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Structure of *N*-(Dichlorophosphinoyl)phosphorimidic Trichloride, $Cl_3PNP(O)Cl_2$, at 100 K

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Dedicated to Professor Dr Edgar Nachbaur on the occasion of his 60*th birthday*

Abstract

N-(Dichlorophosphinoyl)phosphorimidic trichloride, $Cl_3PNP(O)Cl_2$, $M_r = 269.22$, monoclinic, $P2_1/c$, $a = 12.573\,(5)$, $b = 19.183\,(4)$, $c = 14.985\,(4)$ Å, $\beta = 110.14\,(2)°$, $V = 3393\,(1)$ Å^3, $Z = 16$, $D_x = 2.108$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.02$ mm^{-1}, $F(000) = 2080$, $T = 100$ K, $R = 0.030$, $wR = 0.032$ for 4458 unique observed reflections and 325 parameters. There are four molecules in the asymmetric unit. The P—N bonds show a pronounced multiple-bond character, the P—N 'double' bonds [1.517 (3)–1.530 (3) Å] being substantially shorter than the P—N 'single' bonds [1.583 (3)–1.593 (3) Å], and the P—Cl bonds of the $P(O)Cl_2$ groups [1.998 (2)–2.018 (2) Å] are clearly longer than the P—Cl bonds of the $NPCl_3$ groups [1.956 (2)–1.978 (2) Å]. The very flexible P—N—P bond angles lie in the range 137.8 (2)–144.1 (2)°. All four molecules show approximate *cisoid* conformations with respect to their Cl—P···P—Cl and Cl—P···P—O torsion angles. The packing consists of layers normal to the monoclinic axis, each built up of two crystallographically independent molecules with similar environments. In opposition to this, the molecules in alternating layers show very different arrangements.

Introduction

N-(Dichlorophosphinoyl)phosphorimidic trichloride, the stable fundamental substance of neutral linear chlorophosphazenes, can be obtained by many different reactions (Becke-Goehring, Debo, Fluck & Goetze, 1961; Becke-Goehring & Lehr, 1961, 1963; Becke-Goehring, Mann & Euler, 1961; Becke-Goehring & Fluck, 1966; Emsley, Moore & Udy, 1971; Fluck, Hösle & Zischka, 1981). The evidence of three rotamers derived from ^{31}P NMR data (Glidewell, 1979) was disproved by semiempirical theoretical calculations (Glidewell, 1980; Glidewell, Keat & Rycroft, 1981) and by temperature-dependent ^{31}P NMR experiments (Thomas, Scheller & Grossmann, 1982). The ^{35}Cl NQR spectrum (Kaplansky, Clipsham & Whitehead, 1969) shows a line splitting presumably due to crystallographic inequivalence of the Cl atoms.

An X-ray crystal structure analysis performed at room temperature was repeated at 223 K because of an extremely high degree of thermal motion in the bridging N atoms and because of a phase transition below 223 K generating a slightly different packing arrangement (Allcock, Tollefson, Arcus & Whittle, 1985). But the results of the structure redetermination showing two molecules in the asymmetric unit are unsatisfactory, exhibiting positional disorder, very different bond lengths of equivalent bonds in the two molecules [P=O 1.453 (8) and 1.398 (10) Å, P—N 1.580 (8) and 1.53 (2) Å, P=N 1.519 (8) and 1.54 (2) Å in molecules *A* and *B*, respectively], which are unrealistic in molecule *B*, and gross violation of Hirshfeld's 'rigid-bond' postulate (Hirshfeld, 1976), in particular for the P—N bonds of molecule *B*.

As part of a continuing study of phosphazene structures, the crystal structure of the title compound was determined at 100 K. At this temperature an ordered structure was obtained with the same space-group type but with a doubled cell, more accurate structural parameters and realistic thermal parameters. The asymmetric unit consists of four molecules

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and thus the variability of equivalent interatomic parameters and the conformational variability of the molecule can be studied in detail.

Experimental

A colourless single crystal (0.25 × 0.30 × 0.45 mm) obtained by a Kirsanov reaction of $OP(OH)_2NH_2$ with PCl_5 in *sym*-$C_2H_2Cl_4$ (Becke-Goehring, Mann & Euler, 1961) was immersed in oil and immediately cooled to 100 K. All the measurements were performed on a modified Stoe four-circle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation with Nonius low-temperature equipment. Cell parameters were determined from a least-squares fitting of 60 well positioned reflections (2θ range 10–19°). 6310 reflections were measured using ω–2θ scans (scan range 2.0°) for 2θ from 3 to 50° (h 0 to 14, k 0 to 22, l −17 to 17), 4723 reflections had $I > 3\sigma(I)$, 4465 were unique. Two standard reflections measured every 100 reflections showed ±3.1% variation in intensity. The internal consistency factor was computed to $R_{\rm int} = 0.0123$. Data were corrected for Lorentz–polarization effects, an empirical absorption correction (maximum/minimum transmission factors 1.158/0.852) was applied with *DIFABS* (Walker & Stuart, 1983) and seven low-order reflections were omitted, probably suffering from extinction. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1986). Full-matrix least-squares refinements [on F, weighting scheme $w = 1/\sigma^2(F_o)$] with anisotropic thermal parameters for all atoms until no parameter shifts occurred ($\Delta/\sigma \leq 0.002$) gave $R = 0.0296$, $wR = 0.0321$, $S = 1.59$ (4458 reflections, 325 parameters). The final difference Fourier map maximum and minimum were 0.41 and -0.35 e Å^{-3}, respectively. Scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149). VAX/VMS 6000 computer; programs used: *SHELX*76 (Sheldrick, 1976); *PLATON* (Spek, 1982); *ORTEP* (Johnson, 1965); *PLUTO* (Motherwell, 1976).

Discussion

The final atomic positional and thermal parameters are listed in Table 1;* the bond lengths and angles are given in Table 2. At 100 K there are four molecules in the asymmetric unit; their atom labelling is shown in Fig. 1. In the following the four molecules will be indicated by $M1$ to $M4$; the two molecules in the subcell determined by Allcock, Tollefson, Arcus & Whittle (1985) will be indicated by A and B. To a very rough approximation, the molecules $M1$, $M2$ and $M4$ show C_s symmetry. All the four molecules $M1$ to $M4$ show approximate *cisoid* conformations concerning their Cl—P···P—Cl and Cl—P···P—O torsion angles [maximum 11.4 (1)°], as observed in $[Cl_3PNPCl_3][PCl_6]$ (Faggiani, Gillespie, Sawyer & Tyrer, 1980) or in $[ClP(NPCl_3)_3]^+X^-$, $X^- = Cl^-$, $[PCl_6]^-$ (Belaj, 1992). However, whereas the O—P—N—P torsion angles are −169.1 (3) to −175.5 (3)° for $M1$, $M2$ and $M4$, in $M3$ the —$P(O)Cl_2$ group is rotated 120° about the P—N single bond resulting in an O—P—N—P torsion angle of −49.8 (4)° (see Fig. 1). Nevertheless, these two conformations correspond to the conformations I and II tentatively suggested by Glidewell (1979), and explain the line splitting in the ^{35}Cl-NQR spectrum (Kaplansky, Clipsham & Whitehead, 1969).

Table 1. *Fractional atomic coordinates* (× 10^5) *and equivalent isotropic thermal parameters* (Å^2 × 10^4) *with e.s.d.'s in parentheses*

$U_{\rm eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U_{\rm eq}$
P(11)	97908 (8)	75472 (5)	44842 (6)	141 (5)
O(1)	99878 (22)	70021 (13)	51920 (16)	211 (15)
Cl(11)	111397 (8)	76596 (6)	40624 (7)	309 (6)
Cl(12)	97028 (9)	84821 (5)	50423 (7)	327 (6)
N(1)	86942 (26)	74596 (17)	35697 (20)	195 (18)
P(12)	80377 (8)	77673 (5)	26038 (6)	163 (5)
Cl(13)	72772 (9)	86557 (5)	26194 (7)	306 (6)
Cl(14)	68218 (8)	71260 (5)	19130 (6)	254 (5)
Cl(15)	89170 (8)	79147 (6)	17498 (7)	308 (6)
P(21)	47649 (8)	74700 (5)	95448 (6)	149 (5)
O(2)	49286 (22)	68311 (14)	100980 (17)	220 (15)
Cl(21)	61643 (8)	77142 (7)	92414 (7)	342 (6)
Cl(22)	46019 (9)	82947 (5)	103031 (7)	318 (6)
N(2)	37115 (26)	74751 (16)	85828 (20)	187 (17)
P(22)	31258 (8)	79117 (5)	77047 (6)	151 (5)
Cl(23)	24966 (9)	87984 (5)	79340 (7)	295 (6)
Cl(24)	18316 (8)	73974 (5)	68483 (6)	266 (5)
Cl(25)	40479 (8)	81378 (6)	69083 (7)	312 (6)
P(31)	55012 (8)	101402 (5)	78016 (6)	165 (5)
O(3)	44710 (23)	101012 (16)	80425 (19)	302 (18)
Cl(31)	53576 (9)	96400 (5)	65961 (6)	267 (6)
Cl(32)	58007 (9)	111150 (5)	74746 (7)	299 (6)
N(3)	66720 (27)	98511 (17)	85176 (21)	230 (19)
P(32)	73788 (8)	99213 (5)	95653 (6)	162 (5)
Cl(33)	82102 (8)	108117 (5)	98969 (7)	256 (5)
Cl(34)	85573 (8)	92021 (5)	99053 (7)	261 (6)
Cl(35)	65596 (8)	98273 (5)	104715 (6)	230 (5)
P(41)	2866 (8)	49528 (5)	77905 (6)	167 (5)
O(4)	−9349 (22)	50395 (14)	74405 (18)	245 (16)
Cl(41)	10573 (9)	56499 (6)	72173 (7)	309 (6)
Cl(42)	7427 (10)	40522 (6)	73496 (7)	375 (7)
N(4)	8828 (25)	49798 (16)	89123 (20)	185 (17)
P(42)	20578 (8)	50239 (5)	96783 (6)	157 (5)
Cl(43)	30225 (8)	41874 (5)	98209 (7)	237 (5)
Cl(44)	18779 (8)	51403 (5)	109211 (6)	230 (5)
Cl(45)	30361 (8)	57965 (5)	95597 (6)	222 (5)

The interatomic parameters are almost the same for $M1$ and $M2$ but are often somewhat different from $M3$ and $M4$. This can only be understood by analysing the packing of the molecules in the unit

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* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55654 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE0101]

Table 2. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°) *in the four molecules M*1 *to M*4 *of the asymmetric unit*

	$n = 1$	$n = 2$	$n = 3$	$n = 4$
Cl(*n*1)—P(*n*1)	2.015 (2)	2.018 (2)	1.998 (1)	2.010 (2)
Cl(*n*2)—P(*n*1)	1.998 (2)	1.999 (2)	2.001 (2)	2.003 (2)
P(*n*1)—O(*n*)	1.449 (3)	1.454 (3)	1.461 (3)	1.452 (3)
P(*n*1)—N(*n*)	1.583 (3)	1.587 (3)	1.593 (3)	1.588 (3)
P(*n*2)—N(*n*)	1.517 (3)	1.519 (3)	1.520 (3)	1.530 (3)
Cl(*n*3)—P(*n*2)	1.958 (2)	1.956 (2)	1.975 (2)	1.978 (2)
Cl(*n*4)—P(*n*2)	1.958 (2)	1.957 (2)	1.959 (2)	1.964 (2)
Cl(*n*5)—P(*n*2)	1.978 (2)	1.977 (2)	1.975 (2)	1.973 (2)
P(*n*1)···P(*n*2)	2.949 (2)	2.942 (2)	2.905 (2)	2.940 (2)
Cl(*n*1)—P(*n*1)—O(*n*)	110.9 (1)	111.2 (1)	112.8 (1)	112.0 (1)
Cl(*n*2)—P(*n*1)—O(*n*)	111.2 (1)	111.4 (1)	111.5 (1)	111.5 (1)
Cl(*n*1)—P(*n*1)—N(*n*)	108.4 (1)	108.3 (1)	102.5 (1)	108.0 (1)
Cl(*n*2)—P(*n*1)—N(*n*)	107.5 (1)	107.1 (1)	106.4 (1)	107.0 (1)
Cl(*n*1)—P(*n*1)—Cl(*n*2)	102.1 (1)	102.3 (1)	101.2 (1)	101.4 (1)
O(*n*)—P(*n*1)—N(*n*)	115.8 (2)	115.7 (2)	120.5 (2)	115.7 (2)
P(*n*1)—N(*n*)—P(*n*2)	144.1 (2)	142.6 (2)	137.8 (2)	141.1 (2)
Cl(*n*3)—P(*n*2)—Cl(*n*4)	104.9 (1)	105.0 (1)	104.8 (1)	104.8 (1)
Cl(*n*3)—P(*n*2)—Cl(*n*5)	105.5 (1)	105.8 (1)	105.2 (1)	103.9 (1)
Cl(*n*4)—P(*n*2)—Cl(*n*5)	104.8 (1)	104.1 (1)	106.5 (1)	106.2 (1)
Cl(*n*3)—P(*n*2)—N(*n*)	115.8 (1)	115.6 (1)	114.0 (1)	115.7 (1)
Cl(*n*4)—P(*n*2)—N(*n*)	109.2 (1)	109.6 (1)	109.1 (1)	108.7 (1)
Cl(*n*5)—P(*n*2)—N(*n*)	115.5 (1)	115.7 (2)	116.4 (2)	116.4 (1)
O(*n*)—P(*n*1)—N(*n*)—P(*n*2)	−175.5 (3)	−175.3 (3)	−49.8 (4)	−169.1 (3)
Cl(*n*1)—P(*n*1)—N(*n*)—P(*n*2)	−50.1 (4)	−49.8 (4)	−176.0 (3)	−42.6 (3)
Cl(*n*2)—P(*n*1)—N(*n*)—P(*n*2)	59.5 (4)	59.8 (4)	78.3 (3)	65.9 (3)
Cl(*n*3)—P(*n*2)—N(*n*)—P(*n*1)	−71.0 (4)	−64.5 (4)	−76.2 (4)	−69.2 (3)
Cl(*n*4)—P(*n*2)—N(*n*)—P(*n*1)	170.9 (3)	177.2 (3)	167.0 (3)	173.2 (3)
Cl(*n*5)—P(*n*2)—N(*n*)—P(*n*1)	53.0 (4)	59.9 (4)	46.6 (4)	53.4 (4)
Cl(*n*2)—P(*n*1)···P(*n*2)—Cl(*n*3)	−7.9 (1)	−1.6 (1)	5.0 (1)	0.1 (1)

cell (Fig. 2): layers normal to the monoclinic *b* axis formed by *M*1 and *M*2 (at $y \simeq \frac{1}{4}$, $y \simeq \frac{3}{4}$) alternate with layers formed by *M*3 and *M*4 (at $y \simeq 0$, $y \simeq \frac{1}{2}$). *M*1 and *M*2 are alternating but in the same orientation arranged in chains parallel to [101] with contacts between the chains. *M*3 and *M*4 lie around centres of symmetry and show two Cl···O interactions each (Fig. 3). Beside these six short contacts [2.854 (3) to 3.265 (3) Å] there are six other short Cl···O contacts [2.868 (3) to 3.252 (3) Å] between the layers [next Cl···O distance 3.436 (3) Å]. Each of the Cl atoms of the $NPCl_3$ groups of the four molecules is involved in just one interaction. However, the shortest intermolecular distance from the Cl atoms of the $P(O)Cl_2$ group to the O atoms is 3.530 (3) Å. Fig. 3 shows the relationship between the unit cell of the disordered structure as determined at 223 K by Allcock, Tollefson, Arcus & Whittle (1985) and the doubled unit cell of the ordered structure at 100 K (transformation matrix $\bar{1}0\bar{1}/0\bar{1}0/\bar{1}01$): molecules *M*1 and *M*2 of the supercell with nearly identical conformations result in the ordered molecule *A*; the superimposition of molecules *M*3 and *M*4 with rather different conformations (compare the O—P—N—P torsion angles) produces the disordered molecule *B* in the subcell.

According to the 'rigid-bond' postulate (Hirshfeld, 1976), the difference $\Delta = |z^2_{A,B} - z^2_{B,A}|$ should be less than about 0.001 Å^2 for every covalently bonded pair of atoms *A* and *B*, where $z^2_{A,B}$ denotes the mean-square amplitude of vibration of the atom *A* along the direction of the bond. From the vibrational parameters refined in this structure determination, maximum differences Δ of 0.0018 (7) Å^2 for intramolecular P—Cl bonds and 0.0041 (17) Å^2 for other intramolecular bonds are obtained. Averaging the molecules *M*1 to *M*4, the r.m.s. values of Δ are 0.0015 Å^2 for bonded pairs of atoms, 0.0015 Å^2 for non-bonded pairs of atoms of the $NPCl_3$ group and 0.0019 Å^2 for non-bonded pairs of atoms of the $NP(O)Cl_2$ group, but 0.0054 Å^2 for all other non-bonded pairs of atoms within the molecules. There-

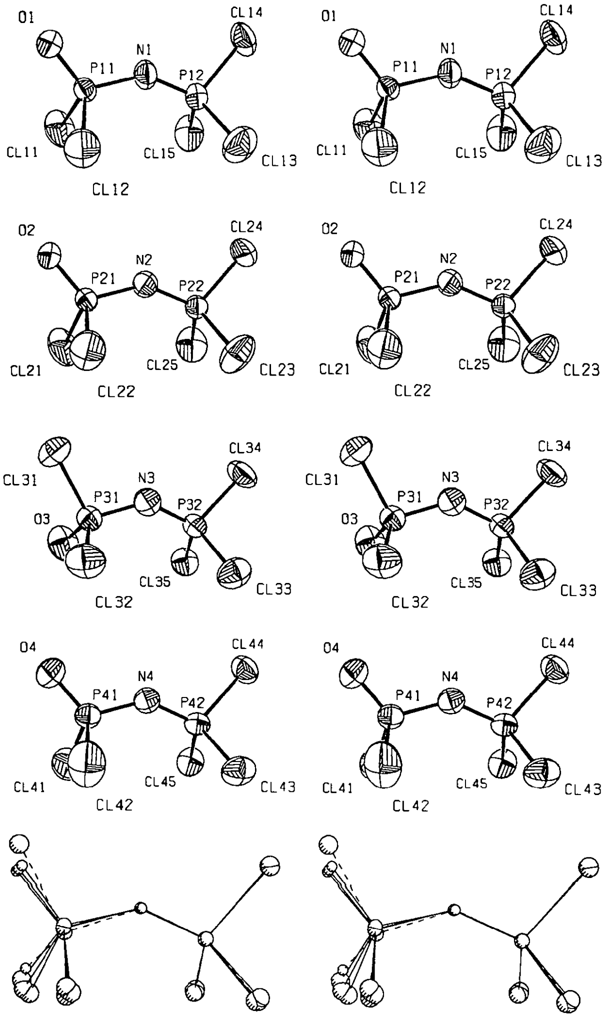

Fig. 1. *ORTEP* plots showing the atomic labelling scheme of the four molecules *M*1 to *M*4 of the asymmetric unit with thermal ellipsoids drawn at the 90% probability level. The *PLUTO* plot shows the conformational variability of the compound. The $NPCl_3$ groups of the four molecules *M*1 to *M*4 were fitted together by minimization of the r.m.s. deviations of the atomic positions of equivalent atoms. The molecule *M*3 is drawn with dashed bonds to indicate its different conformation.

fore, there are some internal motions within the molecules between the rigid $NPCl_3$ and $NP(O)Cl_2$ groups. The molecule *M*3 shows larger r.m.s. values of Δ than the other three molecules, *e.g.* 0.0023 Å^2 compared with 0.0010 Å^2 for bonded pairs of atoms, owing to overlarge temperature factors of N(3) and O(3).

As expected, the P—N bonds show a pronounced multiple-bond character and are substantially shorter than the length of an 'ideal' P—N single bond such as the 1.800 (4) Å found in $K[H_3N—PO_3]$ (Cameron, Chan & Chute, 1980). A comparison of the bond lengths (Table 2) shows that the P—N 'single' bond of the $NP(O)Cl_2$ groups is only slightly longer and the P—N 'double' bond of the $NPCl_3$ groups is distinctly shorter than 1.575 (3) Å, as observed in $(NPCl_2)_3$ (Bullen, 1971). This is in good agreement with the P—N distances [1.575 (2)–1.590 (3) *vs* 1.502 (2)–1.543 (2) Å] found in $[ClP(NPCl_3)_3]Cl$ and $[ClP(NPCl_3)_3]PCl_6.\frac{1}{2}C_2H_2Cl_4$ (Belaj, 1992). However, in the less accurate structure determinations of the higher homologous compound $OP(Cl_2)NP(Cl_2)$-$NPCl_3$ (Allcock, Tollefson, Arcus & Whittle, 1985) and of $OP(R_2)NP(R_2)NPR_3$ with $R = O—C_6H_4—C_6H_5$ (Allcock, Ngo, Parvez, Whittle & Birdsall, 1991), the P—N bond lengths are not resolved into alternating short and long bonds.

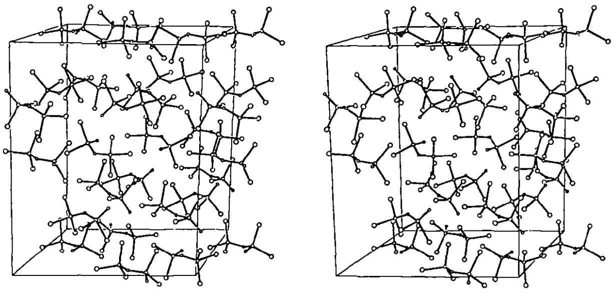

Fig. 2. Stereographic projection of the packing of the molecules in the crystal. The atoms are drawn as spheres with arbitrary radii.

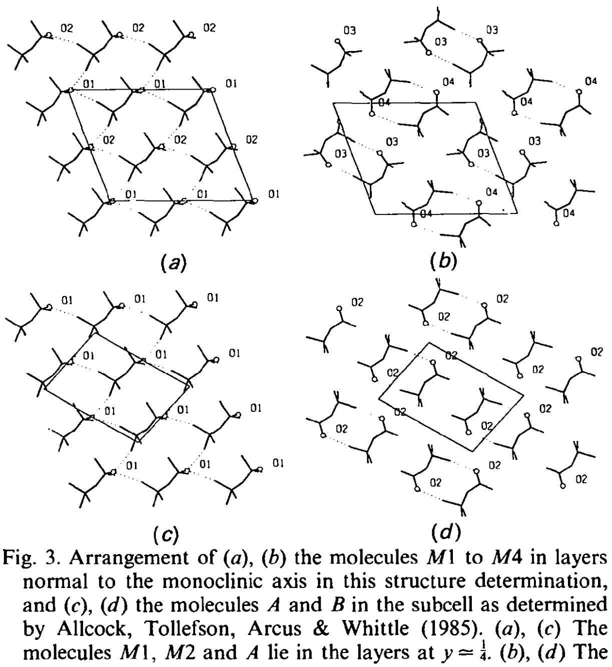

Fig. 3. Arrangement of (*a*), (*b*) the molecules *M*1 to *M*4 in layers normal to the monoclinic axis in this structure determination, and (*c*), (*d*) the molecules *A* and *B* in the subcell as determined by Allcock, Tollefson, Arcus & Whittle (1985). (*a*), (*c*) The molecules *M*1, *M*2 and *A* lie in the layers at $y \simeq \frac{1}{4}$. (*b*), (*d*) The molecules *M*3, *M*4 and *B* lie in the layers at $y \simeq 0$. O atoms are labelled and drawn as spheres. Dashed lines indicate short Cl···O contacts below 3.3 Å.

The P═O bond lengths agree well with the bond lengths of 1.456 (10), 1.455 (4) and 1.456 (5) Å found in $POCl_3$ (Olie, 1971), $CH_2(POCl_2)_2$ (Sheldrick, 1975) and $C_6H_5NHPOCl_2$ (Nöth & Storch, 1984), respectively. The P—Cl bond lengths of the $POCl_2$ groups are significantly longer and the Cl—P—Cl and Cl—P—N angles are distinctly smaller than those of the PCl_3 groups.

A search in the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) for compounds with an acyclic P—N—P substructural fragment resulted in 405 error-free hits (*R* factors less than 0.1) with P—N—P bond angles lying in the range 124.8–180.0°. The bulk of 376 hits involve the bis(triphenylphosphino)iminium cation $[(C_6H_5)_3P═]_2N^+$. With the single exception of the linear tetraphenylimidobis(phosphinic acid) (Nöth, 1982), all compounds with linear (7 hits) or almost linear (25 hits) P—N—P geometries (bond angles greater than 150°) contain the $[(C_6H_5)_3P═]_2N^+$ cation. In two cases (Kirtley, Chanton, Love, Tipton, Sorrell & Bau, 1980; Müller, Ha-Eierdanz, Kräuter & Dehnicke, 1991) linear and bent (139.1, 140.2°) forms of this cation coexist in the same crystal. The mean value of the P—N—P angle in bent fragments is 141.3 (3)° with a large standard deviation of the sample of 5.1°. All the compounds with linear P—N—P geometries lie on centres of symmetry ($\bar{1}$ or $\bar{3}$), have two short P—N distances of 1.51–1.56 Å and show larger (3.03–3.11 Å) P···P distances than the bent compounds (2.90–3.03 Å). This indicates that the linearity is not simulated by a disorder of the N atoms (whose positions are always less accurately determined than the positions of the heavier P atoms) around a centre of symmetry, as assumed by Müller, Ha-Eierdanz, Kräuter & Dehnicke (1991).

The high flexibility of the P—N—P angle suggests that packing energies may exceed the small differences in energy between the linear and the presumably more stable bent forms. This is reflected by semiempirical MNDO (modified neglect of diatomic overlap; Dewar & Thiel, 1977), AM1 (Austin model 1; Dewar, Zoebisch, Healy & Stewart, 1985) and MNDO-PM3 (parametric method 3; Stewart, 1989) calculations for $Cl_3PNP(O)Cl_2$, which resulted in P—N—P angles of 135.6, 121.0 and

179.5°, respectively. The local energy minima were confirmed by the calculated complete set of harmonic vibrational frequencies.

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The Modulated Structure of the Commensurate Misfit-Layer Compound $(BiSe)_{1.09}TaSe_2$

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Abstract

Single-crystal X-ray diffraction (Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å) was used to determine the structure of the commensurate inorganic misfit-layer compound $(BiSe)_{\alpha_0}TaSe_2$, $\alpha_0 = 12/11 \simeq 1.09$. The structure is described as a (3 + 1)-dimensional intergrowth compound with two subsystems and with symmetry according to the superspace group $P{:}Fm2m(\alpha_0,0,0)\bar{1}\bar{1}1$. The $TaSe_2$ subsystem has a_{11} = 3.421 (1), a_{12} = 5.970 (1) and a_{13} = 24.341 (7) Å, with subsystem space group $Fm2m$ and subsystem superspace group $P{:}Fm2m(\alpha_0,0,0)\bar{1}\bar{1}1$. The BiSe subsystem has lattice parameters a'_{21} = 3.135 (1), a'_{22} = 2.984 (1)

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