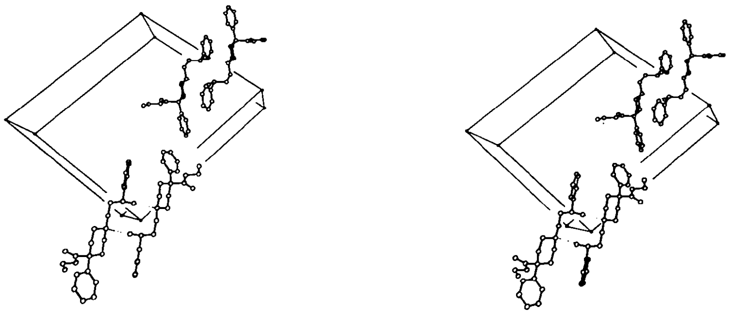

Fig. 3. Stereoscopic view of the molecular packing.

Fig. 3 shows that the molecular packing is essentially due to hydrogen bonds which arise between the piperidine N of one molecule and the alcohol O atom of the one opposite, in order to form a dimeric association.

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1-Phenyl-1,1′-spirobi[3*H*-2,1-benzoxaphosphole]-3,3′-dione

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Abstract. $C_6H_5P(C_7H_4O_2)_2$, monoclinic, $C2/c$, a = 25·252 (6), b = 8·549 (9), c = 15·252 (6) Å, β = 97·15 (9)°, Z = 8, U = 3267 Å^3, D_x = 1·416 g cm^{-3}, μ(Cu $K\alpha$) = 15·8 cm^{-1}. The structure was solved by direct methods and refined to an R of 0·036 for 2047 unique diffractometer data. The coordination at P is close to ideal trigonal bipyramidal, with axial O atoms. The mean P–O and P–C lengths are 1·781 (2) and 1·801 (2) Å respectively.

Introduction. Segall, Granoth, Kalir & Bergmann (1975) have reported the synthesis of stable spiro bicyclic acyloxyphosphoranes by the spontaneous acid-catalysed intramolecular dehydration of bis(*o*-carboxyphenyl)phosphine oxides. Structural elucidation of these phosphoranes was based mainly on ^{31}P NMR data. In view of the isolation of the corresponding *P*-hydroxyphosphorane by Segall & Granoth (1977) crystallographic structural confirmation was desirable, and is reported here for the *P*-phenyl phosphorane.

Intensities were measured with a Syntex $P2_1$ four-circle diffractometer, graphite-monochromated Cu $K\alpha$ radiation, and a crystal 0·15 × 0·23 × 0·50 mm. No corrections were applied for absorption. Equivalent reflexions were averaged, reducing the 3364 measured data to 2047 unique reflexions with $F > 4\sigma(F)$ based on counting statistics. Cell dimensions were obtained from the diffractometer settings for 15 strong reflexions. Intensity statistics indicated the space group $C2/c$ rather than Cc; $C2/c$ was confirmed by the successful structure refinement. All the non-hydrogen atoms were located from the best E map obtained by multisolution Σ_2 sign expansion; a subsequent difference synthesis revealed the H atoms. The structure was refined by blocked-matrix least squares, with complex neutral-atom scattering factors and the weighting scheme $w = [\sigma^2(F) + 0{\cdot}00037F^2]^{-1}$, to $R' = \Sigma w^{1/2}\Delta/\Sigma w^{1/2}F_o$ = 0·040 and R = 0·036. The H atoms were allowed to refine freely, with individual isotropic temperature factors; the remaining atoms were anisotropic. An

Table 1. *Atom coordinates* (× 10⁴)

	x	*y*	*z*
P	1260 (1)	4498 (1)	3446 (1)
O(11)	1769 (1)	3382 (1)	3031 (1)
O(12)	1972 (1)	998 (2)	2579 (1)
O(21)	751 (1)	5597 (1)	3875 (1)
O(22)	582 (1)	7060 (2)	5023 (1)
C(10)	1668 (1)	1867 (2)	2890 (1)
C(11)	1142 (1)	1447 (2)	3163 (1)
C(12)	876 (1)	2727 (2)	3462 (1)
C(13)	377 (1)	2507 (2)	3753 (1)
C(14)	168 (1)	1010 (2)	3741 (1)
C(15)	441 (1)	−243 (3)	3441 (1)
C(16)	930 (1)	−35 (2)	3146 (1)
C(20)	893 (1)	6311 (2)	4651 (1)
C(21)	1462 (1)	6046 (2)	4953 (1)
C(22)	1714 (1)	5103 (2)	4391 (1)
C(23)	2248 (1)	4744 (3)	4603 (1)
C(24)	2519 (1)	5328 (3)	5379 (2)
C(25)	2267 (1)	6249 (3)	5937 (1)
C(26)	1734 (1)	6630 (3)	5727 (1)
C(31)	718 (1)	5918 (2)	1950 (1)
C(32)	1203 (1)	5713 (2)	2473 (1)
C(33)	1653 (1)	6470 (2)	2247 (1)
C(34)	1609 (1)	7454 (3)	1527 (2)
C(35)	1128 (1)	7642 (3)	1009 (1)
C(36)	684 (1)	6870 (3)	1209 (1)

Table 2. *Hydrogen atom coordinates* (× 10⁴) *and isotropic temperature factors* (Å² × 10³)

	x	*y*	*z*	*U*
H(13)	170 (8)	3364 (23)	3940 (12)	54 (5)
H(14)	−186 (9)	873 (23)	3975 (13)	63 (6)
H(15)	306 (9)	−1247 (27)	3463 (13)	70 (6)
H(16)	1123 (8)	−929 (24)	2935 (12)	61 (6)
H(23)	2421 (10)	4133 (27)	4211 (16)	79 (8)
H(24)	2894 (11)	5059 (27)	5529 (15)	73 (7)
H(25)	2449 (10)	6642 (27)	6484 (16)	79 (7)
H(26)	1553 (10)	7281 (27)	6076 (16)	76 (7)
H(31)	431 (9)	5360 (23)	2116 (13)	57 (6)
H(33)	1979 (8)	6319 (21)	2580 (12)	47 (5)
H(34)	1924 (11)	8047 (31)	1415 (16)	91 (8)
H(35)	1111 (10)	8358 (28)	464 (16)	83 (7)
H(36)	362 (10)	7052 (26)	872 (15)	70 (7)

Table 3. *Bond lengths* (Å)

O(11)–P	1·780 (3)	O(21)–P	1·782 (3)
C(12)–P	1·799 (4)	C(22)–P	1·803 (4)
C(32)–P	1·802 (4)	C(32)–C(31)	1·386 (3)
C(33)–C(32)	1·389 (4)	C(34)–C(33)	1·377 (4)
C(35)–C(34)	1·374 (4)	C(36)–C(35)	1·367 (5)
C(36)–C(31)	1·387 (4)	C(10)–O(11)	1·332 (3)
C(20)–O(21)	1·340 (3)	C(10)–O(12)	1·205 (3)
C(20)–O(22)	1·208 (3)	C(11)–C(10)	1·485 (4)
C(21)–C(20)	1·472 (4)	C(12)–C(11)	1·391 (3)
C(22)–C(21)	1·388 (4)	C(13)–C(12)	1·398 (4)
C(23)–C(22)	1·381 (4)	C(14)–C(13)	1·384 (4)
C(24)–C(23)	1·386 (4)	C(15)–C(14)	1·382 (4)
C(25)–C(24)	1·372 (5)	C(16)–C(15)	1·377 (4)
C(26)–C(25)	1·381 (5)	C(16)–C(11)	1·375 (4)
C(26)–C(21)	1·382 (4)		

Table 4. *Bond angles* (°)

C(12)–P–O(11)	88·2 (2)	C(12)–P–O(21)	91·4 (2)
C(22)–P–O(11)	91·2 (2)	C(22)–P–O(21)	88·3 (2)
C(32)–P–O(21)	90·6 (2)	C(32)–P–O(11)	90·2 (2)
C(22)–P–C(12)	121·4 (2)	C(32)–P–C(12)	120·6 (2)
C(32)–P–C(22)	118·1 (2)	O(21)–P–O(11)	179·1 (1)
C(10)–O(11)–P	116·5 (2)	C(20)–O(21)–P	116·0 (2)
O(12)–C(10)–O(11)	123·0 (3)	C(11)–C(10)–O(11)	110·4 (2)
C(11)–C(10)–O(12)	126·6 (3)	C(12)–C(11)–C(10)	112·9 (2)
C(16)–C(11)–C(10)	125·3 (3)	C(16)–C(11)–C(12)	121·8 (3)
C(11)–C(12)–P	111·9 (2)	C(13)–C(12)–P	128·7 (2)
C(13)–C(12)–C(11)	119·4 (3)	C(15)–C(14)–C(13)	121·0 (3)
C(16)–C(15)–C(14)	120·9 (3)	C(14)–C(13)–C(12)	118·5 (3)
C(15)–C(16)–C(11)	118·4 (3)	O(22)–C(20)–O(21)	122·5 (3)
C(21)–C(20)–O(21)	110·6 (3)	C(21)–C(20)–O(22)	126·9 (3)
C(22)–C(21)–C(20)	113·6 (2)	C(26)–C(21)–C(20)	125·1 (3)
C(26)–C(21)–C(22)	121·3 (3)	C(21)–C(22)–P	111·5 (2)
C(23)–C(22)–P	129·0 (3)	C(23)–C(22)–C(21)	119·5 (3)
C(24)–C(23)–C(22)	118·9 (3)	C(25)–C(24)–C(23)	121·2 (3)
C(26)–C(25)–C(24)	120·3 (3)	C(25)–C(26)–C(21)	118·6 (3)
C(36)–C(31)–C(32)	120·2 (3)	C(31)–C(32)–P	121·4 (2)
C(33)–C(32)–P	119·3 (2)	C(33)–C(32)–C(31)	119·4 (3)
C(34)–C(33)–C(32)	119·7 (3)	C(35)–C(34)–C(33)	120·6 (3)
C(36)–C(35)–C(34)	120·4 (3)	C(35)–C(36)–C(31)	119·7 (3)

empirical isotropic extinction parameter x refined to 3·2 (3) × 10^{-6}, where $|F_c|$ was multiplied by $(1 - x|F_c|^2/\sin\theta)$. Final positional parameters are given in Tables 1 and 2, bond lengths and angles for the non-hydrogen atoms in Tables 3 and 4.* C–H lengths were in the range 0·92 to 1·03 Å (mean 0·96 Å), and C–C–H angles in the range 116·3 to 123·4° (mean 120·0°), consistent with sp^2-hybridized C atoms.

Discussion. The molecule (Fig. 1) possesses an approximate non-crystallographic twofold symmetry axis along P–C(32). The coordination of P is close to ideal trigonal bipyramidal, with, as usual, the most electronegative ligands axial; three C atoms occupy the equatorial positions. The unstrained geometry possibly accounts for the high thermal stability of the compound. Much more distorted trigonal-bipyramidal coordination (Cadogan, Gould, Gould, Sadler, Swire & Tait, 1975; Carrell, Berman, Ricci, Hamilton, Ramirez, Marecek, Kramer & Ugi, 1975) or square-pyramidal structures (Wunderlich, Mootz, Schmutzler & Wieber, 1974; Howard, Russell & Trippett, 1973) have been found for other phosphoranes studied by X-ray diffraction. A similar ligand arrangement is found in $Se(C_7H_4O_2)_2$ (Dahlén, 1974) and $S(C_7H_4O_2)_2$ (Kálmán, Sasvári & Kapovits, 1973), but the replacement of the equatorial phenyl group by a lone pair causes much larger distortions from idealized trigonal-bipyramidal geometry. The phenyl group is twisted by 35·7° out of the equatorial plane, possibly to minimize

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33350 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

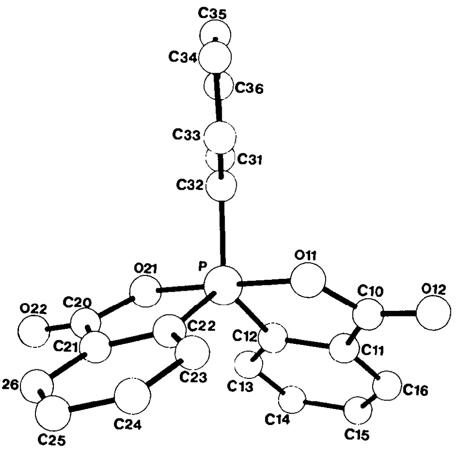

Fig. 1. The labelling scheme of the title compound.

repulsions involving the *ortho* H atoms. C(10)–C(11) [1·485 (4)] and C(20)–C(21) [1·472 (4) Å] are consistent with single bonds between sp^2-hybridized C atoms, indicating little electron delocalization in the five-membered P–O–C–C–C– rings, but the shortness of C(10)–O(11) and C(20)–O(21) suggests that significant multiple-bond character should be assigned to them.

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Hydrogen-Bond Motifs of Carboxylic Acids: The α Form of Cyanoacetic Acid at −150°C

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Abstract. $C_3H_3NO_2$, monoclinic, $P2_1/c$, a = 11·629 (6), b = 7·761 (3), c = 13·758 (3) Å, β = 108·92 (3)°, Z = 12, D_c = 1·460 g cm^{-3} at −150 °C. The structure contains two types of hydrogen-bond motifs. The asymmetric unit consists of three independent molecules. One molecule forms cyclic dimers by carboxyl-group coupling across centres of symmetry, the other two form separate infinite O–H···N-linked polymers.

Introduction. $C_3H_3NO_2$ exists in two distinct crystalline varieties (Schaum, Schaeling & Klausing, 1916). Sublimation *in vacuo* at a temperature of 70 °C yielded the monoclinic modification, which was also obtained by recrystallization from ether. Since Sinha & Katon (1972), from changes upon cooling of IR and Raman spectra of cyanoacetic acid, inferred an order–disorder transition relating to the hydrogen-bond system, the structure has been determined at room and liquid-nitrogen temperatures. As the results of both structure determinations, which were performed to elucidate the hydrogen-bond motif, only differ within experimental error, the low-temperature structure is reported.

A hexagonal rod-like crystal 0·5 × 0·2 × 0·1 mm was sealed in a capillary tube because of its very hygroscopic character. Cell dimensions and 1075 intensities (sin θ/λ < 0·48 Å^{-1}) were measured with an ω–2θ scan and Mo $K\alpha$ radiation (λ = 0·71069 Å) on a Nonius CAD-4 computer-controlled diffractometer. 195 reflexions with I < $2{\cdot}5\sigma(I)$ were considered unobserved and given zero weight in the refinement. After Lorentz and polarization corrections the data were placed on an approximate absolute scale by means of a Wilson (1942) plot and a correction for