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2-Methyl-2,2′-spirobi(1,3-dimethyl-1,3,2λ^5-benzodiazaphosphole)*

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Abstract. $C_{17}H_{23}N_4P$, monoclinic, $P2_1/n$, a = 11·761 (6), b = 11·861 (5), c = 11·776 (3) Å, β = 90·28 (3)°, Z = 4, D_m = 1·27, D_x = 1·27 Mg m^{-3}, M_r = 314·4, μ(Mo $K\alpha$) = 0·18 mm^{-1}. Final R = 0·065 for 1564 reflections. The geometry at the P atom is trigonal bipyramidal with the methyl group at an equatorial site. The axial angle N—P—N is 178·2° and the equatorial angles are 121·8 (N—P—N), 118·6 and 119·6° (N—P—C). The average of the axial P—N lengths is 0·08 Å longer than that of the equatorial. The structure departs by 5% from a trigonal bipyramid with the deviation from the ideal geometry following closely the Berry exchange coordinate.

Introduction. Preparation and crystallization of the title compound and a preliminary report on its crystal structure are given by Wieber, Mulfinger & Wunderlich (1981). The needle-shaped, colorless crystals are air-sensitive and had to be sealed in capillaries. The direction of the needle axis was identified as [100]. A crystal 0·15 × 0·18 × 0·38 mm was used for data collection and determination of lattice parameters (15 reflections with 20 < 2θ < 25 °, Mo $K\alpha$). The symmetry yielded the Laue group $2/m$ and systematic absences were unique for the space group $P2_1/c$ with a large monoclinic angle of 134·82°. Therefore, the setting $P2_1/n$ containing β = 90·28° was preferred for data collection, determination, and description of the structure. The intensities of all 2586 symmetry-independent reflections up to 2θ = 48° (Mo $K\alpha$, crystal monochromator) were measured with an ω-scan of 0·6° on an automated diffractometer (Syntex $P2_1$). 1566 reflections were classified observed ($I > 1{\cdot}96\sigma_I$) and used for the analysis. In a later stage the reflections $31\bar{1}$ and $33\bar{2}$ showed large discrepancies with $F_o > F_c$ and were removed from the data because of probable *Umweganregung*. The phase problem was solved from the Patterson function. The structure, including all H atoms, was completed in the usual way. The final refinement including isotropic temperature factors of the H atoms (291 parameters) converged at R = 0·065 (0·118) and R_w = 0·069 (0·076) for the observed (all) reflections. Weights were derived from counting statistics by $1/w = \sigma_F^2 + (0{\cdot}02F)^2$; scattering factors were taken from Cromer & Waber (1974), those of the P atom being corrected for anomalous dispersion. The final residual electron densities were <0·3 e Å^{-3}. The parameters of the non-H atoms are listed in Table 1.† The anisotropic temperature factors B_{ii} range from 2·0 to 8·4 Å^2 and show no unusual features. All calculations were carried out on an Eclipse computer (Data General) with a local version of the *E-XTL* system (Syntex).

Table 1. *Positional parameters of the non-*H *atoms with e.s.d.'s in parentheses*

The equivalent isotropic temperature factors B_{eq} (Å^2) are defined by $B_{eq} = \frac{1}{3}(B_{11}a^{*2}a^2 + B_{12}a^*b^*ab\cos\gamma + \ldots)$.

	x	y	z	B_{eq}
P(1)	0·2233 (1)	0·0178 (1)	0·4381 (1)	3·1
N(1)	0·3586 (4)	0·0505 (4)	0·3963 (4)	3·3
N(2)	0·2273 (4)	0·1475 (4)	0·5165 (4)	3·9
N(3)	0·1976 (4)	−0·0603 (4)	0·5575 (3)	3·2
N(4)	0·2217 (4)	−0·1137 (4)	0·3637 (4)	3·8
C(5)	0·1053 (7)	0·0683 (8)	0·3537 (8)	4·6
C(1)	0·4411 (7)	−0·0255 (8)	0·3438 (7)	4·3
C(2)	0·1307 (8)	0·1976 (8)	0·5746 (8)	5·5
C(3)	0·2188 (8)	−0·0262 (8)	0·6755 (6)	4·2
C(4)	0·2238 (10)	−0·1243 (7)	0·2402 (6)	5·1
C(11)	0·3236 (5)	0·2095 (5)	0·5058 (5)	3·5
C(12)	0·4016 (5)	0·1541 (5)	0·4355 (4)	3·1
C(13)	0·5072 (7)	0·2001 (7)	0·4142 (7)	4·9
C(14)	0·5318 (8)	0·3064 (8)	0·4664 (8)	6·1
C(15)	0·4555 (9)	0·3581 (7)	0·5328 (7)	5·7
C(16)	0·3508 (7)	0·3117 (6)	0·5523 (5)	4·3
C(21)	0·1881 (5)	−0·2054 (5)	0·4262 (4)	3·1
C(22)	0·1755 (5)	−0·1764 (5)	0·5420 (5)	3·3
C(23)	0·1447 (5)	−0·2553 (6)	0·6196 (5)	3·9
C(24)	0·1256 (6)	−0·3660 (6)	0·5848 (6)	4·3
C(25)	0·1353 (6)	−0·3948 (6)	0·4705 (6)	4·7
C(26)	0·1669 (6)	−0·3149 (5)	0·3902 (5)	4·0

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[*] Crystal Structures of Pentacoordinate Phosphorus Compounds. VII. Part VI: Wunderlich & Wussow (1978).

[†] Lists of structure factors, anisotropic thermal parameters and H atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35826 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Discussion. Many molecular structures with pentacoordinated main-group elements have been studied and the trigonal bipyramid (tbp) has been established as the predominant conformational arrangement. The alternative of a square pyramid (sp) is regarded as an important transition stage in solution. From the crystal structures of many cyclic and spirocyclic phosphoranes it is evident that here the conformations range continuously from tbp to sp. The geometry of an individual compound is determined by steric hindrance, different electronegativities of the atoms bonded to the P atom, saturation, size of the rings *etc.* (Holmes, 1979). This result is documented by a series of spirocyclic oxyphosphoranes $(C_6H_4O_2)_2PR$ derived from catechol with different fifth ligands *R* showing geometries between a tbp (*R* = H, Wunderlich & Wussow, 1978) and an sp which is reduced by the chelation to a rectangular pyramid (rp) [*R* = CH_3, Wunderlich, 1974; *R* = OC_6H_5, Sarma, Ramirez & Marecek, 1976; *R* = $C(CH_3)_3$, Wunderlich, 1978*b*]. Only a few crystal structures of dioxadiazaspirophosphoranes are known (Newton, Collier & Wolf, 1974; Meunier, Day, Devillers & Holmes, 1978; Devillers, Garrigues & Wolf, 1979). In all these structures O atoms are located at the axial sites of a slightly distorted tbp. The compound under study is the first spirobi(diazaphosphorane) and extends this series to molecules without O atoms in the spiro system adjacent to the P atom. Hereby the differences of electronegativities are reduced and should not influence the conformation as much as in the structures cited above.

Table 2. *Bond angles* (°) *in* $[C_6H_4(NCH_3)_2]_2PCH_3$

(i) Angles at the P atom

The e.s.d.'s are 0·2–0·3°.

	N(1)	N(2)	N(3)	N(4)
N(2)	86·1			
N(3)	121·8	92·6		
N(4)	93·7	178·2	85·9	
C(5)	118·6	90·9	119·6	90·8

(iii) Other angles in and around the five-membered rings

The e.s.d.'s are 0·4–0·6°.

P–N(1)–C(12)	115·9	P–N(3)–C(22)	117·0
P–N(1)–C(1)	126·9	P–N(3)–C(3)	126·8
C(1)–N(1)–C(12)	116·1	C(3)–N(3)–C(22)	114·9
N(1)–C(12)–C(11)	111·6	N(3)–C(22)–C(21)	110·0
N(1)–C(12)–C(13)	127·5	N(3)–C(22)–C(23)	129·4
C(12)–C(11)–N(2)	110·5	C(22)–C(21)–N(4)	110·9
C(16)–C(11)–N(2)	129·6	C(26)–C(21)–N(4)	129·0
C(11)–N(2)–P	115·9	C(21)–N(4)–P	115·5
C(11)–N(2)–C(2)	118·4	C(21)–N(4)–C(4)	118·2
C(2)–N(2)–P	125·0	C(4)–N(4)–P	124·3

(iii) Angles in the benzene rings

The e.s.d.'s are 0·5–0·8°.

	n = 1	*n* = 2
C(*n*6)–C(*n*1)–C(*n*2)	119·9	120·2
C(*n*1)–C(*n*2)–C(*n*3)	120·9	120·7
C(*n*2)–C(*n*3)–C(*n*4)	116·8	119·7
C(*n*3)–C(*n*4)–C(*n*5)	121·2	120·1
C(*n*4)–C(*n*5)–C(*n*6)	121·3	120·8
C(*n*5)–C(*n*6)–C(*n*1)	119·9	118·6

Fig. 1 shows the molecule with bond lengths; bond angles are given in Table 2. The geometry at the P atom is clearly tbp with the methyl group at an equatorial position. The axial angle N—P—N is 178·2°; the equatorial angles are 121·8 (N—P—N), 118·6, and 119·6° (N—P—C). The mean bond lengths are $(P—N)_{ax}$ 1·792 and $(P—N)_{eq}$ 1·712 Å. The difference of 0·08 Å together with the bond angles define two axial [N(2), N(4)] and three equatorial [N(1), N(3), C(5)] sites of a tbp. The unequal P—N lengths agree with values reported for similar pentacoordinations [*e.g.*

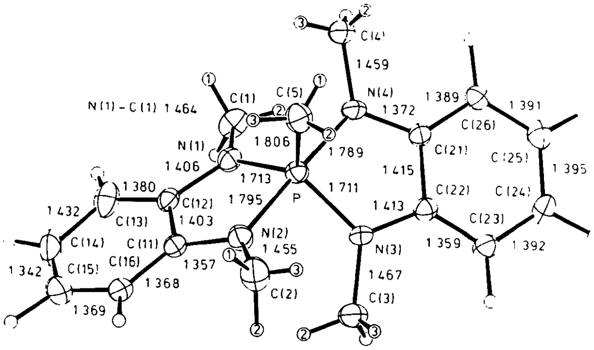

Fig. 1. The molecule of $[C_6H_4(NCH_3)_2]_2PCH_3$ in an arbitrary crystallographic orientation with bond lengths (Å). The non-H atoms are represented by thermal ellipsoids of 25% probability (*ORTEP* II, Johnson, 1976). The radius of the H atoms was set to B = 1·0 Å^2. The H atoms of the methyl groups are identified as far as possible by their last digit. The e.s.d.'s are: P–N 0·004–0·005, P–C 0·009, N–C 0·007–0·011, C–C 0·008–0·013 Å.

Table 3. *Analysis of the dihedral angles* (°)

The e.s.d.'s are *ca* 0·3°. The angles δ are between the normals of the two adjacent triangular faces with the common edge as listed. Nomenclature of δ and angles of idealized tbp and rp are according to Holmes & Deiters (1977).

Edge	δ	tbp	Δ(tbp)	Observed	Δ(rp)	rp
N(1),N(4)	45	101·5	1·1	100·4	18·9	119·3
N(3),N(4)	25	101·5	3·0	104·5	13·1	117·6
N(1),N(2)	14	101·5	2·3	103·8	13·8	117·6
N(2),N(3)	12	101·5	0·2	101·3	18·0	119·3
N(4),C(5)	35	101·5	0·6	102·1	25·2	76·9
N(2),C(5)	13	101·5	0·3	101·8	24·9	76·9
N(3),C(5)	23	53·1	0·4	52·7	24·2	76·9
N(1),C(5)	34	53·1	1·2	54·3	22·4	76·9
N(1),N(3)	24	53·1	4·5	48·6	48·6	0·0
$\Sigma\Delta$			13·6		209·1	

dicyclenphosphorane $C_{16}H_{32}N_8P_2$ (Richman, Day & Holmes, 1980)] and are paralleled by opposite differences of the adjacent C—N lengths of up to 0·056 Å. Analysis of the dihedral angles (Table 3) between all adjacent triangular faces of the tbp polyhedron yields an overall deviation of 13·6° from ideal tbp and 209·1° from ideal rp, following closely the Berry exchange coordinate (Berry, 1960). From these values the structure is 5% away from ideal tbp along the Berry coordinate. A criterion of a least-squares plane (Wunderlich, 1978*a*) defined by N(1), N(2), N(3), and N(4) yields a 94% tbp geometry for this structure, while the corresponding oxyphosphorane, with each NCH_3 group replaced by an O atom (Wunderlich, 1974), with 83% is located almost at the other end of this scale.

The two five-membered rings deviate significantly from planarity. While the two N and C atoms in each ring are coplanar within 2σ, the P atom lies 0·046 (2) and 0·161 (2) Å, respectively, out of the corresponding least-squares planes. The two six-membered rings do not deviate significantly from planarity and are coplanar with the five-membered rings within 3°. The geometry of the H atoms is in the usual range with mean C—H lengths of 0·93 Å for the methyl groups and 1·02 Å for the rings.

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Structure of Tris(2-cyanoethyl)phosphine Oxide, $P(CH_2CH_2CN)_3O$

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Abstract. $C_9H_{12}N_3OP$, trigonal, $R3c$; a = 13·484 (1), c = 10·162 (1) Å, V = 1600·1 (3) Å^3, Z = 6 (hexagonal axes); a = 8·490 (1) Å, α = 105·14 (2)°, V = 533·4 (1) Å^3, Z = 2 (rhombohedral axes); D_c = 1·306, D_o = 1·316 Mg m^{-3}. The final R value for 100 reflections is 0·064. The structure consists of columns of $P(CH_2CH_2CN)_3O$ molecules, with internal C_3 molecular symmetry, arranged head-to-tail along the direction of the hexagonal c axis. The P—O bond length (1·446 Å) is almost identical with that in $POCl_3$.

Introduction. In preliminary crystallographic and spectroscopic studies of the tris(2-cyanoethyl)phosphine derivatives $P(CH_2CH_2CN)_3X$ (X = O, S, Se) it became apparent that the crystal structure and molecular geometry, in the solid, of the oxide is quite different from that of the sulphide or selenide (Blake, 1980; Blake, Howie & McQuillan, 1979). Crystal structure determinations were desirable as a matter of general interest and to facilitate interpretation of the vibrational spectra of these molecules.

Tris(2-cyanoethyl)phosphine oxide, obtained by peroxide oxidation of the parent phosphine in glacial acetic acid, crystallizes from 50% aqueous 2-propanol as colourless needles (Rauhut, Hechenbleikner, Currier, Schafer & Wystrach, 1959). The compound was identified by chemical analysis and unit-cell parameters were determined as described previously (Blake *et al.*, 1979). The systematic absences [hkl, $-h + k + l \neq 3n$; hhl, $l \neq 3n$ and $h\bar{h}l$ ($h + l = 3n$), $l \neq 2n$ (hexagonal axis system)] identify the crystal as trig-

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