mon edge and these double polyhedra are isolated in space from one another, which means that they have no Bi–O–Bi contacts. The distance between the Bi atoms within a double polyhedron is 4·28 Å and of the other Bi–Bi distances 4·64 Å is the shortest one, all the others being longer than 6·5 Å.

The overall structure

Fig. 3 shows a projection of the structure. Every double polyhedron connects four polyphosphate chains and conversely every chain four rows of double polyhedra.

The authors wish to thank Dr Tschudinowa for placing the substance at their disposal, Dr Fichtner for the measurements on the diffractometer of ZIPC, Mrs Schrauber, ZfR, for her help in data processing, and Mr Schubert, who made the DTA.

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Crystal Structure of the Polyphosphate $[BiH(PO_3)_4]_x$

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$[BiH(PO_3)_4]_x$ forms triclinic crystals, space group $P\bar{1}$, with unit-cell dimensions $a=8{\cdot}625$, $b=8{\cdot}866$, $c=7{\cdot}062$ Å, $\alpha=112{\cdot}17°$, $\beta=108{\cdot}54°$, $\gamma=98{\cdot}49°$. In the anion PO_4 tetrahedra are connected *via* corners to infinite chains. The identity period in the chains is the lattice constant c and four tetrahedra form the motif. Bi is surrounded by seven oxygen atoms at distances ranging from 2·27 to 2·55 Å. The shape of the coordination polyhedron is irregular. The position of the hydrogen atom was determined with high probability from a difference map.

Introduction

In the course of investigations of the crystal chemistry of condensed bismuth phosphate the crystal structure of a compound of composition $BiH(PO_3)_4$ was determined. In paper chromatography this compound, which was synthesized by Tschudinowa, Lawrow & Tananajew (1972), behaves like a linear polyphosphate. Proton resonance absorption shows the substance to contain chemically bound water (Grimmer & Tschudinowa, 1972). This confirms the above-mentioned result.

Crystal data

Crystals of $BiH(PO_3)_4$ are colourless and have the shape of columns (axis parallel to z) with a rectangular cross section. Mechanical stress causes the crystals to split into fibres parallel to the column axis. The dimensions of the reduced cell, determined from measurements with Mo $K\alpha$ radiation ($\lambda=0{,}71069$ Å) on a diffractometer, and some other crystal data are collected in Table 1.

Table 1. *Crystal data*

$a=8{\cdot}625\pm0{\cdot}001$, $b=8{\cdot}866\pm0{\cdot}001$, $c=7{\cdot}062\pm0{\cdot}001$ Å
$\alpha=112{\cdot}17\pm0{\cdot}01°$, $\beta=108{\cdot}54\pm0{\cdot}01°$, $\gamma=98{\cdot}49\pm0{\cdot}01°$
(values at 20 °C)
$V=451{\cdot}47$ Å^3 $Z=2BiH(PO_3)_4$
$D_m=3{\cdot}86$ $D_x=3{\cdot}87$ g cm^{-3}
Laue class: $\bar{1}$
Space group: $P\bar{1}$ (from the structure analysis)

Intensity data and structure determination

The intensity data were collected as described in Table 2. In structure determination 2432 crystallographically independent reflexions were used of which 2256 were observed.

The structure was determined by the heavy-atom method. The final R value, calculated with 2390 reflexions, after three isotropic and two anisotropic

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Table 2. *Measurement of intensities*

Hilger four-circle diffractometer
Radiation: Mo $K\alpha$, selected by graphite monochromator
Scan and range: Reflexions with $\theta \leq 5°$ by ω-scan, $\theta > 5°$ by $\omega/2\theta$-scan, $\theta_{max} = 30°$
Crystal used in data collection: Rectangular prism, $0{\cdot}034 \times 0{\cdot}090 \times 0{\cdot}132$ mm
Correction of intensities: p, L, absorption.

block-diagonal least-squares cycles, was 0·040. In the calculations the correction terms $\Delta f'$ and $\Delta f''$ to the atomic scattering factor of bismuth were taken in account.

In order to find the position of the hydrogen atom a difference electron-density map was calculated. Excluded were all reflexions with $\theta > 23{\cdot}6°$ and nine reflexions below this limit, which seem to be affected by extinction. In this map the highest maximum is at the position of bismuth. Of the remaining maxima the second highest seems to be due to hydrogen. From crystallochemical considerations the other high maxima (one of the same height, five which are 10–20 % lower) cannot be hydrogen. The atomic parameters and the $|F_o|/F_c$ values are presented in Tables 3–5.

Table 3. *Atomic coordinates*

In brackets: $10^4 \times \sigma$.
For discussion of the position of hydrogen atom see the text.

	x	y	z
Bi	0·2634 (1)	0·2621 (1)	0·0984 (1)
P(2)	0·3884 (4)	0·6614 (4)	0·0835 (5)
P(3)	0·1955 (4)	0·8947 (4)	0·2110 (5)
P(4)	0·8717 (4)	0·1597 (4)	0·4308 (5)
P(5)	0·7103 (4)	0·4188 (4)	0·3883 (5)
O(6)	0·5707 (12)	0·6969 (12)	0·1175 (16)
O(7)	0·3176 (13)	0·5520 (11)	0·1736 (16)
O(8)	0·3574 (12)	0·8435 (11)	0·1774 (15)
O(9)	0·2162 (14)	0·0745 (12)	0·2480 (17)
O(10)	0·0314 (12)	0·7566 (13)	0·0348 (16)
O(11)	0·2296 (12)	0·9012 (13)	0·4512 (15)
O(12)	0·9379 (11)	0·8094 (13)	0·4294 (17)
O(13)	0·8028 (14)	0·0440 (13)	0·1910 (16)
O(14)	0·8612 (12)	0·3460 (12)	0·4823 (16)
O(15)	0·2415 (13)	0·4008 (12)	0·4408 (15)
O(16)	0·5372 (11)	0·2969 (13)	0·3181 (16)
O(17)	0·7373 (12)	0·4234 (12)	0·1791 (15)
H	0·854	0·759	0·468

The structure

$[BiH(PO_3)_4]_x$ is a polyphosphate. The anion consists of infinite chains of PO_4 tetrahedra, which share by common corners bridging oxygen atoms. The type of chain is similar to that found in $[Pb(PO_3)_2]_x$ ('4er Kette'). The chain is shown in two projections in Fig. 1 and details of the geometry are given in Tables 6 and 7. Of the bond lengths within the chain, only P(4)–O(11) and P(4)–O(12) are unusual (see Table 6). The first, a bridging bond, is rather short. Its deviation from the mean value of bridging bonds in polyphosphate is more than 3σ. The second bond mentioned is rather long for a bond with a terminal oxygen atom. This leads to the suggestion that O(12) forms an OH group. This suggestion is supported by two facts; firstly in $(\varrho_o - \varrho_c)$ there is a maximum at the proper position for hydrogen near O(12) and secondly O(12) is the only terminal oxygen atom which does not take part in the coordination of the bismuth atom. The geometry of the assumed hydrogen bridge explains Fig. 2. Whether the bond P(4)–O(12)–H influences the length of the bridging bonds from P(4), especially the one to O(11), cannot be said.

Bismuth is coordinated by seven terminal oxygen atoms, which form an irregular polyhedron. The Bi–O distances are between 2,27 and 2,55 Å (Fig. 3) and the shortest distance Bi–O to an oxygen atom outside the coordination sphere is longer than 3·3 Å. The coordination polyhedra of Bi are isolated in space from one another, each connecting four polyphosphate chains. Pairs of chains are also coupled by hydrogen bridges (Fig. 4). The shortest Bi–Bi vectors have

Table 4. *Thermal parameters*

$B_{11} = 10^4 \cdot 2\pi^2 a^{*2} U_{11} + \ldots$. In brackets: standard deviations.

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Bi	19 (0)	7 (1)	28 (1)	15 (1)	26 (1)	13 (1)
P(2)	26 (4)	18 (5)	28 (7)	24 (9)	37 (9)	24 (7)
P(3)	28 (4)	13 (5)	40 (8)	28 (9)	34 (10)	22 (7)
P(4)	34 (5)	9 (5)	44 (8)	32 (10)	52 (10)	28 (7)
P(5)	28 (4)	14 (5)	33 (8)	20 (10)	30 (10)	21 (7)
O(6)	26 (13)	33 (15)	89 (25)	49 (31)	48 (31)	44 (22)
O(7)	92 (16)	14 (13)	88 (25)	22 (29)	124 (33)	6 (23)
O(8)	40 (13)	3 (13)	65 (23)	22 (28)	59 (29)	28 (20)
O(9)	107 (18)	19 (14)	121 (28)	102 (33)	169 (37)	86 (26)
O(10)	36 (14)	62 (16)	63 (24)	38 (32)	34 (31)	12 (24)
O(11)	52 (15)	45 (16)	40 (22)	47 (31)	69 (30)	30 (24)
O(12)	15 (12)	45 (16)	150 (29)	109 (35)	57 (31)	53 (22)
O(13)	101 (18)	42 (16)	56 (24)	25 (31)	94 (35)	47 (27)
O(14)	45 (14)	2 (13)	84 (25)	21 (29)	41 (31)	29 (21)
O(15)	87 (16)	8 (14)	58 (23)	25 (29)	93 (32)	50 (24)
O(16)	19 (12)	56 (16)	85 (25)	46 (32)	−4 (28)	−8 (22)
O(17)	46 (14)	45 (15)	20 (22)	37 (29)	37 (29)	20 (23)
H	–	–	–	–	–	–

lengths of 5·37 and 5·40 Å. In the structure they form zigzag chains parallel to [111] in the $(1\bar{1}0)$ planes; see Fig. 5. Bi atoms in neighbouring planes are further apart than $d_{110}=6·6$ Å.

Comparison with other condensed Bi phosphates

So far as is known to us the structures of only two other condensed Bi phosphates have been determined

Table 5. *Structure factors*

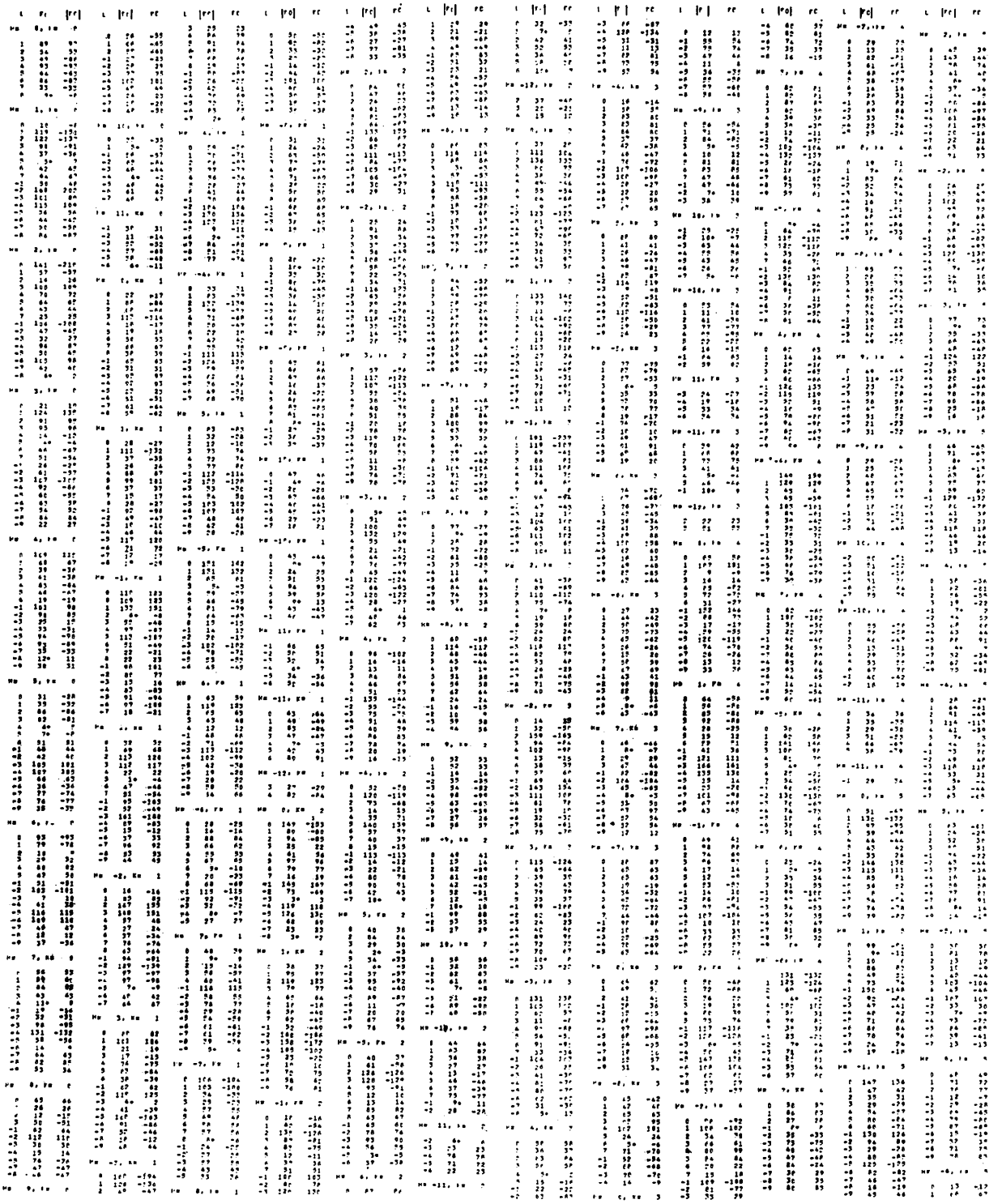


Table 5 (*cont.*)

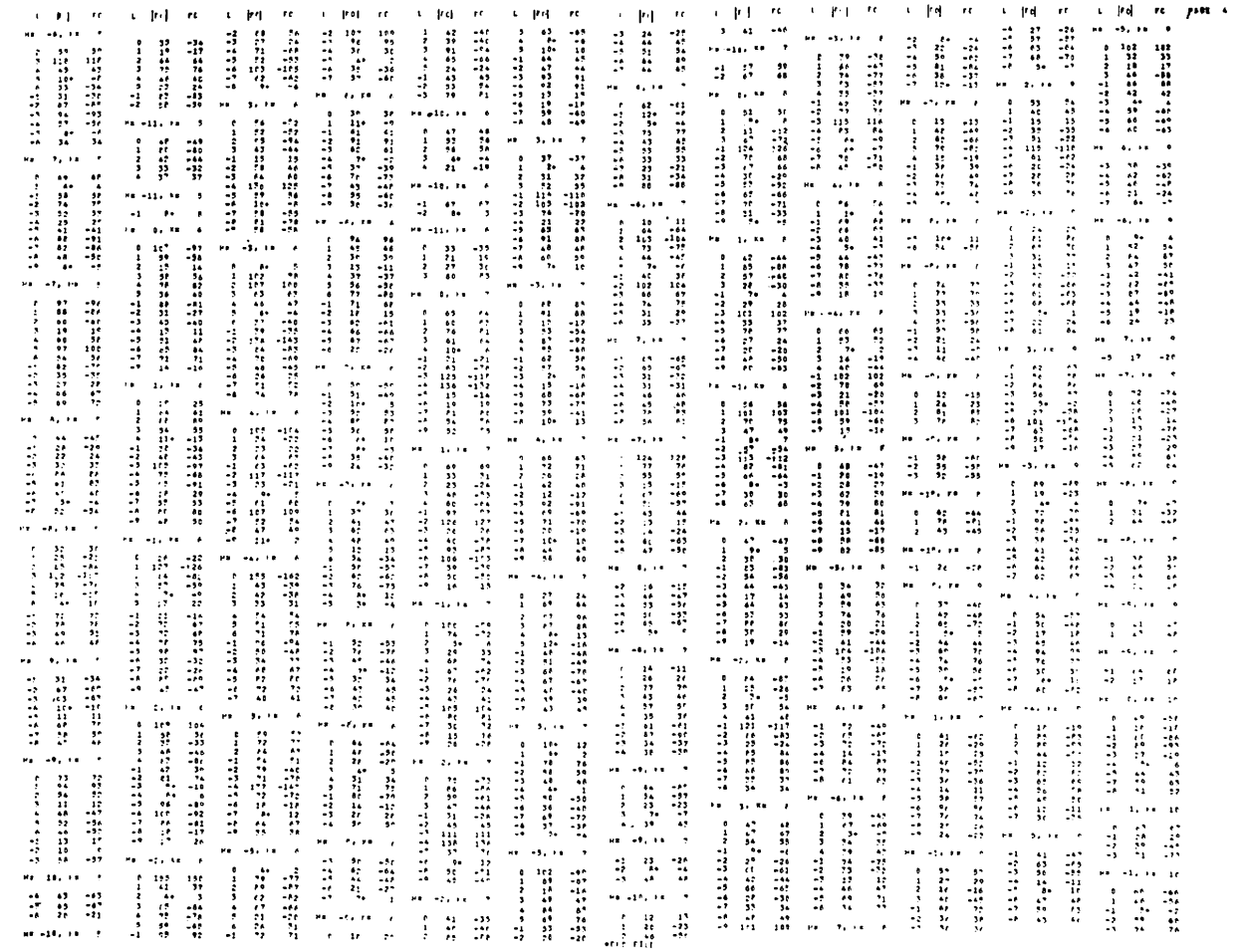


Fig. 1. The polyphosphate chain. (*a*) Projection along the chain (*z* axis). PO_4 tetrahedra are outlined. (*b*) Projection on the plane (110).

Table 6. *Bond lengths in the polyphosphate chain*

Standard deviations ≃0·01 Å.
b = bridging oxygen atom.

P(2)–O(6)	1·478 Å	P(4)–O(11′)*b*	1·553 Å
O(7)	1·502	O(12′)	1·542
O(8)*b*	1·597	O(13)	1·464
O(17′)*b*	1·615	O(14)*b*	1·575
P(3)–O(8)*b*	1·590 Å	P(5)–O(14)*b*	1·604 Å
O(9″)	1·488	O(15′)	1·488
O(10)	1·506	O(16)	1·513
O(11)*b*	1·603	O(17)*b*	1·581

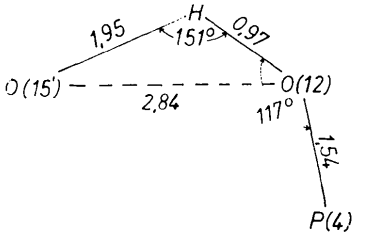


Fig. 2. Distances and angles in the hydrogen bridge. For details see text.

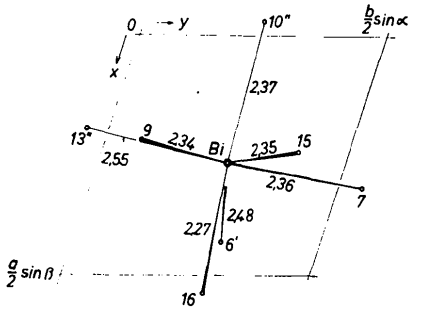


Fig. 3. Oxygen coordination of Bi.

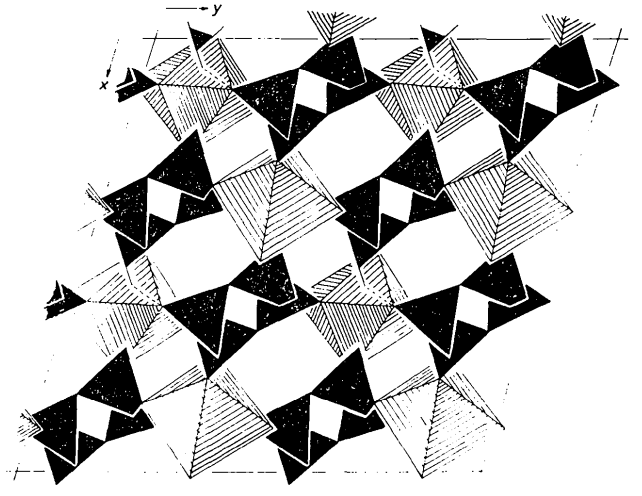


Fig. 4. Projection of the structure along *z*. The area of four cells is outlined. Black: PO_4 tetrahedra. Hatched: coordination polyhedra of Bi. Broken lines: assumed hydrogen bridges (see text).

Table 7. *Valence angles within the polyphosphate chain*

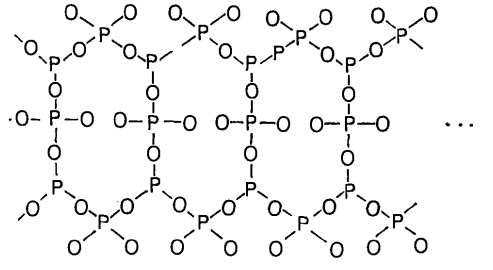
O(6)—P(2)–O(7)	120·2°	O(11′)*b*	P(4)——O(12′)	105·5°
O(6)	O(8)*b*	106·1	O(11′)*b*	O(13)	112·0
O(6)	O(17′)*b*	111·2	O(11′)*b*	O(14)*b*	104·8
O(7)	O(8)*b*	110·4	O(12′)	O(13)	117·1
O(7)	O(17′)*b*	105·6	O(12′)	O(14)*b*	103·1
O(8)*b*	O(17′)*b*	102·0	O(13)	O(14)*b*	113·2
O(8)*b*–P(3)–O(9″)	109·0°	O(14)*b*–P(5)——O(15′)	105·9°
O(8)*b*	O(10)	110·7	O(14)*b*	O(16)	110·2
O(8)*b*	O(11)*b*	100·1	O(14)*b*	O(17)*b*	101·3
O(9″)	O(10)	119·6	O(15′)	O(16)	119·2
O(9″)	O(11)*b*	105·3	O(15′)	O(17)*b*	107·2
O(10)	O(11)*b*	110·4	O(16)	O(17)*b*	111·4
			P(2)——O(8)*b*—P(3)	131·2°
			P(3)——O(11)*b*–P(4′)	138·9
			P(4)——O(14)*b*–P(5)	133·1
			P(5′)——O(17′)*b*–P(2)	132·5

or proved to be isotypic with a compound of which the crystal structure is known. These are the ultraphosphate, BiP_5O_{14}, and the polyphosphate, $Bi(PO_3)_3$.

Tschudinowa & Jost (1973) have shown BiP_5O_{14} to be isotypic or clearly related in structure to some rare-earth phosphates. This has now been confirmed by the structure determination of NdP_5O_{14} (Albrand, Attig, Fenner, Jeser & Mootz, 1974; Hong, 1974). Both NdP_5O_{14} and BiP_5O_{14} crystallize in space group C_{2h}^5 and so good is the agreement in unit-cell dimensions that the interatomic distances should be the same:

NdP_5O_{14}	BiP_5O_{14}
a = 8·77 Å	c = 8·77 Å
b = 8·99	b = 9·02
c = 13·03	a = 13·06
β = 90·48°	β = 90·6° .

Therefore the anion in BiP_5O_{14} should be a ribbon with the chemical constitution:



Bismuth should be coordinated by eight oxygen atoms with Bi–O distances of 2,40 to 2,50 Å. The shortest distances Bi–Bi should be arranged in zigzag chains parallel to the *x* axis and have values of 5,19 and 5,94 Å.

In $Bi(PO_3)_3$ (structure determined by Palkina & Jost, 1975) the anions are spiral-like chains of corner-connected PO_4 tetrahedra with six tetrahedra per winding. Bi is irregularly coordinated by six oxygen atoms with Bi–O distances of 2,20 to 2,43 Å and one with 2,79 Å. Each pair of coordination polyhedra of Bi

has a common edge. The distance between the two Bi atoms within such a double polyhedron is 4,28 Å; the shortest of the others is 4·64 Å. The corresponding Bi and Nd polyphosphates are not isomorphous but the anion chains are related (Hong, 1974).

Both in $BiH(PO_3)_4$ and in $Bi(PO_3)_3$ the anion chains contain large jolts. The reason for this may be that in this way it is possible to give the cation enough oxygen contacts in spite of the high (P:Bi) ratios of four and three respectively.

We wish to thank Dr Tschudinowa, Dr Fichtner and Mrs Schrauber for their kind support.

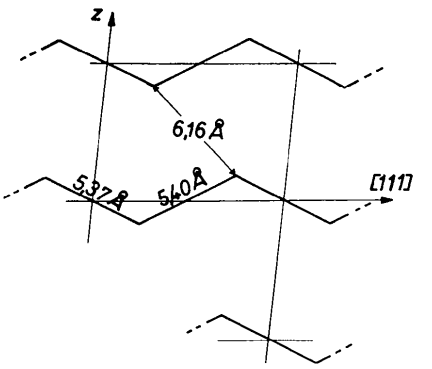


Fig. 5. Shortest Bi–Bi contacts.

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Structure Cristalline de la Δ9–10 Méthyl-17α Nor-19 Progestérone

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(*Reçu le* 5 *mars* 1975, *accepté le* 21 *mars* 1975)

$C_{21}H_{28}O_2$, orthorhombic, $P2_12_12_1$, $Z=8$, $a=30{\cdot}966$ (8), $b=8{\cdot}053$ (3), $c=14{\cdot}070$ (4) Å. The conformations of the two independent molecules are identical. Cohesion of the crystal is achieved by van der Waals forces only.

Dans le but d'étudier l'influence de l'adjonction d'une double liaison en 9–10 sur la géométrie des cycles *A* et *B* des dérivés du nor-19 androstène, nous avons déjà présenté la structure de la Δ9–10 méthyl-21 norprogestérone (Busetta, Comberton, Courseille & Hospital, 1974). Le présent article est consacré à l'étude du dérivé non méthylé.

Les cristaux de Δ9–10 méthyl-17α nor-19 progestérone ont été obtenus par évaporation d'une solution dans l'alcool éthylique; les différentes mesures expérimentales ont été effectuées sur un diffractomètre automatique Siemens. 2974 réflexions indépendantes ont été mesurées dont 2437 observées.

La structure a été déterminée par méthodes directes (multisolution). Tous les atomes d'hydrogène ont été localisés à partir de sections différences. Les coordonnées atomiques et les paramètres d'agitation thermique sont réportés sur le Tableau 1. Le facteur *R* final est égal à 0,061.*

Discussion

Généralement, quand un cristal est formé de plusieurs molécules indépendantes, celles-ci présentent des conformations relativement différentes, du fait qu'elles ne se trouvent pas dans le même environnement et notamment qu'elles contractent des liaisons hydrogène d'énergie et de directions différentes. Les interactions du type van der Waals, beaucoup plus

* La liste des facteurs de structure a été déposée au dépôt d'archives de la British Library Lending Division (Supplementary Publication No. SUP 31005: 31 pp., 1 microfiche). On peut en obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, Angleterre.