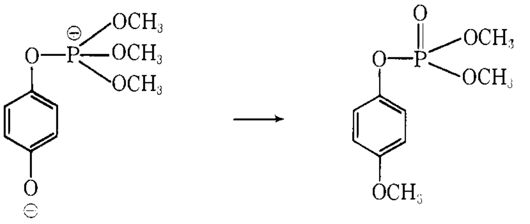
Crystal and Molecular Structures of Pentacoordinated Group V Compounds. I. 2,2,2-Triisopropoxy-4,5-(2′,2″-biphenyleno)-1,3,2-dioxaphospholene. Orthorhombic[1,2]

Walter C. Hamilton, Sam J. LaPlaca, Fausto Ramirez, and C. P. Smith

Contribution from the Departments of Chemistry, Brookhaven National Laboratory, Upton, New York 11973, and the State University of New York, Stony Brook, New York. *Received December 5, 1966*

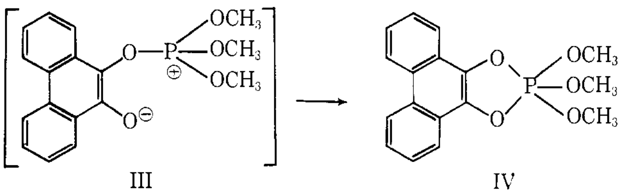
Abstract: The reaction of triisopropyl phosphite with phenanthrenequinone forms a 1:1 adduct, 2,2,2-triisopropoxy-4,5-(2′,2″-biphenyleno)-1,3,2-dioxaphospholene. This cyclic unsaturated pentaoxyphosphorane crystallizes in two allotropic forms. The preparation of these forms and the crystal structure of the orthorhombic form are described in this paper. The space group is Pbca with eight molecules in a cell of dimensions $a = 18.18 \pm 0.01$ A, $b = 25.03 \pm 0.01$ A, and $c = 10.14 \pm 0.01$ A. The phosphorus atom is at the center of a PO_5 trigonal bipyramid, with two isopropoxy groups in equatorial positions and one in an apical position. The phenanthrenequinone moiety forms a bridge between one apical and one equatorial position as it forms a C_2O_2P five-membered ring. The apical P–O bond length in the ring is 1.76 ± 0.02 A. The apical bond length to the isopropoxy group is 1.66 ± 0.02 A. The equatorial bond lengths have an average value of 1.61 A. The C–C bond length in the five-membered ring is considerably shorter than the corresponding bond in phenanthrene. More accurate values for the geometrical parameters were obtained for the monoclinic form, discussed in paper II of this series.

The reaction of trialkyl phosphites with *p*-quinones involves an attack by phosphorus on oxygen. The product seems to be a 1:1 dipolar adduct (I), which undergoes a very rapid alkyl group translocation to a stable alkyl ether of a *p*-quinol monophosphate (II).[3]



I II

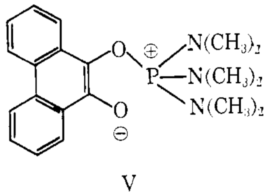
When this reaction was investigated in the series of *o*-quinones, a different and new type of structure was isolated.[4] The product, again, was a 1:1 adduct of the phosphite and the quinone, in which the phosphorus had attacked an oxygen atom of the latter. However, no alkyl group translocation was observed in this case. The product was formulated as a cyclic unsaturated pentaoxyphosphorane (IV), a derivative of the 1,3,2-dioxaphospholene ring system.



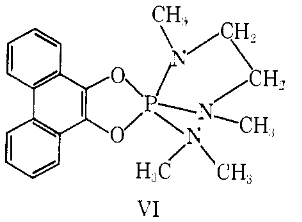
III IV

The oxyphosphorane structure IV was originally based on the relatively large positive shift of the P^{31} nmr signal of these adducts relative to H_3PO_4. For instance, the trimethyl phosphite adduct has $\delta P^{31} = +44.7$ ppm, and the triphenyl phosphite adduct has $\delta P^{31} = +58.7$ ppm. These positive P shifts, indicative of a rather effective shielding of the phosphorus nucleus by electrons, seem to favor the cyclic structure IV over the open-chain dipolar structure III. Moreover, the adducts are remarkably soluble in hexane and in benzene, a behavior not expected for dipolar structures like III. The infrared spectrum also favors the phospholene formulation IV.

More recently,[5] dipolar structures like V have been made from *o*-quinones and tris(dimethylamino)phosphine; they give negative P shifts; for example, $\delta P^{31} = -38.6$ ppm for V. On the other hand, the cyclic *spirotriaminodioxyphosphoranes* (VI), made from cyclic triaminophosphines, have positive shifts; $\delta P^{31} = +29.8$ ppm.



V



VI

The behavior of α-diketones, RCOCOR, toward tertiary phosphite esters was found to be analogous to the behavior of *o*-quinones. These results were reported by three independent groups of investigators.[4,6,7]

---

[1] Research supported by the U. S. Atomic Energy Commission, by Public Health Service Research Grant CA-04769-07 from the National Cancer Institute, and by the National Science Foundation, Grant GP-3341.

[2] A preliminary account of this work is given by W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *J. Am. Chem. Soc.*, **87**, 127 (1965).

[3] (a) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 856 (1957); (b) *ibid.*, **23**, 778 (1958); (c) *J. Am. Chem. Soc.*, **81**, 587 (1959); (d) F. Ramirez, E. H. Chen, and S. Dershowitz, *ibid.*, **81**, 4338 (1959).

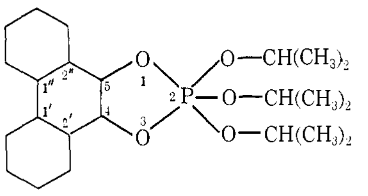
[4] (a) F. Ramirez and N. B. Desai, *ibid.*, **82**, 2652 (1960); (b) *ibid.*, **85**, 3252 (1963); (c) F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964).

[5] (a) F. Ramirez, A. V. Patwardhan, and C. P. Smith, *J. Am. Chem. Soc.*, **87**, 4973 (1965); (b) F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *Tetrahedron Letters*, **26**, 3053 (1966).

[6] (a) G. H. Birum and J. L. Dever, U. S. Patents 2,961,455 (1960) and 3,014,949 (1961); (b) Abstracts, Division of Organic Chemistry, 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1958, p 101-P.

[7] (a) V. A. Kukhtin, *Dokl. Akad. Nauk SSSR*, **121**, 466 (1958); *Chem. Abstr.*, **53**, 1105*b* (1959); (b) V. A. Kukhtin and K. M. Orekhova, *J. Gen. Chem. USSR*, **30**, 1229 (1960); (c) V. A. Kukhtin and K. M. Kirillova, *ibid.*, **32**, 2755 (1962).

This paper describes the initial investigation of the crystal and molecular structure of the adduct made from phenanthrenequinone and triisopropyl phosphite, 2,2,2-triisopropoxy-4,5-(2′,2′′-biphenyleno)-1,3,2-dioxaphospholene (VII). This adduct was obtained in two crystalline forms, monoclinic and orthorhombic. We discuss here the crystal structure of the orthorhombic form; the preliminary results have already been reported.[2] The following paper[8] describes the structure of the monoclinic form and compares the two.



VII

The reaction of the quinone with the phosphite was carried out in the absence of solvent. The reaction was exothermic and the heat of the reaction raised the temperature of the mixture to 120°. The melt crystallized in the monoclinic form. Recrystallization from hexane gave the monoclinic form if the crystallization was carried out very slowly and without disturbances. If the hexane solution was cooled rapidly and crystallization was induced by scratching, the orthorhombic form resulted. Both forms had the same P^{31} and H^1 nmr spectra and the same infrared spectra in solutions. The crystal data for $C_{23}H_{29}O_5P$, mol wt 416.45, showed for the orthorhombic form probable space group Pbca: $a = 18.18 \pm 0.01$ A, $b = 25.03 \pm 0.01$ A, $c = 10.14 \pm 0.01$ A, $Z = 8$, $\rho_{\text{X-ray}} = 1.20$ g cm^{-3}. The monoclinic form showed probable space group $P2_1/c$: $a = 25.997 \pm 0.001$ A, $b = 8.894 \pm 0.001$ A, $c = 9.880 \pm 0.001$ A, $\beta = 94.25 \pm 0.01°$, $Z = 4$, $\rho_{\text{X-ray}} = 1.213$ g cm^{-3}.

Experimental Section

Preparation of the Phenanthrenequinone–Triisopropyl Phosphite 1:1 Adduct, 2,2,2-Triisopropoxy-4,5-(2′,2′′-biphenyleno)-1,3,2-dioxaphospholene. The quinone was recrystallized from benzene, and the phosphite ester was kept over sodium wire, decanted from it, and distilled with protection against moisture.

Triisopropyl phosphite (6.5 ml, 25.5 mmoles) was added to phenanthrenequinone (5.3 g, 25 mmoles) at 20°. The temperature of the mixture began to rise within 2 min; when it reached 37°, the reaction became strongly exothermic and the temperature rose to 122° in 1 min. The resulting reddish brown thick oil became solid at 20°; this material proved to be the *monoclinic form* of the 1:1 adduct. The crystals were dissolved in 20 ml of boiling hexane. (Although the 1:1 adduct is pale yellow, this solution was red and contained traces of undissolved phenanthrenequinone; these traces of quinone can be removed by filtration, but they do not affect subsequent steps in the purification of the adduct. The red color seems to be due to a very deeply colored complex between the 1:1 adduct as donor and the quinone as acceptor.)

The hexane solution was allowed to cool to 20°, very slowly (12 hr) and without any disturbances. The first crop of reddish crystals (6.3 g, 60% of the theory) proved to be the *monoclinic form* of the adduct. The same monoclinic form is obtained by recrystallization of the monoclinic crystals, using 2 ml of hexane/g of adduct, provided that the solution is allowed to cool to 20° very slowly as indicated above. However, if cooling is rapid and if the crystallization process is disturbed, the crystals that result have the *orthorhombic form.* It has not been possible to obtain the monoclinic crystals by recrystallization of the orthorhombic crystals from hexane by slow cooling.[9]

The *monoclinic form* of the 1:1 adduct had a softening point of 97–98°, but it melted completely at 107–108° (in an open capillary tube). The *orthorhombic form*, made by dissolving monoclinic crystals in hexane and cooling rapidly while scratching the sides of the flask with a glass rod, had a sharp melting point of 107–108°. The P^{31} and the H^1 nmr spectra of both forms were indistinguishable in $CDCl_3$ solution. The infrared spectra of both forms in CCl_4 solution were also identical.

The infrared spectrum was taken in a Perkin-Elmer Model 21 spectrometer and had the following bands (in cm^{-1}; w, weak; m, medium; s, strong; with respect to the C–H stretching at 2960 cm^{-1} regarded as medium): 1650 (m), 1600 (w), 1505 (w), 1455 (m), 1380 (s), 1330 (w), 1170 (m), 1135 (w), 1105 (ms), 1060 (mw); *1015* (*vs*), 980 (m), 890 (w), 875 (w), and 865 (w).

The H^1 nmr spectrum, in CCl_4 solution, was taken at 60 Mcps. The spectrum examined at a 500-cps sweep width showed an 8 H^1 multiplet centered at τ 2.2 (aromatic H^1) (τ = shift in ppm from tetramethylsilane taken as 10); the methine H^1 gave a 3 H^1 multiplet at τ 5.40 (*vide infra*); the methyl H^1 gave an 18 H^1 doublet, $J_{\text{HCCH}} = 6.1$ cps, centered at τ 8.75. When the spectrum was examined at a 50-cps sweep width, the methine H^1 gave a doublet, $J_{\text{HCOP}} = 8.2$ cps, of septets, $J_{\text{HCCH}} = 6.2$ cps; the methyl H^1 gave a doublet, $J_{\text{HCCH}} = 6.2$ cps, of doublets, $J_{\text{HCCOP}} = 0.7$ cps. Examination of the methine region at 100 Mcps gave the couplings, $J_{\text{HCOP}} = 8.4$ and $J_{\text{HCCH}} = 6.4$ cps; there was no indication of further fine structure and no indication of nonequivalence of the three isopropoxy groups at 30°.

The P^{31} nmr data are summarized in Table I.

Table I

Crystalline form	Solvent	δP^{31}, ppm *vs.* H_3PO_4
Monoclinic	Benzene	+49.2
Monoclinic	$CDCl_3$	+48.6
Monoclinic	Dimethylformamide	+49.0
Monoclinic	Benzene–methanol (1:1)	+49.2
Monoclinic	Chloroform–methanol (1:9)	+49.0
Orthorhombic	$CDCl_3$	+48.6

The adduct, in both crystalline forms, is sparingly soluble in methanol, but quite soluble in hexane, benzene, methylene chloride, carbon tetrachloride, and chloroform.

Anal. Calcd for $C_{23}H_{29}O_5P$: C, 66.4; H, 6.9; P, 7.4. Found: C, 66.0; H, 6.8; P, 7.3.

When the hexane filtrate (from which about 60% of the monoclinic form had been removed by the slow crystallization described above) was concentrated under vacuum until crystals appeared, an additional 20% of adduct resulted; this crop proved to be the orthorhombic form by X-ray examination.

Crystal Structure Determination

A sealed vial containing orthorhombic crystals was opened in a dry nitrogen atmosphere, and single crystals suitable for X-ray photography were sealed in glass capillaries with a wall thickness of 0.01 mm. The needle-like crystals were approximately 0.2 mm in diameter and 0.4 mm long. The *c* axis of the crystal was in each case parallel to the capillary axis. The unit cell and space group were determined from precession and Weissenberg photographs. The systematic absences, *h*0*l* for *l* odd, 0*kl* for *k* odd, and *hk*0 for *h* odd, are consistent with the assigned space group.

Intensities of 754 reflections were visually estimated from integrated Weissenberg photographs of the *hk*0, *hk*1, *hk*2, *hk*3, *hk*4, *hk*6, and *hk*7 reciprocal lattice layers.

---

[8] R. D. Spratley, W. C. Hamilton, and J. Ladell, *J. Am. Chem. Soc.*, **89**, 2272 (1967).

[9] This curious behavior is undoubtedly due to the presence of seeds of the orthorhombic form being present. Clearly, there can be no difference between solutions prepared from the two crystalline forms.

Table II. Final Positional Parameters and Rm.s Displacements[a]

Atom	x	y	z	$\langle \delta r^2 \rangle^{1/2}$, A
P	0.1365(3)	0.1545(2)	0.1462(4)	0.43(4)
O_2	0.2135(5)	0.1491(4)	0.0671(8)	0.44
O_1	0.1005(5)	0.1026(4)	0.0485(8)	0.45
O_4	0.0731(5)	0.1945(4)	0.0958(8)	0.45
C_{41}	0.0096(7)	0.1865(6)	0.0137(15)	0.45
C_{42}	−0.0062(11)	0.2448(8)	−0.0441(19)	0.65
C_{43}	−0.0528(9)	0.1639(7)	0.0915(17)	0.58
O_5	0.1189(6)	0.1161(4)	0.2662(8)	0.47
C_{51}	0.1362(9)	0.1257(6)	0.4069(14)	0.46
C_{52}	0.0778(11)	0.0926(7)	0.4808(13)	0.57
C_{53}	0.2148(10)	0.1049(7)	0.4256(16)	0.54
O_3	0.1755(6)	0.2019(4)	0.2322(8)	0.48
C_{31}	0.2085(12)	0.2513(6)	0.1800(15)	0.56
C_{32}	0.2912(11)	0.2510(10)	0.2124(23)	0.71
C_{33}	0.1595(11)	0.2963(6)	0.2415(15)	0.56
C_1	0.1487(9)	0.0837(6)	−0.0367(13)	0.44
C_2	0.2112(11)	0.1054(6)	−0.0310(14)	0.46
C_3	0.2774(9)	0.0982(7)	−0.1109(15)	0.47
C_4	0.3454(9)	0.1270(6)	−0.1029(13)	0.45
C_5	0.4009(11)	0.1156(9)	−0.1889(21)	0.64
C_6	0.3973(15)	0.0763(11)	−0.2801(25)	0.76
C_7	0.3323(15)	0.0456(9)	−0.2954(17)	0.69
C_8	0.2684(12)	0.0557(7)	−0.2088(17)	0.56
C_9	0.2005(11)	0.0299(6)	−0.2150(12)	0.53
C_{10}	0.1823(11)	−0.0159(8)	−0.3069(15)	0.56
C_{11}	0.1096(11)	−0.0354(7)	−0.3063(18)	0.57
C_{12}	0.0511(11)	−0.0244(7)	−0.2255(15)	0.58
C_{13}	0.0685(10)	0.0180(6)	−0.1332(14)	0.52
C_{14}	0.1390(11)	0.0402(6)	−0.1340(13)	0.47

[a] Standard deviations for x, y, and z are those obtained from the least-squares analysis as described in the text and are indicated in parentheses in terms of the least significant figure in the parameter value. The atoms are identified in Figure 1.

Table III. Observed (FO) and Calculated (FC) Structure Factors in Electrons for Orthorhombic Crystals (all values have been multiplied by 10)

H	K	L	FO	FC
0	0	0		15456
0	0	2	1411	1456
0	0	4	505	534
0	0	6	542	518
0	0	8	174	181
0	2	0	542	457
0	2	1	1041	918
0	2	2	1048	981
0	2	3	1412	1229
0	2	5	519	466
0	2	6	262	284
0	2	7	99	91
0	4	0	1560	1651
0	4	1	2498	2401
0	4	2	3989	2452
0	4	3	827	810
0	4	4	419	455
0	4	5	341	716
0	4	6	155	124
0	4	7	175	195
0	6	0	788	118
0	6	1	1181	1047
0	6	2	768	623
0	6	3	108	105
0	6	4	1116	1181
0	6	5	128	144
0	6	6	161	59
0	8	0	1118	898
0	8	1	165	667
0	8	2	155	280
0	8	3	419	382
0	8	4	119	241
0	8	5	497	446
0	8	7	217	194
0	10	0	105	320
0	10	1	99	89
0	10	2	576	611
0	10	3	759	745
0	10	4	959	947
0	10	5	509	506
0	10	6	591	891
0	12	0	145	772
0	12	1	227	211
0	12	2	1015	949
0	12	3	461	464
0	12	4	405	428
0	12	5	761	110
0	12	6	561	596
0	14	0	1025	1007
0	14	1	156	193
0	14	2	128	91
0	14	4	100	102
0	14	5	445	404
0	16	0	412	196
0	16	1	254	189
0	16	4	279	240
0	16	5	85	91
0	18	0	400	194
0	18	1	270	220
0	18	3	342	347
1	0	2	60	67
1	0	4	1013	994
1	1	1	1127	1107
1	1	2	1257	1104
1	1	3	284	244
1	1	4	51	79
1	1	5	227	202
1	1	6	281	281
1	1	7	231	165
1	2	1	2059	2100
1	2	2	1549	1498
1	2	3	589	559
1	2	4	201	212
1	2	5	116	89
1	2	6	98	77
1	2	7	174	195
1	3	1	1062	972
1	3	2	435	795
1	3	3	265	258
1	3	4	277	273
1	3	5	151	142
1	3	6	115	102
1	3	7	118	189
1	4	2	678	930
1	4	3	119	87
1	4	4	162	171
1	4	5	251	216
1	4	6	185	188
1	5	1	1465	1221
1	5	2	1975	1808
1	5	3	562	561
1	5	4	77	48
1	5	5	215	198
1	5	6	171	154
1	6	1	189	212
1	6	2	1091	1004
1	6	3	565	510
1	6	4	301	156
1	6	5	91	229
1	6	6	85	86
1	6	7	279	299
1	7	3	285	387
1	7	4	421	454
1	7	7	165	434
1	8	1	460	188
1	8	2	208	221
1	8	3	856	694
1	8	4	260	280
1	8	6	98	92
1	8	7	179	155
1	9	1	577	547
1	9	2	524	451
1	9	3	604	612
1	9	4	165	114
1	9	7	114	161
1	10	1	122	115
1	10	2	816	857
1	10	3	164	306
1	10	5	219	145
1	11	1	409	416
1	11	2	156	117
1	11	3	215	171
1	11	4	401	405
1	11	5	121	121
1	11	6	141	174
1	12	2	611	592
1	12	4	288	251
1	12	5	176	117
1	12	6	195	180
1	13	1	416	419
1	14	1	165	744
1	14	2	424	401
1	14	3	210	212
1	15	1	195	219
1	16	1	168	111
1	16	2	271	204
1	17	1	227	209
1	17	3	112	109
1	18	1	181	405
1	18	2	169	176
1	18	3	240	206
1	19	2	214	165
0	20	0	685	710
2	0	0	2005	1900
2	0	2	1714	1461
2	0	4	68	88
2	0	6	181	167
2	0	6	146	107
2	1	0	3145	2945
2	1	1	817	881
2	1	2	202	179
2	1	3	186	188
2	1	4	159	111
2	1	5	414	114
2	1	6	211	191
2	1	7	110	141
2	2	0	449	441
2	2	1	591	559
2	2	2	1151	1024
2	2	3	111	190
2	2	4	70	89
2	2	5	128	167
2	2	6	44	67
2	2	7	81	64
2	3	0	461	509
2	3	1	1151	1022
2	3	2	2111	1964
2	3	3	768	714
2	3	4	162	120
2	3	5	119	340
2	3	7	117	192
2	4	0	426	467
2	4	1	821	889
2	4	1	781	689
2	4	2	1747	1592
2	4	3	490	502
2	4	4	464	501
2	4	5	119	122
2	4	6	291	272
2	4	7	168	172
2	5	0	1512	1496
2	5	1	1846	1866
2	5	2	1076	918
2	5	3	120	255
2	5	5	271	391
2	5	6	100	115
2	6	0	895	864
2	6	1	816	817
2	6	2	199	158
2	6	3	244	211
2	6	4	105	121
2	7	0	401	164
2	7	1	162	102
2	7	2	510	406
2	7	3	594	621
2	7	4	1008	1027
2	7	5	392	747
2	7	6	94	106
2	8	0	666	569
2	8	1	214	216
2	8	2	568	574
2	8	3	952	869
2	8	4	282	106
2	8	1	158	111
2	9	0	711	594
2	9	1	191	195
2	9	2	256	246
2	9	3	166	195
2	9	4	872	860
2	9	5	642	601
2	9	6	164	119
2	9	7	191	162
2	10	0	429	417
2	10	2	166	118
2	10	3	516	526
2	10	5	200	155
2	10	5	119	119
2	11	0	649	618
2	11	2	152	116
2	11	4	776	819
2	11	6	644	703
2	12	0	249	241
2	12	1	241	198
2	12	3	492	501
2	12	4	218	284
2	12	5	125	272
2	12	6	215	161
2	13	0	94	170
2	13	2	549	544
2	13	5	721	710
2	13	6	224	205
2	14	0	141	118
2	14	1	154	196
2	14	2	215	205
2	14	3	219	191
2	15	0	270	272
2	15	4	256	280
2	16	0	140	210
2	16	1	240	281
2	16	3	295	108
2	17	0	196	254
2	17	1	177	111
2	17	3	256	260
2	18	2	170	350
2	19	0	444	457
2	19	1	111	186
3	0	2	111	131
3	0	4	241	254
3	0	6	144	95
3	1	2	657	617
3	1	3	101	102
3	1	4	242	214
3	1	5	221	231
3	1	6	159	172
3	1	7	211	211
3	2	1	492	474
3	2	4	256	244
3	2	5	318	125
3	2	6	481	541
3	2	7	121	145
3	3	1	281	311
3	3	2	665	585
3	3	3	519	501
3	3	4	194	206
3	3	5	192	214
3	3	6	558	579
3	3	7	299	267
3	4	1	170	194
3	4	2	655	569
3	4	3	150	391
3	4	5	194	218
3	4	6	217	268
3	4	7	129	135
3	5	1	450	440
3	5	2	1090	1102
3	5	3	781	769
3	5	4	561	561
3	5	5	416	114
3	5	7	118	185
3	6	1	572	550
3	6	2	518	186
3	6	3	181	117
3	6	4	621	600
3	6	5	527	484
3	6	6	197	208
3	7	2	571	497
3	7	3	125	151
3	7	4	267	341
3	7	7	170	357
3	8	2	882	854
3	8	3	561	569
3	8	4	518	555
3	8	7	642	711
3	9	1	496	567
3	9	2	288	288
3	9	3	911	859
3	9	4	624	645
3	9	5	262	258
3	9	6	191	201
3	9	7	99	110
3	10	2	512	506
3	10	3	111	181
3	10	4	1008	999
3	10	7	104	164
3	11	1	144	96
3	11	2	158	726
3	11	3	378	161
3	11	4	260	215
3	12	1	466	455
3	12	3	147	66
3	12	5	271	264
3	12	6	121	112
3	13	1	490	519
3	13	3	219	181
3	13	5	118	112
3	13	6	108	294
3	14	1	129	126
3	14	3	247	214
3	14	4	522	547
3	14	5	177	110
3	14	6	215	222
3	15	1	210	261
3	15	2	190	159
3	15	3	98	10
3	16	2	252	247
3	16	3	101	51
3	16	4	219	220
3	17	1	411	452
3	17	3	211	204
3	18	1	154	176
3	19	1	291	151
4	0	0	2082	2171
4	0	2	1119	1258
4	0	4	188	184
4	1	0	1091	1055
4	1	1	514	500
4	1	2	561	560
4	1	3	147	241
4	1	4	139	117
4	1	5	121	112
4	1	7	154	194
4	2	0	1024	1026
4	2	1	711	811
4	2	2	521	504
4	2	4	229	216
4	2	5	246	214
4	2	6	161	151
4	3	0	16	12
4	3	1	206	213
4	3	2	254	100
4	3	3	277	270
4	3	4	159	111
4	3	5	122	66
4	3	6	65	40
4	4	0	1665	1111
4	4	1	278	264
4	4	2	429	191
4	4	3	211	189
4	4	4	186	141
4	4	5	557	578
4	4	7	161	111
4	5	0	651	614
4	5	1	165	141
4	5	2	181	220
4	5	3	412	795
4	5	4	270	119
4	5	5	444	415
4	5	7	120	101
4	6	0	412	415
4	6	1	191	141
4	6	2	465	506
4	6	4	791	874
4	6	6	316	112
4	6	7	121	101
4	7	0	265	276
4	7	1	144	151
4	7	2	457	191
4	7	3	1060	1065
4	7	4	111	131
4	7	5	120	123
4	7	6	244	260
4	7	7	94	6
4	8	0	261	168
4	8	1	124	129
4	8	2	146	111
4	8	3	194	405
4	8	5	671	651
4	8	7	220	169
4	9	0	487	488
4	9	1	186	405
4	9	2	551	575
4	9	4	151	147
4	9	5	269	262
4	9	7	110	151
4	10	0	117	371
4	10	1	202	249
4	10	2	151	111
4	10	3	250	216
4	10	4	741	891
4	10	5	575	514
4	10	6	507	469
4	11	0	416	185
4	11	1	252	287
4	11	2	674	605
4	11	3	254	394
4	11	4	114	182
4	11	5	285	255
4	11	6	116	151
4	12	0	600	444
4	12	2	152	281
4	12	3	127	84
4	12	5	567	517
4	12	6	342	721
4	13	0	146	141
4	13	1	139	114
4	13	3	425	411
4	14	0	290	299
4	14	1	168	108
4	14	3	270	246
4	14	5	516	462
4	15	0	271	295
4	15	1	112	147
4	15	5	215	214
4	16	0	452	409
4	17	0	215	204
4	17	4	250	384
4	18	1	188	196
4	19	0	251	217
4	19	2	251	341
5	0	2	716	657
5	0	4	1019	1161
5	1	1	57	100
5	1	2	261	267
5	1	3	104	795
5	1	4	279	253
5	1	5	612	601
5	1	6	128	121
5	1	7	214	219
5	2	1	546	504
5	2	2	709	117
5	2	3	282	269
5	2	4	165	171
5	2	6	215	221
5	2	7	476	462
5	3	1	256	102
5	3	2	152	104
5	3	3	311	131
5	3	5	244	242
5	3	6	114	711
5	4	1	229	222
5	4	2	98	63
5	4	3	669	704
5	4	4	101	85
5	4	5	154	112
5	4	6	135	778
5	4	7	125	112
5	5	1	781	145
5	5	2	231	744
5	5	3	251	219
5	5	4	474	511
5	5	6	129	111
5	5	7	159	273
5	6	1	260	226
5	6	2	556	544
5	6	3	161	114
5	6	4	155	405
5	6	5	121	80
5	6	6	181	117
5	6	7	211	171
5	7	1	211	204
5	7	3	128	84
5	7	4	470	416
5	7	5	290	295
5	7	6	164	154
5	7	7	157	151
5	8	1	241	214
5	8	3	740	828
5	8	4	212	194
5	8	5	204	194
5	8	6	242	327
5	8	7	140	129
5	9	1	225	252
5	9	2	270	270
5	9	3	100	252
5	9	4	441	505
5	9	5	251	311
5	9	6	119	118
5	9	7	154	177
5	10	1	176	174
5	10	2	120	134
5	10	3	154	166
5	10	4	286	119
5	10	5	151	120
5	10	6	87	41
5	11	1	329	117
5	11	2	245	170
5	11	3	211	292
5	11	4	210	240
5	11	5	119	216
5	11	6	415	799
5	12	1	162	143
5	12	2	519	577
5	12	3	197	181
5	12	4	98	171
5	12	5	121	297
5	12	6	555	551
5	13	2	168	169
5	13	3	411	417
5	13	4	177	142
5	13	5	506	521
5	13	6	148	390
5	14	1	421	484
5	14	2	151	144
5	14	3	217	208
5	14	4	118	310
5	14	5	184	191
5	15	4	347	111
5	15	5	229	184
5	18	2	550	581
5	18	1	270	245
5	18	1	271	101
5	19	1	160	152
6	0	0	141	156
6	0	2	412	401
6	0	4	251	245
6	0	6	122	155
6	1	0	525	492
6	1	1	750	768
6	1	2	514	497
6	1	3	442	461
6	1	4	177	746
6	1	5	121	11
6	2	0	856	810
6	2	2	176	216
6	2	3	640	670
6	2	4	407	418
6	2	5	551	540
6	3	0	110	168
6	3	1	194	418
6	3	2	144	117
6	3	3	102	278
6	3	4	296	256
6	3	5	614	582
6	4	0	718	656
6	4	1	151	198
6	4	4	591	641
6	4	5	182	159
6	4	7	214	240
6	5	0	129	715
6	5	1	244	364
6	5	2	567	555
6	5	3	254	261
6	5	4	196	442
6	5	5	149	122
6	5	6	271	291
6	6	0	570	554
6	6	1	159	171
6	6	2	282	298
6	6	3	171	110
6	6	4	201	213
6	6	5	102	114
6	6	6	158	144
6	7	0	112	114
6	7	1	909	915
6	7	2	110	65
6	7	3	127	102
6	7	4	164	416
6	7	5	166	195
6	7	6	176	791
6	8	0	141	121
6	8	2	191	158
6	8	3	416	482
6	8	4	471	524
6	8	5	262	260
6	9	0	295	112
6	9	1	221	144
6	9	2	117	110
6	9	3	220	215
6	9	5	466	500
6	10	0	446	494
6	10	1	111	95
6	10	2	471	512
6	10	3	172	111
6	10	4	565	565
6	11	0	292	101
6	11	2	69	87
6	11	4	119	745
6	11	6	177	771
6	12	0	141	155
6	12	1	157	147
6	12	2	251	241
6	12	6	215	201
6	13	1	210	201
6	13	5	621	628
6	14	0	129	118
6	14	1	219	141
6	14	3	201	179
6	14	5	410	347
6	15	0	228	240
6	15	1	102	159
6	16	1	105	101
6	16	2	264	294
6	17	0	145	743
6	18	0	127	211
7	0	2	199	196
7	0	4	576	576
7	0	6	184	194
7	1	1	117	75
7	1	2	120	296
7	1	3	731	164
7	1	4	421	502
7	1	6	218	191
7	1	7	158	185
7	2	1	262	104
7	2	3	148	279
7	2	5	117	171
7	2	6	191	201
7	3	1	278	248
7	3	3	427	421
7	3	4	111	105
7	3	5	401	416
7	3	7	512	542
7	4	1	119	65
7	4	2	294	282
7	4	4	208	184
7	4	5	229	256
7	4	7	177	214
7	5	1	299	714
7	5	2	199	411
7	5	3	281	282
7	5	4	177	447
7	5	5	161	159
7	5	6	246	245
7	6	1	107	14
7	6	2	204	211
7	6	3	194	173
7	6	4	165	316
7	6	6	169	712
7	7	1	479	509
7	7	2	111	46
7	7	3	190	419
7	7	4	261	275
7	8	1	257	114
7	8	4	108	70
7	8	5	200	110
7	9	1	289	241
7	9	2	297	118
7	9	3	166	791
7	9	4	213	191
7	9	6	274	380
7	10	1	203	199
7	10	4	278	297
7	10	5	161	114
7	11	1	171	241
7	11	2	157	185
7	11	3	315	184
7	11	4	249	249
7	11	6	197	767
7	12	2	89	117
7	12	3	168	150
7	12	5	186	116
7	13	1	152	115
7	13	3	362	794
7	15	1	256	275
7	15	2	429	197
7	15	4	141	144
7	16	1	187	192
7	18	1	191	181
8	1	2	769	816
8	0	0	161	164
8	0	2	249	211
8	0	4	114	222
8	0	6	299	240
8	1	1	121	144
8	1	3	296	705
8	1	5	444	411
8	1	6	231	215
8	2	0	91	14
8	2	1	241	216
8	2	2	190	182
8	2	5	102	297
8	2	6	217	255
8	3	0	296	125
8	3	2	275	276
8	3	3	161	198
8	3	4	412	452
8	3	5	197	189
8	3	6	207	220
8	4	0	1019	1031
8	4	2	701	749
8	4	5	113	111
8	5	0	115	704
8	5	1	101	101
8	5	2	230	251
8	5	4	126	91
8	5	5	255	309
8	5	6	115	152
8	6	0	150	711
8	6	1	615	617
8	6	2	112	168
8	6	4	225	224
8	6	6	178	416
8	7	0	151	160
8	7	1	291	751
8	7	2	148	794
8	7	3	206	255
8	7	4	189	187
8	7	5	256	267
8	7	6	157	149
8	8	0	116	156
8	8	1	185	190
8	8	5	356	109
8	8	6	108	159
8	9	0	118	118
8	9	1	176	221
8	9	2	115	108
8	[illegible]	[illegible]	174	119
8	9	6	134	144
8	10	0	571	517
8	10	1	297	211
8	10	2	141	141
8	10	4	272	292
8	11	0	118	115
8	11	1	210	253
8	11	2	151	162
8	11	3	259	275
8	11	4	149	19
8	12	5	306	290
8	13	0	278	244
8	14	1	256	217
8	15	0	241	201
9	0	2	148	120
9	0	4	195	422
9	0	6	291	298
9	1	1	184	404
9	2	1	112	124
9	2	3	140	152
9	3	1	139	124
9	3	2	245	275
9	3	3	162	174
9	3	4	114	107
9	3	6	89	79
9	4	1	125	61
9	4	2	197	211
9	4	3	147	126
9	4	4	482	494
9	4	5	189	174
9	4	6	151	124
9	5	5	190	94
9	6	2	111	127
9	6	3	220	229
9	6	4	139	267
9	6	6	112	104
9	7	1	241	200
9	7	2	68	49
9	8	1	220	242
9	8	3	451	114
9	10	1	277	274
9	10	2	291	245
9	11	1	172	127
9	11	5	217	268
9	12	1	271	240
9	12	2	149	162
9	12	3	118	400
9	13	1	261	217
9	14	1	265	210
9	14	2	212	101
9	14	3	190	184
9	15	2	251	179
9	16	2	162	149
10	0	0	181	224
10	0	2	161	102
10	0	4	655	674
10	1	0	171	267
10	1	1	165	199
10	1	2	281	242
10	1	4	219	186
10	1	6	229	199
10	2	0	98	67
10	2	1	124	105
10	2	3	166	215
10	2	5	525	489
10	3	0	494	579
10	3	1	129	164
10	3	2	15	102
10	3	3	188	245
10	3	5	158	109
10	3	6	250	271
10	4	0	166	208
10	4	1	114	164
10	4	2	141	144
10	4	3	284	258
10	4	4	148	781
10	4	5	192	212
10	4	6	115	162
10	5	0	655	797
10	5	1	261	704
10	5	5	158	151
10	6	0	510	548
10	6	1	160	140
10	6	4	254	252
10	6	5	286	219
10	7	1	154	414
10	7	2	152	114
10	7	3	195	255
10	8	0	288	308
10	8	1	229	221
10	9	0	816	705
10	10	0	454	425
10	11	0	116	110
10	11	4	101	215
10	11	1	378	197
10	11	3	221	198
10	14	0	575	417
10	14	1	295	701
11	0	2	251	250
11	1	1	94	58
11	1	2	197	279
11	1	3	167	211
11	1	5	261	91
11	2	1	155	113
11	2	3	211	231
11	3	1	151	178
11	3	4	248	274
11	4	4	116	119
11	5	2	198	772
11	5	3	192	202
11	5	5	241	349
11	7	1	200	714
11	7	2	101	249
11	7	3	292	712
11	8	1	151	121
11	8	2	312	241
11	9	2	311	117
11	9	3	100	212
11	10	1	382	123
11	10	2	259	294
11	11	2	441	485
11	12	1	156	17
11	12	3	111	25
11	14	1	161	198
12	0	0	431	142
12	0	4	269	217
12	1	0	791	170
12	1	4	291	251
12	1	5	261	787
12	2	1	146	117
12	3	0	195	116
12	3	1	246	172
12	3	3	185	391
12	3	5	152	216
12	4	0	468	169
12	4	1	140	122
12	5	0	256	75
12	5	2	202	146
12	5	4	195	114
12	6	0	164	84
12	6	1	144	156
12	6	2	204	80
12	6	3	181	210
12	7	0	161	117
12	7	1	215	197
12	7	3	152	144
12	7	4	304	729
12	8	0	448	400
12	8	1	262	380
12	8	3	188	272
12	9	0	272	221
12	9	1	151	124
12	10	0	511	491
12	11	0	218	701
12	12	0	221	397
12	12	1	191	151
13	0	4	281	264
13	2	2	119	281
13	2	3	186	217
13	3	4	161	727
13	4	3	186	195
13	4	4	212	398
13	6	1	241	11
13	6	2	102	294
13	6	3	296	91
14	0	0	567	700
14	0	2	195	790
14	1	2	125	141
14	2	0	271	282
14	2	1	156	117
14	3	0	216	261
14	3	2	178	114
14	4	0	280	127
14	6	0	179	171

Structure factors were derived in the usual way by application of Lorentz and polarization factors. No absorption correction was applied; the linear absorption coefficient for Cu Kα radiation is 12.96 cm^{-1}. The structure was solved by location of the phosphorus atom from a three-dimensional Patterson function and by a series of difference electron density syntheses. No attempt was made to locate the hydrogen atoms.

A separate isotropic temperature factor was applied to each atom, and a series of least-squares refinements reduced the value of

$$R = \frac{\Sigma \left| |F_o| - |F_c| \right|}{\Sigma |F_o|}$$

to 0.13. We had hoped for better agreement at this stage of the refinement. This fact together with the fact that the estimated errors of the bond lengths in the phenanthrene ring were rather large led us to collect a complete new set of data, this time using a scintillation counter and a 2θ-θ-scan technique with the crystal mounted on a General Electric single crystal orienter.[10] Nickel-filtered Cu Kα radiation was again used. Refinement of the structure based on this data set resulted in parameter values substantially the same as those obtained previously and an agreement factor R which was no better. It now seemed probable that the lack of agreement at this stage was due to the fact that the relatively large thermal motions were not being accounted for properly by the individual isotropic temperature factors. The final series of refinements was based on the 893 independent reflections from the two data sets and a model in which each atom was described as an anisotropic harmonic oscillator. Eight scale

---

(10) T. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1966.

Table IV. Some Bond Distances in Angstroms and Angles in Degrees in Orthorhombic Phenanthrenequinone–Triisopropylphosphite[a]

Bond		Angle		Bond		Angle	
	PO_5 Trigonal Bipyramid				Five-Membered Ring		
$P-O_1$	1.76	O_1-P-O_2	89	C_1-O_1	1.32	C_1-O_1-P	113
$P-O_2$	1.62	O_2-P-O_3	87	C_2-O_2	1.48	C_2-O_2-P	112
$P-O_3$	1.63	O_1-P-O_5	85	C_1-C_2	1.26	$O_2-C_2-C_1$	112
$P-O_4$	1.60	O_5-P-O_3	97	$P-O_1$	1.76	$O_1-C_1-C_2$	114
$P-O_5$	1.58	O_1-P-O_4	91	$P-O_2$	1.62	O_1-P-O_2	89
		O_4-P-O_3	92				
		O_2-P-O_5	120				
		O_2-P-O_4	121				
		O_4-P-O_5	119				

Phenanthrene Ring

C_1-C_2, 1.26 (σ = 0.04); mean of 15 other C–C, 1.42 (σ = 0.05); C–C–C angles, 109–132; mean, 120 (σ = 6)

Isopropoxy Groups (Mean Values)

O–C 1.47 (σ = 0.02)	P–O–C 128 (σ = 3)
C–C 1.54 (σ = 0.04)	O–C–C 106 (σ = 3)
	C–C–C 115 (σ = 2)

[a] These values are not as accurate as those for the monoclinic allotrope.[8] The standard deviations of P–O, O–C, and C–C distances are about 0.02, 0.03, and 0.04 A, respectively. The standard deviations of the bond angles range from 1° for O–P–O angles to 5° for some of C–C–C angles. The atoms are labeled as in Figure 1.

factors, one for each of the Weissenberg layers and one for the counter data, were also included as parameters in the least-squares refinements. The least-squares refinement was carried out on the structure amplitudes, with the counter data being weighted by $w = (\sigma^2 + 0.0025F^2)^{-1}$, where σ^2 is the estimated variance of F based on the Poisson counting statistics, and the visual photographic data by $w = (0.01F^2)^{-1}$, except that reflections with intensities lying below a preassigned minimum value were given constant weight. As the least-squares program used did not permit simultaneous refinement of the 269 parameters, the final refinement consisted of alternating cycles of refinement of partial parameter sets as shown in tabular form below.

Cycle	Parameters refined
N-3	Scale and 14 atoms in phenanthrene ring
N-2	15 other atoms
N-1	3 × 29 position parameters
N	6 × 29 thermal parameters

The value of R had converged at this point to 0.088 for calculated structure amplitudes based on the positional parameters in Table II and the anisotropic thermal parameters which are not quoted. The standard deviations are those estimated by the usual methods from the least-squares refinements on cycles N and N-1. These will be underestimates of the marginal standard deviations if there is any correlation between the two parameter sets refined as blocks.

A final difference Fourier synthesis, $\rho_{obsd} - \rho_{calcd}$, was calculated. The maximum electron density in this synthesis was 0.463 e A^{-3}, indicating that no atoms other than hydrogen remain to be located.

The observed and calculated structure factors are presented in Table III.

Description of the Molecular Structure

Interesting interatomic distances and angles are presented in Table IV. These are not as accurate as those for the monoclinic form,[8] to which reference should be made for definitive bond lengths.

As shown in Figure 1, the phosphorus atom lies at the center of a trigonal bipyramid of the five oxygen atoms which are covalently bound to the phosphorus. The distortions from the ideal O–P–O angles of 90 and 120° are slight. Two of the isopropoxy groups are bound to the phosphorus in equatorial positions and one in an apical position. The phenanthrenequinone thus forms with the phosphorus a five-membered ring which bridges the remaining equatorial and apical positions.[11] The bonding in this compound is discussed in the following paper.[8] We remark here only that the apical bonds are lengthened relative to the equatorial bonds, as is typical of pentacoordinated phosphorus compounds, and that, further, the bonds to the phenanthrene ring are longer than equivalent bonds to the isopropoxy groups.

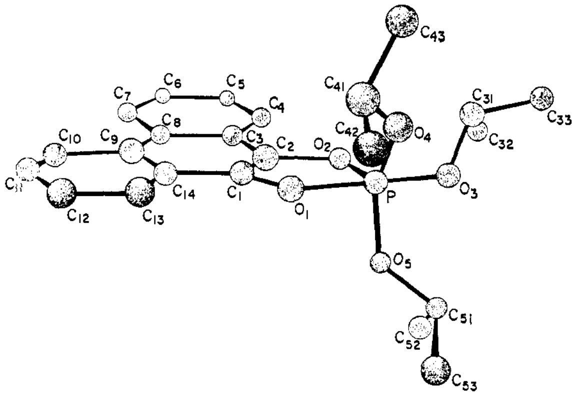


Figure 1. Molecular structure of orthorhombic phenanthrenequinone–triisopropyl phosphite 1:1 adduct.

The phenanthrene ring, the phosphorus atom, and three of the oxygen atoms lie within 0.07 A of the plane

$$5.904x - 16.753y + 6.7784z = -0.7855$$

where x, y, and z are the fractional coordinates of the atoms in question.

---

(11) In a discussion of the possible geometries of the *transition states* in the acid-catalyzed hydrolysis of ethylene hydrogen phosphate, and in the exchange of oxygen between the latter and the water solvent, P. C. Haake and F. H. Westheimer (*J. Am. Chem. Soc.*, **83**, 1102 (1961)) suggested structures in which the five-membered ring is in an apical–equatorial position, found here.

The large amplitudes of thermal motion and the size of the molecule with the attendant complexity of possible vibrations, librations, and other motions would make any detailed discussion of the thermal motion somewhat pretentious. Since the accuracy of these parameters is quite low, we have not quoted the individual values but have given only the root-mean-square displacements in Table II. There are significant anisotropies, and the amplitudes of motion are in general larger as the distance from the P atom increases.

The intermolecular packing is apparently determined entirely by interactions between carbon atoms or the hydrogens attached to them. There are six independent distances less than 4.0 A between carbon atoms of phenanthrene groups in adjacent molecules: 3.55, 3.73, 3.77, 3.78, 3.79, 3.87. There are two such distances between carbon atoms of isopropyl groups: 3.86, 3.90. The remaining eleven distances are between phenanthrene carbon and isopropyl carbon: 3.50, 3.72, 3.72, 3.75, 3.75, 3.76, 3.89, 3.89, 3.94, 3.95, 3.97. There is nothing singular to be noted about these distances. Any detailed discussion of the intermolecular forces would require knowledge of the hydrogen-atom positions—which were not determined.

The intramolecular nonbonded distances are normal except for the four short distances between oxygen atoms and the central carbon atom of neighboring isopropyl groups. These are (in A) O_2–C_{31}, 2.804; O_1–C_{41}, 2.695; O_4–C_{31}, 2.960; O_3–C_{51}, 2.700. This represents what must be an extreme overcrowding of the molecule, a factor which perhaps explains the relative instability of these kinds of molecules and perhaps the advantage derived from having a five-membered ring involving two of the oxygen atoms which may minimize such interactions. Intramolecular overcrowding might be, at least partially, responsible for the differences in molecular structure observed among adducts of phenanthrenequinone with tris(dialkylamino)phosphines, for example, V and VI.

Crystal and Molecular Structures of Pentacoordinated Group V Compounds. II. 2,2,2-Triisopropoxy-4,5-(2′,2″-biphenyleno)-1,3,2-dioxaphospholene. Monoclinic[1a]

Richard D. Spratley,[1b] Walter C. Hamilton,[1b] and Joshua Ladell[1c]

Contribution from the Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, and Philips Laboratories, Briarcliff Manor, New York.

Received December 5, 1966

Abstract: The crystal and molecular structures of the monoclinic allotrope of the phenanthrenequinone-triisopropyl phosphite 1:1 adduct have been determined by single crystal X-ray diffraction techniques. The space group is $P2_1/c$ with four molecules in a unit cell of dimensions $a = 25.997 \pm 0.001$ A, $b = 8.894 \pm 0.001$ A, $c = 9.880 \pm 0.001$ A, and $\beta = 94.25 \pm 0.01°$. The final R factor for 2183 independent reflections is 0.109. The molecular structure is a trigonal bipyramid of oxygen atoms around the phosphorus with two isopropoxy groups in equatorial positions and one in an apical position. The phenanthrenequinone moiety bridges one apical and one equatorial position, thereby forming a C_2O_2P five-membered ring. The apical P-O bonds show the lengthening (relative to the equatorial bonds) commonly observed in PX_5 structures. In addition, P-O bonds in the five-membered ring are further lengthened, an effect that can be attributed to molecular π bonding.

A preliminary account of the molecular and crystal structures of the phenanthrenequinone–triisopropyl phosphite 1:1 adduct (PQTP), orthorhombic form, has been given.[2] A fuller account of this work including details of the preparative chemistry is in paper I of this series.[3] This paper reports the results of a single crystal X-ray investigation of a second crystal modification of this species. Although the work reported in paper I established the molecular geometry in the compound beyond any doubt, the present study has resulted in bond lengths of much greater accuracy. The crystal data show a monoclinic form of probable space group $P2_1/c$; $a = 25.997 \pm 0.001$ A, $b = 8.894 \pm 0.001$ A, $c = 9.880 \pm 0.001$ A, $\beta = 94.25 \pm 0.01°$, $\rho_{\text{X-ray}} = 1.213$ g cm^{-3}.

Experimental Section

A suitable crystal prepared as described in **I** was ground into a sphere of diameter 0.432 mm and mounted in a Lindemann glass capillary; the intensities of 2817 reflections were measured on the automatic single crystal X-ray diffractometer PAILRED[4] using monochromatized copper Kα radiation. The following reciprocal lattice layers were investigated: $hk0$, $hk\bar{1}$, $hk\bar{2}$, $hk\bar{3}$, $hk\bar{4}$, $hk\bar{5}$, $hk\bar{6}$, $hk\bar{7}$, $0kl$, $2kl$, $3kl$, $4kl$, and $5kl$. Structure factors were derived in the usual way by application of Lorentz and polarization factors and an absorption correction. The absorption correction was calculated by the expression

$$A = K_0 + K_1\theta + K_2\theta^2 + K_3\theta^3$$

where the expansion coefficients K_i were obtained from a least-squares fit to values tabulated for a spherical specimen.[5] The observed intensities were placed on approximate absolute scales by Wilson's method[6] and the resulting 14 scale factors reduced to a

---

(1) (a) This work supported in part by the U. S. Atomic Energy Commission; (b) Brookhaven National Laboratory; (c) Philips Laboratories.

(2) W. C. Hamilton, S. J. LaPlaca, and C. P. Smith, *J. Am. Chem. Soc.*, 87, 127 (1965).

(3) Paper I: W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *ibid.*, 89, 2268 (1967).

(4) See, for example, J. Ladell, *Trans. Am. Cryst. Assoc.*, 1, 86 (1965).

(5) "International Tables for X-Ray Crystallography," Vol. II, The Kynoch Press, Birmingham, 1959.

(6) A. J. C. Wilson, *Nature*, 150, 152 (1942).