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, $P(CH_2CH_2CN)_3O$

By A. J. Blake, R. A. Howie and G. P. McQuillan*

Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE, Scotland

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Abstract. $C_9H_{12}N_3OP$, trigonal, $R3c$; $a = 13\cdot484$ (1), $c = 10\cdot162$ (1) Å, $V = 1600\cdot1$ (3) Å^3, $Z = 6$ (hexagonal axes); $a = 8\cdot490$ (1) Å, $\alpha = 105\cdot14$ (2)°, $V = 533\cdot4$ (1) Å^3, $Z = 2$ (rhombohedral axes); $D_c = 1\cdot306$, $D_o = 1\cdot316$ 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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* To whom correspondence should be addressed.

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onal, space group $R3c$ or $R\bar{3}c$. The six molecules in the hexagonal cell (two in the rhombohedral cell) must occupy special positions, of D_3 or C_{3i} symmetry in $R\bar{3}c$, or C_3 symmetry in $R3c$. The minimum required symmetry in $R\bar{3}c$ is not compatible with the $P(CH_2CH_2CN)_3O$ molecule and the space group is therefore $R3c$ (No. 161).

Intensity data were collected for a single crystal (0·5 × 0·3 × 0·2 mm) set about c (hexagonal) using a Hilger & Watts model Y190 automatic linear diffractometer with balanced filters and Mo $K\alpha$ radiation (λ = 0·7107 Å). A total of 2013 intensities measured for non-extinct reflections over the range $0 < \sin^2\theta < 0{\cdot}31$, with $\Delta\omega = 2{\cdot}5°$, yielded 462 independent Lp-corrected reflections of which 109, with $I > 2\sigma(I)$, were treated as 'observed'.

In space group $R3c$, the six molecules in the hexagonal cell must occupy special positions with the P—O bonds aligned along c. Accordingly, the P atom was fixed at the origin and the O atom placed initially 1·45 Å away along the c axis. A three-dimensional Patterson synthesis produced a $\overrightarrow{PC}$ vector and a subsequent Fourier synthesis located the C and N atoms. Block-diagonal least-squares refinement, employing all 462 measured intensities with all atoms isotropic reduced the conventional R value to 0·13; the refinement was then continued using only the 'observed' reflections with the P atom anisotropic until all parameter shifts were <0·3 e.s.d. The R value at this point (100 reflections) was 0·064; including 'unobserved' reflections and 9 'observed' reflections classed as unsatisfactory in the course of the refinement, the value was 0·090. The computed H atom positions coincided in most cases with small peaks on a difference map. The weighting scheme used throughout was of the form $w = [1 + (a|F_o| - b)^2]^{-1}$ where $a = 0{\cdot}04$ and $b = 1{\cdot}4$. Computer programs were based on those of Ahmed, Hall, Pippy & Huber (1966) and neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

Table 1. *Final positional parameters*

For P, $T = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$ and for the remaining heavy atoms $\exp[-B_{\rm iso}(\sin\theta/\lambda)^2]$.

	x	y	z	$B_{\rm iso}$ (Å^2)
P	0·0000	0·0000	0·0000	1·48†
O	0·0000	0·0000	−0·1423 (7)	2·95
C(1)	0·0315 (6)	0·1367 (7)	0·0753 (8)	3·49
C(2)	−0·0424 (8)	0·1796 (9)	−0·0063 (11)	5·12
C(3)	−0·0058 (7)	0·2978 (6)	0·0250 (8)	3·18
N	0·0256 (6)	0·3923 (7)	0·0377 (9)	4·76
H(11)*	0·009	0·126	0·179	
H(12)*	0·123	0·199	0·071	
H(21)*	−0·030	0·173	−0·111	
H(22)*	−0·132	0·127	0·019	

* Approximate H atom coordinates calculated assuming a tetrahedral HCH angle and C—H bond length of 1·09 Å. The first digit in the H atom number indicates the C atom to which it is attached.

† Equivalent isotropic thermal parameter calculated from anisotropic temperature factors using an eigenvector routine programed by P. D. Cradwick, Macaulay Institute for Soil Research, Aberdeen.

Anisotropic thermal parameters for P (Å^2 × 10^4)

B_{11}	B_{22}	B_{33}	B_{12}
27	27	35	25

Table 2. *Bond lengths* (Å) *and angles* (°)

E.s.d.'s in the last significant figures are given in parentheses.

P—O	1·446 (7)	O—P—C	114·6 (3)
P—C(1)	1·84 (1)	C—P—C	103·9 (4)
C(1)—C(2)	1·61 (2)	P—C(1)—C(2)	105·8 (6)
C(2)—C(3)	1·45 (2)	C(2)—C(2)—C(3)	110·5 (8)
C(3)—N	1·13 (1)	C(2)—C(3)—N	173·7 (10)

The final atomic coordinates are given in Table 1 and details of bond lengths and angles in Table 2.*

Discussion. The structure consists of parallel columns of $P(CH_2CH_2CN)_3O$ molecules, arranged 'head-to-tail' alternately left- and right-handed in the direction of the hexagonal c axis (Fig. 1). The intermolecular non-bonded P—O distance, along the axis, is 3·635 (7) Å, compared with 1·446 (7) Å for the intramolecular P—O bond. The $P(CH_2CH_2CN)_3O$ molecules have the minimum C_3 symmetry compatible with their crystal sites: the individual CCCN chains are not coplanar with the P—O bond (as would be required for a C_{3v} conformation) and in projection the molecule has a twisted propeller-like appearance (Fig. 2). The immediate phosphorus environment is tetrahedral, with the OPC angles slightly greater, and the CPC angles slightly less, than the 'pure' tetrahedral value. Overall, however, the $P(CH_2CH_2CN)_3$ grouping is rather flattened, with the P atom only 0·385 Å above the plane defined by the three N atoms: this arrangement presumably minimizes the inter- and intramolecular CN—CN and O—CN repulsions.

The P—O bond length [1·446 (7) Å] is close to that in $POCl_3$ [1·448 (5) Å, Moritani, Kuchitsu & Morino, 1971] and distinctly shorter than that in $POMe_3$ [1·476 (2) Å, Wilkins, Hagen, Hedberg, Quang Shen & Hedberg, 1975]. The cyanoethyl group thus appears to exert a significant electron-withdrawing effect. The P—C distance of 1·84 Å is typical for a P—C single bond. Within the cyanoethyl group, the C(1)—C(2) and

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35845 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

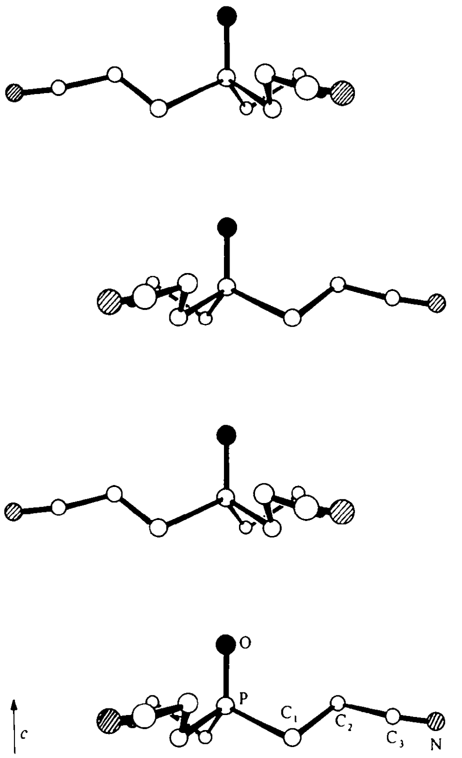

Fig. 1. 'Head-to-tail' arrangement of $P(CH_2CH_2CN)_3O$ molecules in the hexagonal **c** direction.

C(2)–C(3) bond lengths are expected to be unequal because of the difference in the C(1) and C(2) (sp^3) and C(3) (sp) carbon atom radii: this does not imply any significant difference in C–C bond orders. The C(1)–C(2) distance (1·61 Å) appears to be slightly long (a value of about 1·55 Å would be more consistent with related molecules) and probably reflects residual errors in the C atom coordinates: because of the limited number of observed reflections the C atom parameters could not be refined anisotropically and the position of C(2) is marginally less well-defined than are those of C(1), C(3) or N.

The CCN angle of 173·7 (1·0)° is also probably influenced by uncertainties in the C atom positions but the deviation from 180°, relative to the probable accuracy of the structure, is sufficient to suggest that the CCN arrangement is genuinely non-linear. Slightly 'bent' CCN groups can be observed even in the gas phase [*e.g.* CH_3CH_2CN, 178·3° (Mader, Heise & Dreizler, 1974)], and similar or greater departures from strict linearity may well be induced by inter- or intramolecular effects in the crystal.

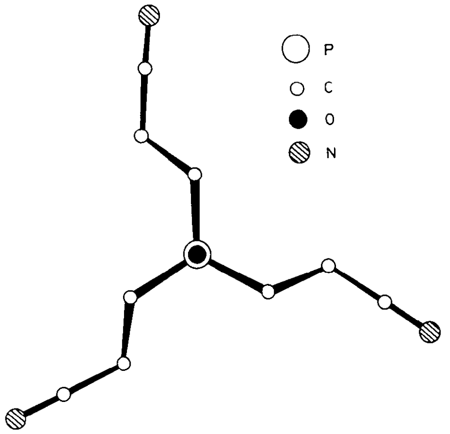

Fig. 2. Projection of $P(CH_2CH_2CN)_3O$ on the plane perpendicular to the O–P bond.

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