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TECHNICAL REPORT No. 5

Structure of Tris(2-cyanoethyl) phosphine Oxide

by

Bruce M. Foxman, Choong Hyun Kim and Harry Mazurek

Prepared for Publication

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Waltham, Massachusetts 02254

December 1, 1979

Structure of Tris(2-cyanoethyl)phosphine Oxide

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Abstract. (O)$P(CH_2CH_2CN)_3$, rhombohedral, R3c, a = 13.501(4) Å, c = 10.177(3) Å (hexagonal setting), z = 6, ρ_o = 1.297 g/cc, ρ_c = 1.30 g/cc. The molecule has three-fold rotational symmetry along the P-O bond axis with a C-P-C angle of 106.43(12)°. The P=O distance is 1.485(3) Å.

Rho sub c

deg.

Rho sub o

Introduction. Square-planar transition metal complexes of the polyfunctional ligand, tris-(2-cyanoethyl)-phosphine, undergo a series of interesting solid-state reactions (Walton and Whyman, 1968; Foxman and Cheng, 1977). This ligand possesses a unique combination of low steric requirements and low basicity, pK_a = 1.37 (Streuli, 1960). In order to examine the effect of ligand basicity on the nature of the P=O bond, the oxide was synthesized and its structure determined.

The space group, R3c, was implied from preliminary Weissenberg (hk0 and hk1) and precession (h0ℓ and h1ℓ) photographs exhibiting systematic absences for 0kℓ ($\ell \neq 2n$), h0ℓ ($\ell \neq 2n$), and hkℓ ($-h+k+\ell \neq 3n$), and density measurements (flotation in xylene and carbon tetrachloride). Subsequent refinement confirmed this choice. Data were collected, on a Syntex $P2_1$ diffractometer using a crystal with dimensions 0.11 x 0.13 x 0.39 mm. Most operations were carried out as described previously (Foxman, 1978). Details of the structure analysis, in outline form, are presented in Table I. An empirical absorption correction was applied to all data. The analytical scattering factors of Cromer and Waber were used (International Tables for X-ray Crystallography, 1974(a)); real and imaginary components of anomalous scattering were included in the calculations for all nonhydrogen atoms (International Tables for

X-ray Crystallography, 1974(b)). From density considerations, it was necessary to place the P atom on the 6a site; (0,0,0) was chosen. The remaining nonhydrogen atoms were located from subsequent structure factor calculations and ΔF syntheses. At the conclusion of isotropic refinement, initial H atoms positions were calculated using the program HPOSN (Syntex, 1976). All nonhydrogen atoms were refined anisotropically (the H atoms, isotropically). At final convergence, R=0.033 and R_w = 0.042. Comparison with the similarly refined enantiomer (R = 0.042; R_w = 0.059) confirmed the initial choice (Hamilton, 1965). The atomic coordinates are listed in Table II.

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 comparable to those found in other phosphine oxides containing alkyl groups, e.g. 1.495(5) in $(O)P(CH_3)(C_6H_5)(C(CH_3)_2CH(OH)(CH_3))$ and 1.492(9) in $(O)P(CH_3)(C_6H_5)(CH(CH_3)(C(CH_3)=CH_2))$ (Allen, Kennard, Nassimbeni, Shepherd, and Warren, 1974). The remaining geometry is similar to that found for tris-(2-cyanoethyl)phosphine complexes (Bennett, Cotton, and Winquist, 1967; Foxman and Cheng, 1977; Foxman and Mazurek, 1979). There appears to be no correlation between ligand basicity and the P=O bond length.

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Table I. Data for the X-ray Diffraction Study of $(O)P(CH_2CH_2CN)_3$.

(A) *Measurement of Intensity Data*

Cell constant determination: 17 high angle values of (hkl) and refined $2\theta,\omega,\chi$ values in the range $82° < |2\theta| < 136°$ ($(CuK\alpha_1)$ = 1.5405 Å)

Radiation: CuKα, Ni β-filter

Reflections measured: ± (hkℓ) (to $2\theta = 158°$)

Scan type, speed: θ-2θ, variable, 1.95-3.91°/min

Scan range: Symmetrical, $[1.8 + \Delta(\alpha_2-\alpha_1)]°$

Background measurement: stationary, for one-quarter of scan time at each of the scan limits

No. of reflections measured: 655 total; 615 in unique set

Standard reflections: 024, 060

(B) *Treatment of Intensity Data*[a]

Data reduction: intensities as before[b]; esd's of |Fo| values calculated by method of finite differences[c]

Statistical information: $R_s = 0.009$ (I > 1.96 (I))

Table I. (cont'd)

(C) Refinement[d]

Weighting of reflections: $w = [\sigma^2(|Fo|) + (p|Fo|)^2]^{-1}$; $p = 0.035$

Isotropic refinement, all nonhydrogen atoms: $R = 0.069$; $R_w = 0.100$

Anisotropic refinement, all hydrogen atoms included: $R = 0.033$; $R_w = 0.042$

Standard deviation of an obsvn of unit weight (SDU): 1.0499

Final dffce Fourier map: Random peaks $\leq$ 0.16 e/Å

References:

(a) $R_s = \Sigma\sigma(|Fo|)/\Sigma|Fo|$.

(b) Foxman, 1978.

(c) Churchill, Lashewycz, and Rotella, 1977.

(d) $R = \Sigma(|Fo| - |Fc|)/\Sigma|Fo|$; $R_w = [\Sigma w(|Fo| - |Fc|)^2/\Sigma w|Fo|^2]^{\frac{1}{2}}$

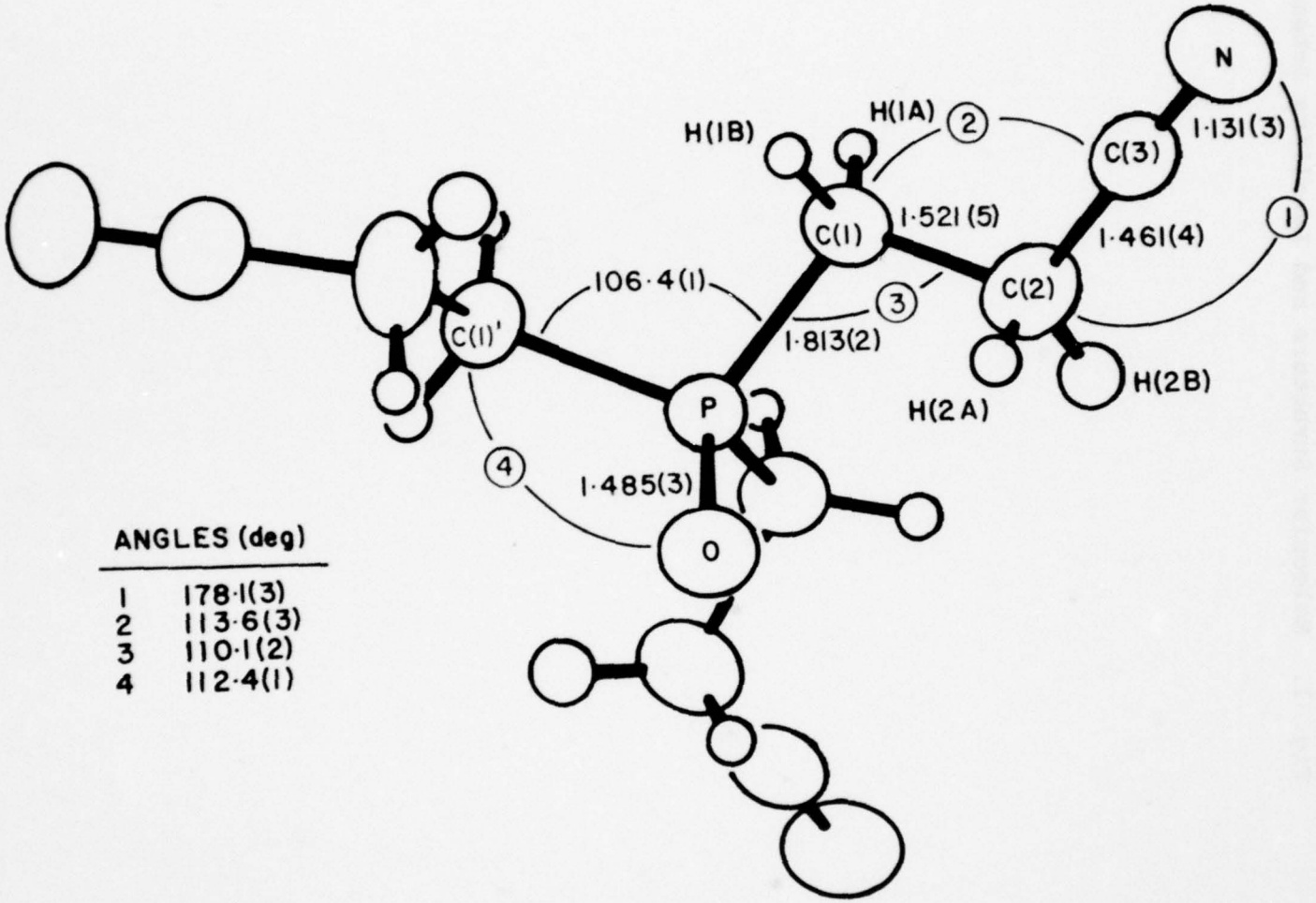
SDU = $[\Sigma w(|Fo| - |Fc|)^2/(m-n)]^{\frac{1}{2}}$ where m = 615 is the number of obsvns and n = 58 is the number of parameters

Table II. Atomic Coordinates for $(O)P(CH_2CH_2CN)_3$ [a]

Atom	x	y	z
P	0	0	0
O	0	0	-0.14596(32)
C1	0.03035(20)	0.13655(18)	0.06779(23)
C2	-0.04451(28)	0.17685(23)	0.00213(36)
C3	-0.00494(21)	0.29802(20)	0.02302(28)
N	0.02271(21)	0.39126(20)	0.03863(28)
H1A	0.1143(34)	0.1945(35)	0.0511(37)
H1B	0.0183(27)	0.1301(24)	0.1590(35)
H2A	-0.1239(57)	0.1250(56)	-0.0057(60)
H2B	-0.0176(36)	0.1823(36)	-0.0884(42)

[a] Standard deviations in the least significant digit appear in parentheses.

Fig. 1. Molecular Structure and Labelling Scheme.



ANGLES (deg)	
1	178·1(3)
2	113·6(3)
3	110·1(2)
4	112·4(1)

Supplemental Information

for

Referees and Deposition

A. Thermal Parameters

B. Structure Factor Tables

Temperature Parameters ($Å^2$) for $(O)P(CH_2CH_2CN)_3$ [a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	3.173(23)	U_{11}	2.582(32)	$U_{11}/2$	0	0
O	4.67(8)	U_{11}	2.71(10)	$U_{11}/2$	0	0
C1	3.73(8)	3.22(8)	3.08(8)	1.72(7)	-0.18(6)	-0.23(6)
C2	5.17(11)	3.55(10)	6.50(14)	2.20(9)	-1.83(12)	-0.38(9)
C3	4.49(9)	4.08(11)	3.55(9)	2.43(9)	-0.68(7)	-0.11(8)
N	6.80(13)	4.14(10)	5.32(11)	2.95(10)	-1.12(10)	-0.39(9)
H1A	6.7(9)					
H1B	4.8(6)					
H2A	13.3(22)					
H2B	7.2(10)					

[a] The form of the thermal ellipsoid is

$\exp[-2\pi^2(a^{*2}U_{11}h^2+\ldots+2b^*c^*U_{23}k\ell)]$.

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