn(1)–O(7)	108·1	O(6)—P(3)–C(6)	109·5
Zn(2)–O(5)	1·93	O(3)–Zn(1)–O(7)	106·7	C(5)—P(3)–C(6)	105·3
Zn(2)–O(6)	1·97	O(4)–Zn(2)–O(5)	109·2	O(7)—P(4)–O(8)	115·7
Zn(2)–O(8)	1·87	O(4)–Zn(2)–O(6)	110·2	O(7)—P(4)–C(7)	109·3
P(1)—O(1)	1·50	O(4)–Zn(2)–O(8)	113·3	O(7)—P(4)–C(8)	107·6
P(1)—O(4)	1·51	O(5)–Zn(2)–O(6)	108·7	O(8)—P(4)–C(7)	106·2
P(2)—O(2)	1·53	O(5)–Zn(2)–O(8)	106·9	O(8)—P(4)–C(8)	107·8
P(2)—O(5)	1·48	O(6)–Zn(2)–O(8)	108·3	C(7)—P(4)–C(8)	110·2
P(3)—O(3)	1·50	O(1)–P(1)—O(4)	117·5	Zn(1)–O(1)–P(1)	136·3
P(3)—O(6)	1·49	O(1)–P(1)—C(1)	107·8	Zn(1)–O(2)–P(2)	137·9
P(4)—O(7)	1·51	O(1)–P(1)—C(2)	108·3	Zn(1)–O(3)–P(3)	136·3
P(4)—O(8)	1·52	O(4)–P(1)—C(1)	107·7	Zn(2)–O(4)–P(1)	137·5
P(1)—C(1)	1·89	O(4)–P(1)—C(2)	105·8	Zn(2)–O(5)–P(2)	139·8
P(1)—C(2)	1·79	C(1)–P(1)—C(2)	109·6	Zn(2)–O(6)–P(3)	132·3
P(2)—C(3)	2·09	O(2)–P(2)—O(5)	116·7	Zn(1)–O(7)–P(4)	147·0
P(2)—C(4)	1·75	O(2)–P(2)—C(3)	103·6	Zn(2)–O(8)–P(4)	154·9
P(3)—C(5)	1·93	O(2)–P(2)—C(4)	109·6		
P(3)—C(6)	1·81	O(5)–P(2)—C(3)	103·7		
P(4)—C(7)	1·89	O(5)–P(2)—C(4)	104·3		
P(4)—C(8)	1·81	C(3)–P(2)—C(4)	119·5		

Table 9. *Bond lengths and angles of the refined butyl and phenyl groups*

Length		Angle	
C(5)——C(5Bu1)	1·76 Å	P(3)——C(5)——C(5Bu1)	105°
C(5Bu1)–C(5Bu2)	1·38	C(5)——C(5Bu1)–C(5Bu2)	122
C(5Bu2)–C(5Bu3)	1·21	C(5Bu1)–C(5Bu2)–C(5Bu3)	155
Average	1·45	Average	128
C(6)——C(6Ph1)	1·37	C(6Ph5)–C(6)——C(6Ph1)	121
C(6Ph1)–C(6Ph2)	1·37	C(6)——C(6Ph1)–C(6Ph2)	117
C(6Ph2)–C(6Ph3)	1·33	C(6Ph1)–C(6Ph2)–C(6Ph3)	126
C(6Ph3)–C(6Ph4)	1·30	C(6Ph3)–C(6Ph3)–C(6Ph4)	118
C(6Ph4)–C(6Ph5)	1·45	C(6Ph3)–C(6Ph4)–C(6Ph5)	122
C(6Ph5)–C(6)	1·41	C(6Ph4)–C(6Ph5)–C(6)	115
Average	1·37	Average	120
C(8)——C(8Ph1)	1·30	C(8Ph5)–C(8)——C(8Ph1)	114
C(8Ph1)–C(8Ph2)	1·56	C(8)——C(8Ph1)–C(8Ph2)	125
C(8Ph2)–C(8Ph3)	1·29	C(8Ph1)–C(8Ph2)–C(8Ph3)	119
C(8Ph3)–C(8Ph4)	1·21	C(8Ph2)–C(8Ph3)–C(8Ph4)	121
C(8Ph4)–C(8Ph5)	1·62	C(8Ph3)–C(8Ph4)–C(8Ph5)	125
C(8Ph5)–C(8)	1·46	C(8Ph4)–C(8Ph5)–C(8)	114
Average	1·39	Average	120

Ripamonti, 1969). As a consequence of this disorder it seems logical to expect at least a partial orientational disorder of the organic side groups. In the present structure this seems to be reflected in the localization of only one butyl group, and of two phenyl groups with an occupancy factor of 0·5 (out of four butyl and four phenyl groups contained in the asymmetric unit), from inspection of the electron density maps, and in the very large thermal parameters obtained for some carbon atoms by the least-squares refinement. Thus the carbon atom positions are affected by large errors and they could not be reasonably improved. The P–C lengths range from 1·75 to 2·09 Å with a mean value of 1·87 Å. The C–C bond lengths and C–C–C angles of the refined side groups together with the average value of each group are given in Table 9.

Because of the large shifts of the carbon atoms attached to the phosphorus atoms during the least-squares refinement, the positions of the side groups held fixed are physically meaningless. The inclusion of these side groups in the structure factors calculation is therefore justified only by the improvement of some strong low-angle reflexions. Further evidence that both the difficulty in placing the organic substituents, and the large thermal parameters for some carbon atoms localized in the Fourier syntheses, result from a disordering due to random occupancy of butyl and phenyl groups rather than from large thermal motions, might be obtained by noting any decrease in the falling off of the intensities when the crystals are cooled. However no change was noted in the diffraction photographs when monoclinic crystals were cooled to −150°C, in agreement with the assumed disordered model of the structure.

The packing of the main chains is remarkably similar in the orthorhombic and monoclinic forms. Furthermore the intensity distributions indicate that the same type of disorder is present in the two forms. The crystal packing is determined by the contacts between the rigid phenyl groups, as indicated by models, in agreement with the similarity between the crystal structure of the n-butylphenylphosphinate and the γ-form of the diphenyl derivative. The layered nature of the chain packing and the close interlocking between chains related by a symmetry centre, found in the β form of $\{Zn[(n\text{-}C_4H_9)_2PO_2]_2\}_n$ and in the copolymer $\{Zn[(n\text{-}C_4H_9)_2PO_2]\,[(n\text{-}C_6H_{13})_2PO_2]\}_n$ are not permitted in the present structure by the more bulky phenyl side groups. These very groups, however, may promote an increase in the rigidity of the chain backbone and thus allow for the crystalline character of the material in spite of the disordering of side groups different in nature and size. The results of a study on the properties of beryllium polymers containing diphenylphosphinate bridging groups have already been interpreted on similar considerations (Gemiti, Giancotti & Ripamonti, 1968).

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