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BRANDEIS UNIV WALTHAM MASS DEPT OF CHEMISTRY
STRUCTURE OF TRIS (2-CYANOETHYL) PHOSPHINE OXIDE.(U)
DEC 79 B M FOXMAN , C H KIM , H MAZUREK

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4. TITLE (and Subtitle) (6) Structure of Tris(2-cyanoethyl) phosphine Oxide.		5. TYPE OF REPORT & PERIOD COVERED (9) Interim / rept.
7. AUTHOR(s) (10) Bruce M. Foxman, Choong Hyun Kim and Harry Mazurek		8. CONTRACT OR GRANT NUMBER(s) (15) N00014-76-C-0822
9. PERFORMING ORGANIZATION NAME AND ADDRESS Brandeis University Department of Chemistry Waltham, Massachusetts 02254		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-619
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		12. REPORT DATE (11) 1 December 1979
14. MONITORING AGENCY NAME (If DD Form 101 is different from Controlling Office) LEVEL 1		13. NUMBER OF PAGES 16
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release; its distribution is unlimited (12) 16		15. SECURITY CLASS. (of this report) Unclassified
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Phosphine-oxides, polyfunctional ligands, solid-state reaction ligands.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) See page 3.		

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OFFICE OF NAVAL RESEARCH

Contract No. N00014-76-C-0822

Task No. NR 053-619

TECHNICAL REPORT No. 5

Structure of Tris(2-cyanoethyl) phosphine Oxide

by

Bruce M. Foxman, Choong Hyun Kim and Harry Mazurek

Prepared for Publication

in

Acta Crystallographica

Brandeis University

Department of Chemistry

Waltham, Massachusetts 02254

December 1, 1979

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Structure of Tris(2-cyanoethyl)phosphine Oxide

By Bruce M. Foxman, Choong Hyun Kim* and Harry Mazurek

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Waltham, Massachusetts 02154, U.S.A.

Abstract. $\rightarrow$ (O)P(CH₂CH₂CN)₃, rhombohedral, R3c, $a = 13.501(4)$ Å,
 $c = 10.177(3)$ Å (hexagonal setting), $z = 6$, $\rho_o = 1.297$ g/cm³,
 $\rho_c = 1.30$ g/cm³. 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. $\leftarrow$

Rho sub c

deg.

Rho sub o

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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 hkl) and precession ($h0l$ and $h1l$) photographs exhibiting systematic absences for $0kl$ ($l \neq 2n$), $h0l$ ($l \neq 2n$), and hkl ($-h+k+l \neq 3n$), and density measurements (floatation in xylene and carbon tetrachloride). Subsequent refinement confirmed this choice. Data were collected, on a Syntex P2₁ diffractometer using a crystal with dimensions $0.11 \times 0.13 \times 0.39$ 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 $0.969(23) \text{ \AA}$. The P=O bond length, $1.485(3) \text{ \AA}$, 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.

We wish to thank the Office of Naval Research for partial support of this work.

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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 $82^\circ < |2\theta| < 136^\circ$ ($(CuK\alpha_1) = 1.5405 \text{ \AA}$)

Radiation: $CuK\alpha$, Ni β -filter

Reflections measured: $\pm (hkl)$ (to $2\theta = 158^\circ$)

Scan type, speed: θ - 2θ , variable, 1.95 - $3.91^\circ/\text{min}$

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

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 $|F_o|$ values calculated by method of finite differences^c

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

Table I. (cont'd)

(C) Refinement^d

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

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 obsv of unit weight (SDU): 1.0499

Final diffce Fourier map: Random peaks ≤ 0.16 e/Å

References:

(a) $R_s = \Sigma(|F_o|)/\Sigma|F_o|$.

(b) Foxman, 1978.

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

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

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

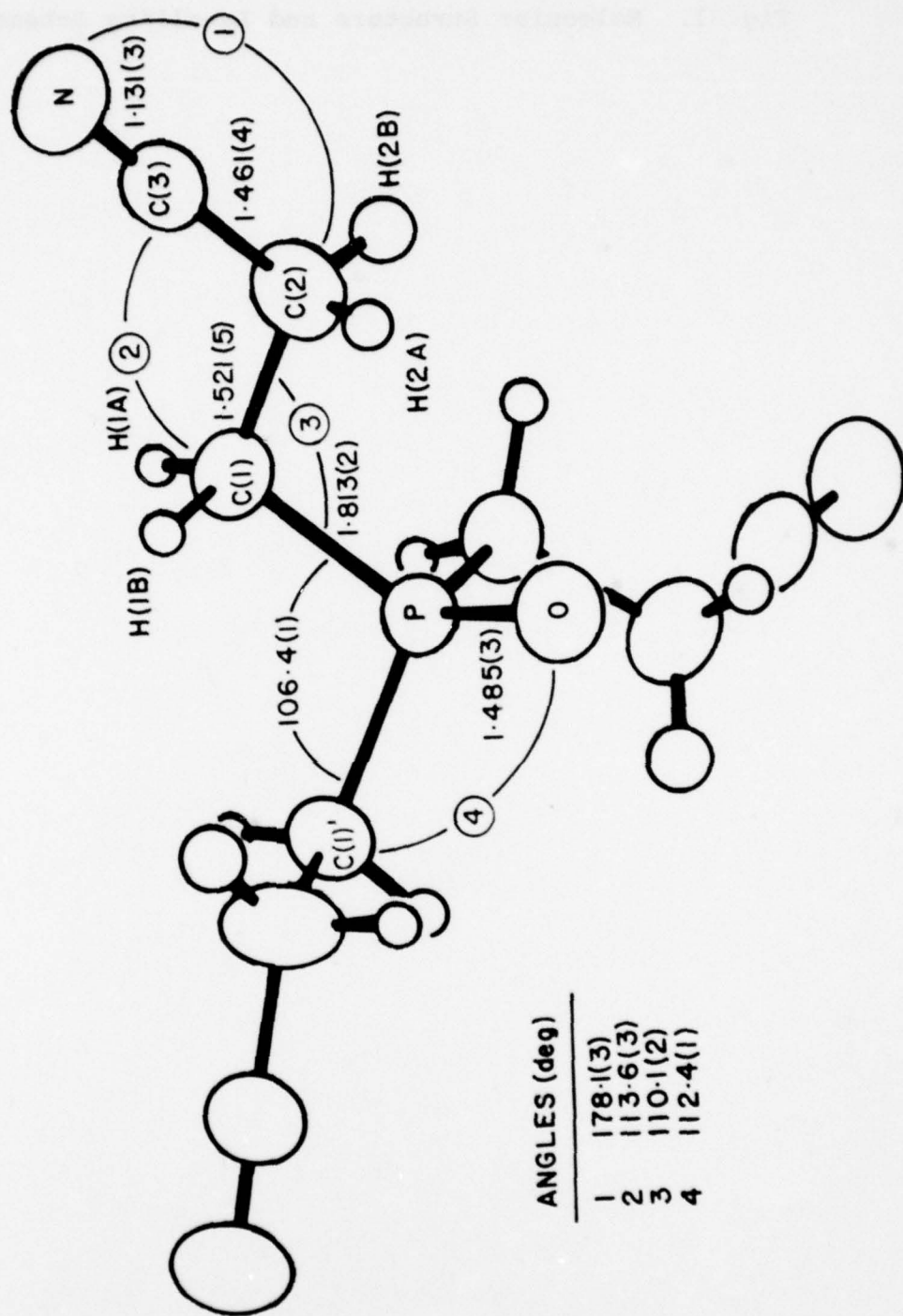
Table II. Atomic Coordinates for $(O)P(CH_2CH_2CN)_3$ ^a

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 ($\text{\AA}^2$) for $(\text{O})\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ ^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

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

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