weakening of the hydrogen-bond interaction relative to compounds such as 2,4-dihydroxybenzophenone [$O \cdots O$, 2·550 (4) Å] which have only one intra-molecular hydrogen bond to the carbonyl O is in keeping with the observed IR ν_{O-H} values (Merrill, 1961). Our findings are also consistent with the interpretation of the ^{13}C NMR and IR spectra by Sopchik & Kingsbury (1979) who suggested weaker hydrogen bonding than in single hydroxyl interactions with the carbonyl and also suggested unequal hydrogen bonding by the two hydroxyl groups.

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Structure of Tris(2-cyanoethyl)phosphine Oxide

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Abstract. $C_9H_{12}N_3OP$, $M_r = 209·2$, rhombohedral, $R3c$, $a = 13·501$ (4), $c = 10·177$ (3) Å, $Z = 6$, $D_m = 1·30$ (1), $D_x = 1·30$ Mg m^{-3}; $R = 0·033$ for 615 reflexions. The molecule has threefold symmetry along the P–O bond with a C–P–C angle of 106·43 (12)°. The P=O distance is 1·485 (3) Å.

Introduction. Square-planar transition-metal complexes of the polyfunctional ligand, tris(2-cyanoethyl)-phosphine, undergo a series of interesting solid-state reactions (Walton & Whyman, 1968; Foxman & Cheng, 1977). This ligand has both low steric requirements and the lowest basicity observed for a tertiary phosphine, $pK_a = 1·37$ (Streuli, 1960). In order to examine the structural chemistry of related derivatives, the oxide was synthesized and its structure determined.

The space group, $R3c$, was implied from Weissenberg and precession photographs, and confirmed by the structure analysis and refinement. Density measurements were by flotation in xylene and carbon tetra-

chloride. Data were collected on a Syntex $P2_1$ diffractometer using a crystal with dimensions 0·11 × 0·13 × 0·39 mm, as described previously (Foxman, 1978). Details of the structure analysis are presented in Table 1. An empirical absorption correction (Syntex,

Table 1. *Data for the X-ray diffraction study of* $(O)P(CH_2CH_2CN)_3$

Cell-constant determination of 17 high-angle values in the range $82° < |2\theta| < 136°$ [$\lambda(Cu\ K\alpha_1) = 1·5405$ Å and Ni β-filter]; $T = 294$ K

Intensities measured: 655 total; 615 in unique set (to $2\theta = 158°$)

Data reduction as in Foxman (1978); e.s.d.'s of $|F_o|$ values calculated by method of finite differences (Churchill, Lashewycz & Rotella, 1977) gave $R_s = \sum \sigma(|F_o|)/\sum|F_o| = 0·009$ [$I > 1·96\sigma(I)$]

Full-matrix least-squares refinement: anisotropic thermal parameters for P, C, O, N atoms; isotropic thermal parameters for H atoms, with weights $= [\sigma^2(|F_o|) + (0·035\ |F_o|)^2]^{-1}$

Final $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0·033$,
$R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0·042$

Table 2. *Atomic coordinates and isotropic thermal parameters with e.s.d.'s in the least significant digit in parentheses*

For atoms refined anisotropically,

$$U_{iso} = U_{eq} = \tfrac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{iso} (Å^2)
P	0	0	0	0·0377 (3)
O	0	0	−0·1460 (3)	0·0508 (9)
C(1)	0·0304 (2)	0·13655 (18)	0·0678 (2)	0·0425 (9)
C(2)	−0·0445 (3)	0·1769 (2)	0·0021 (4)	0·0641 (13)
C(3)	−0·0049 (2)	0·2980 (2)	0·0230 (3)	0·0496 (10)
N	0·0227 (2)	0·3913 (2)	0·0386 (3)	0·0674 (12)
H(1A)	0·114 (3)	0·195 (4)	0·051 (4)	0·084 (12)
H(1B)	0·018 (3)	0·130 (2)	0·159 (4)	0·061 (8)
H(2A)	−0·124 (6)	0·125 (6)	−0·006 (6)	0·17 (3)
H(2B)	−0·018 (4)	0·182 (4)	−0·088 (4)	0·091 (12)

Fig. 1. Molecular structure and labelling scheme. (E.s.d.'s for torsion angles are ∼0·2°.)

1976) was applied to all data. The analytical scattering factors of Cromer and Waber were used (*International Tables for X-ray Crystallography*, 1974, pp. 99–101); real and imaginary components of anomalous scattering were included in the calculations for all non-H atoms (*International Tables for X-ray Crystallography*, 1974, pp. 148–150). With $Z = 6$, the P and O atoms must be on the 6(*a*) sites; the P atom was placed at $z = 0$ to fix the origin. The remaining non-H atoms were located from subsequent structure-factor calculations and ΔF syntheses. At the conclusion of isotropic refinement, initial H-atom positions were calculated using the program *HPOSN* (Syntex, 1976). The non-H atoms were refined anisotropically and the H atoms isotropically. At convergence, $R = 0·033$ and $R_w = 0·042$. Comparison with a refinement of the structure of opposite polarity gave $R = 0·042$, $R_w = 0·059$ confirming the choice of coordinates for the particular crystal selected (Hamilton, 1965). The atomic coordinates are listed in Table 2.*

Discussion. Pertinent distances and angles, with their standard deviations, are shown in Fig. 1. The weighted average C—H distance is 0·969 (23) Å. The P=O bond length, 1·485 (3) Å, is normal, and comparable to those found in other phosphine oxides containing alkyl groups, *e.g.* 1·495 (5) Å in (O)P(CH₃)(C₆H₅)-[C(CH₃)₂CH(OH)(CH₃)] and 1·492 (9) Å in (O)P(CH₃)(C₆H₅){CH(CH₃)[C(CH₃)=CH₂]} (Allen, Kennard, Nassimbeni, Shepherd & Warren, 1974). Thus it appears that the complex fails to display P=O bond shortening as expected by analogy with the *M*—P
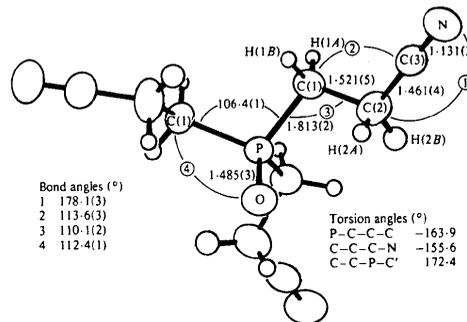
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36276 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Comparison of cell constants and R values*

(*a*) Cell constants reported for (O)P(CH₂CH₂CN)₃

a	c	Reference
13·484 (1) Å	10·162 (1) Å	1
13·487 (3)	10·166 (1)	2
13·501 (4)	10·177 (3)	3*

(*b*) R indices and 'overdetermination ratio' (NO/NP, where NO is the number of observations and NP the number of parameters)

R	NO	NP	Ratio	σ(P—O)	σ(C—C)$_{av}$	Reference
0·064	109	23	4·7	0·007 Å	0·020 Å	1
0·028	397	58	6·8	0·003	0·003	2
0·033	615	58	10·6	0·003	0·004	3

References: (1) Blake *et al.* (1981). (2) Cotton *et al.* (1981). (3) This work.

* $T = 294$ K. Cell-constant determination checked against a 0·15 mm spherical ruby crystal.

bond shortening in $M(CO)_5[P(CH_2CH_2CN)_3]_2$ ($M = $ Cr, Mo) (Cotton, Darensbourg & Ilsley, 1981). The remaining geometry is similar to that found for tris(2-cyanoethyl)phosphine complexes (Bennett, Cotton & Winquist, 1967; Foxman & Mazurek, 1979; Cotton *et al.*, 1981).

Note added in proof: After this paper was accepted for publication, two further studies of the compound appeared in the literature (Blake, Howie & McQuillan, 1981; Cotton, Darensbourg, Fredrich, Ilsley & Troup, 1981). There are significant differences between reported cell constants (Table 3*a*); however, the temperature of the cell-constant determination is available

only for the present work (Table 1). The crystal used in the study by Blake *et al.* (1981) yielded a structure determination of relatively low precision (Table 3*b*); further, no determination of the crystal polarity was carried out. Under these circumstances we feel that a highly detailed comparison of the other two structures to that determination is unwarranted. The present work and the structure determined by Cotton *et al.* (1981) are essentially in agreement, except that the *z* coordinates in the latter are displaced by an average of +0·008 Å from those in the present work. This effect possibly stems from either (*a*) an incorrect polarity determination [*R* values were not given by Cotton *et al.* (1981)], or (*b*) inaccuracies in the value of f'' for P. In any event, the data from the present work should be unaffected by such errors, since both *hkl* and $h\bar{k}l$ were measured for each reflection (Cruickshank & McDonald, 1967, and Supplementary Publication No. SUP 36276). Correction of the P—O bond distance (1·498 Å) in the Cotton *et al.* (1981) structure by −0·008 Å gives 1·490 (3) Å, in close agreement with our value of 1·485 (3) Å. Whether the correction is made or not, both the present work and that of Cotton *et al.* (1981) demonstrate that the P=O bond length is *not* altered by the electron-withdrawing effects of the —CN groups. This is at variance with the results of Blake *et al.* (1981), who observed a short P=O bond length of 1·446 (7) Å.

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Structure de la Citréomontanine

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Abstract. 4-Methoxy-5-methyl-6-(7,9,11-trimethyl-1,3,5,7,9,11-tridecahexaenyl)-2*H*-pyran-2-one (all *E*), $C_{23}H_{28}O_3$, isolated from *Penicillium pedemontanum*, triclinic, P$\bar{1}$, $a = 12·092$ (5), $b = 11·018$ (5), $c = 8·018$ (5) Å, $\alpha = 106·5$ (1), $\beta = 94·8$ (1), $\gamma = 97·7$ (1)°, $Z = 2$, $V = 1007$ Å³, $d_x = 1·162$ (2) g cm⁻³. The structure was solved and refined to $R = 0·059$ with 2913 reflexions considered as observed. Atoms C(18), C(19) and C(20) are out of the mean plane of the chain. In the polyene chain, double bonds [mean value