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The Crystal and Molecular Structure of 2-Oxo-2-phenyl-4,4-dimethyl-1,3,2-dioxaphosphorinane

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Crystals of 2-oxo-2-phenyl-4,4-dimethyl-1,3,2-dioxaphosphorinane are monoclinic, space group $P2_1$, with $Z=2$. Unit-cell dimensions are $a=5\cdot82\pm0\cdot02$, $b=10\cdot23\pm0\cdot03$, $c=9\cdot70\pm0\cdot02$, $\beta=99\cdot0°\pm5'$. The structure has been solved from a three-dimensional Patterson synthesis and refined using an absolute weighting scheme. The final R index was 12% compared with a theoretical R index of 11%. The phosphorinane ring has a chair conformation with the phenyl group lying in the axial position.

Introduction

Although conformations of six-membered rings have been widely studied in the last ten years and reviewed recently (Anderson, 1965), the conformation of six-membered phosphorus heterocyclics has aroused further interest (Hargis & Bentrude, 1968). In studying the nuclear magnetic resonance spectra and resulting coupling constants of phosphorus heterocyclics, some interesting results have been obtained and in the hope of explaining these, crystal structure analysis of some of these compounds is being undertaken. This paper describes one such analysis.

Experimental

Thirty-nine grams of phenylphosphoryl chloride in 100 ml toluene were added slowly to 20·8 g of 2,2-dimethylpropane-1,3-diol and 41 g of trimethylamine in 300 ml toluene at 5 °C. The mixture was heated to 100 °C for one hour and the amine salt filtered off. During evaporation of the solvent, the product crystallized. The compound was recrystallized from benzene.

Crystal data

2-Oxo-2-phenyl-4,4-dimethyl-1,3,2-dioxaphosphorinane. Molecular formula $C_{11}H_{15}O_3P$, m.p. 104 °C, M.W. 226·22.

Monoclinic
$a=5\cdot82\pm0\cdot02$, $b=10\cdot23\pm0\cdot03$, $c=9\cdot70\pm0\cdot02$ Å
$\beta=99\cdot0°\pm5'$
$V=570\cdot42$ Å^3
$D_x=1\cdot32\pm0\cdot02$ g.cm^{-3}
$D_o=1\cdot30\pm0\cdot05$ g.cm^{-3}
$Z=2$

μ(Mo $K\alpha$) $=0\cdot23$ cm^{-1}

Absent spectra: $0k0$ when k is odd
Space group: $P2_1$ (or $P2_1/m$)

Two well formed crystals of approximate dimensions $0\cdot5\times0\cdot2\times0\cdot1$ mm were used, one mounted about the b axis and the other about the c axis. Unit-cell dimensions were obtained from rotation and zero-layer Weissenberg photographs with copper radiation at room temperature.

Equi-inclination data were collected for $k=0\rightarrow9$ on a Hilger & Watts linear diffractometer with the crystal mounted about the b axis. The balanced filter technique was used with Mo $K\alpha$ radiation ($\lambda=0\cdot7107$ Å) and a 30 sec oscillation motor. The data were reduced to structure factors by correction for Lorentz and polarization effects in the usual way. No corrections for absorption were made. The total number of reflexions recorded with net counts greater than zero was 635.

Structure determination

A three-dimensional unsharpened Patterson function showed only two peaks about 1·5 Å from the origin and not four as expected from the approximately tetrahedral $P(O_3-C)$ system. These peaks were identified as vectors between the phosphorus atom and the surrounding four atoms, both being double peaks due to vectors on either side of the mirror plane $y=0$. The corresponding vectors between these four atoms were also identified and the position of the phosphorus atom was obtained from the Harker section $y=\frac{1}{2}$. At this stage the possibility of space group $P2_1/m$ could be excluded.

A structure factor calculation based on these coordinates in space group $P2_1$ gave a reliability factor of 0·40 and from the resulting Fourier summation the positions of the carbon atoms were found. These indicated a chair conformation for the phosphorinane ring and an axial position for the phenyl group. Least-squares refinement using a Hughes weighting scheme with isotropic temperature factors reduced R to 0·15.

Refinement

Further refinement was carried out using an absolute weighting scheme (Killean & Lawrence, 1969). This

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gives a weight $w(\mathbf{h})$ for each structure factor $F(\mathbf{h})$ having a variance $\sigma^2(\mathbf{h})$ of

$$w(\mathbf{h})=\frac{1}{\sigma^2(\mathbf{h})}=\left[\frac{K}{4\mathrm{Lp}}\,\frac{I+B}{I-B}+c^2|F(\mathbf{h})|^2+k^2\langle|F(\mathbf{h})|^2\rangle\right]^{-1}$$

where K is a scale factor, I is the integrated peak count, B is the background count, c is the fractional error in $|F(\mathbf{h})|$ and k is the average fractional error in the scattering curves due to bonding electrons.

Since each integrated reflexion was measured for only 15 sec, the variance of $|F(\mathbf{h})|$ due to counting statistics was fairly large and, assuming values of c^2 and k^2 of 0·0025 and 0·0010 respectively, the theoretically expected R index (Killean, 1967) given by

$$R=\left(\frac{2}{\pi}\right)\frac{\sum\limits_{\mathbf{h}}\sigma(\mathbf{h})}{\sum\limits_{\mathbf{h}}|F(\mathbf{h})|},$$

was 0·11 .

The structure was refined using this weighting scheme with the assumed values of c and k and gave a final R index of 0·134 and a value of

$$\frac{\sum\limits_{\mathbf{h}} w(\mathbf{h})|\Delta(\mathbf{h})|^2}{(m-n)},$$

where m and n represent the number of observations and variables respectively, of 1·24.

Corrected values of c and k were then calculated using the G index (Kitaigorodski, 1957) defined as

$$G^2=\frac{\sum\limits_{\mathbf{h}}|\Delta(\mathbf{h})|^2}{\sum\limits_{\mathbf{h}}|F(\mathbf{h})|^2}=\frac{\sum\limits_{\mathbf{h}}\sigma(\mathbf{h})^2}{\sum\limits_{\mathbf{h}}|F(\mathbf{h})|^2}=S^2+c^2+k^2\,.$$

At this point of refinement, $G^2=0\cdot0200$ and $S^2=0\cdot0153$.

$$c^2+k^2=0\cdot0047\,.$$

Various values of

$$\frac{\sum\limits_{\mathbf{h}} w(\mathbf{h})|\Delta(\mathbf{h})|^2}{(m-n)}$$

were then calculated for values of c and k subject to $c^2+k^2=0\cdot0047$ and the minimum value occurred when $c^2=0\cdot0027$ and $k^2=0\cdot0020$.

Further refinement using this new weighting scheme gave a final R index of 0·119 and a final value of

$$\frac{\sum\limits_{\mathbf{h}} w(\mathbf{h})|\Delta(\mathbf{h})|^2}{(m-n)}$$

of 0·99. In the final refinement only those reflexions for which $|F(\mathbf{h})|>3\sigma(\mathbf{h})$ were included.

As can be seen, the final R index agrees with the theoretically expected value. Obviously, this value could have been reduced by increasing the time taken to measure each reflexion but it was felt that, using the 30 sec motor and thus obtaining an R index of 0·11, sufficient accuracy in the positional and thermal parameters of the atoms would be achieved to determine the stereochemistry unambiguously. The final value of

$$\frac{\sum\limits_{\mathbf{h}} w(\mathbf{h})|\Delta(\mathbf{h})|^2}{(m-n)}$$

was very close to its theoretical value of unity, justifying the choice of weighting scheme. The final value of k of 0·04 suggests about a 4% error in the form factors due to bonding.

No clear evidence of hydrogen atoms was found in a difference synthesis which, in view of the large R index obtained, was not surprising.

Table 1 gives the final coordinates and their standard deviations, Table 2 the anisotropic temperature parameters and Table 3 the structure factors. Large discrepancies between the observed and calculated structure factors occurred for two reflexions 001 and 002; the diffracted beam was almost certainly obscured by the back-stop during the measurement of the 001 intensity. For all other reflexions the discrepancy was less than three times the standard deviation.

Table 1. *Final coordinates and standard deviations*

	x/a	y/b	z/c
P	0·2320 (10)	−0·0008 (7)	0·1624 (6)
O(1)	0·0721 (23)	0·0941 (14)	0·0715 (13)
O(2)	0·1067 (32)	−0·0937 (18)	0·2392 (14)
O(3)	0·3766 (24)	−0·0736 (15)	0·0613 (13)
C(1)	0·1535 (40)	0·1631 (21)	−0·0393 (23)
C(2)	0·2538 (44)	0·0753 (23)	−0·1407 (21)
C(3)	0·4560 (33)	−0·0008 (30)	−0·0519 (20)
C(4)	0·0696 (45)	−0·0213 (25)	−0·2062 (23)
C(5)	0·3702 (47)	0·1519 (29)	−0·2492 (24)
C(6)	0·4407 (38)	0·0963 (19)	0·2802 (17)
C(7)	0·3469 (42)	0·2142 (19)	0·3275 (22)
C(8)	0·4895 (52)	0·2838 (26)	0·4224 (21)
C(9)	0·7074 (44)	0·2376 (30)	0·4727 (21)
C(10)	0·7974 (46)	0·1234 (24)	0·4221 (18)
C(11)	0·6582 (37)	0·0548 (23)	0·3198 (19)

Molecular geometry

Fig. 1 shows the projection of the structure down the a axis, showing the labelling used. Bond lengths and valency angles are listed in Tables 4 and 5.

In the solid state the phosphorinane ring has a chair conformation, slightly flattened compared with the cyclohexane ring. The arrangement around the phosphorus atom is approximately tetrahedral with the phenyl group and phosphorus–oxygen double bond lying in the axial and equatorial positions respectively. The methoxy and phenoxy derivatives of the compound

Table 2. *Final anisotropic temperature factors* $\times 10^5$ *defined as* $\exp[-(B_{ij}h_ih_j)]$

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
P	2261	896	915	−678	−26	−296
O(1)	2022	892	1241	−285	−202	−315
O(2)	6843	1334	943	380	1162	−488
O(3)	2905	1135	1071	677	85	−149
C(1)	4045	596	1266	133	−950	599
C(2)	5157	857	756	−37	−223	1352
C(3)	2067	1219	1357	−692	1152	−2363
C(4)	5698	933	1307	−1228	71	619
C(5)	5109	1871	1113	207	1820	−2368
C(6)	3869	799	302	−273	1541	−263
C(7)	5600	578	1253	304	3822	−252
C(8)	8081	1301	610	−1515	2313	−3376
C(9)	4192	2326	587	508	−1217	−2957
C(10)	6545	1231	329	−784	542	−2832
C(11)	2356	1543	882	1428	126	1111

seem to indicate that this is the sterically preferred conformation (Edmundson, 1964; Geise, 1967).

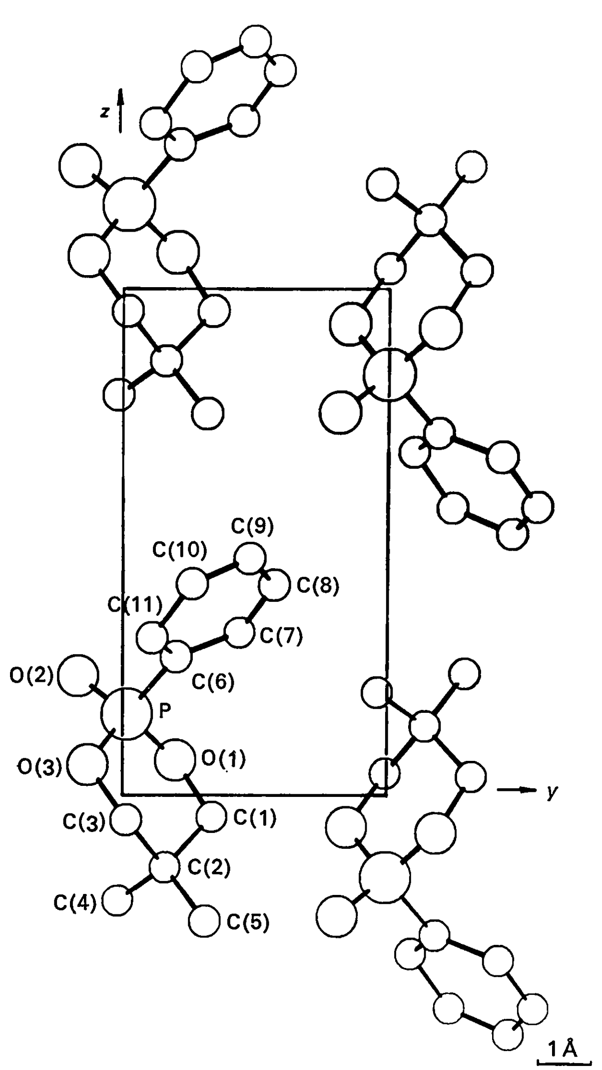

Fig. 1. Projection of the structure down the *a* axis, showing the labelling used.

Table 3. *Measured and calculated values of the structure factors,* $\times 100$, *for reflexions having* $|F(\mathbf{h})| > 3\sigma(\mathbf{h})$

0 0 L		
1	1717	3322
2	1260	604
3	807	811
4	1018	852
5	423	207
6	566	502
8	1220	1097
9	881	799
10	708	804
0 1 L		
1	3621	4185
2	3675	3603
3	1884	1837
4	625	695
5	335	205
6	1092	1279
7	950	854
8	664	636
9	458	741
10	605	535
0 2 L		
1	5481	5202
2	2652	2435
3	2258	2111
4	1161	1036
5	1210	1087
6	667	709
7	856	885
8	512	497
9	945	914
0 3 L		
2	1574	1588
4	1033	1039
5	1063	1190
6	403	437
7	472	469
8	1082	986
0 4 L		
2	315	453
3	1845	1811
4	1579	1687
5	694	727
6	2066	1991
7	891	1010
0 5 L		
2	566	803
3	841	739
4	1506	1527
5	3114	2995
6	1205	1064
7	846	1010
8	610	426
10	497	392
0 6 L		
2	536	720
3	1082	991
4	418	452
5	1255	1443
6	1442	1297
0 7 L		
3	704	736
4	2012	2083
5	1697	1659
6	571	605
8	689	940
0 8 L		
3	1141	1007
4	374	248
6	482	523
7	448	368
1 0 L		
0	1614	1690
1	645	222
−1	2617	2906
2	3045	2952
−2	1899	1780
3	1294	1340
−3	2539	2588
−4	526	325
5	1820	1880
6	551	551
−6	453	355
7	827	870
−8	694	836
9	566	355
10	772	677
1 1 L		
0	6106	5639
1	4654	4693
−1	5781	5647
2	733	617
−2	3985	3711
3	2140	1867
−3	3783	3674
4	841	858
−4	659	714
5	979	975
−5	482	572
6	1077	993
−7	571	657
9	787	786
10	562	648
1 2 L		
0	1141	835
1	4669	4493
−1	1009	1101
2	6017	5255
−2	4212	4083
3	2337	2354
−3	1151	944
4	2219	2042
−4	1707	1711
5	1033	1084
−5	1407	1278
−6	679	567
7	610	629
−7	713	638
8	689	695
−8	1097	1049
10	802	819
1 3 L		
0	1373	1404
1	522	421
−1	1442	1316
2	1791	1696
−2	502	502
3	2499	2324
−3	5412	5531
4	581	594
−4	2691	2652
−5	1510	1673
6	1009	1029
−6	841	813
7	1304	1240
−8	827	1001
9	605	640
1 4 L		
0	1196	1094
1	2598	2384
−1	925	1031
2	2854	2586
−2	1304	1343
3	1068	1032
−3	266	171
4	1333	1309
−4	1383	1419
5	1899	1911
−5	1589	1569
6	772	627
7	551	331
−7	738	1129
8	743	646
−8	1225	1327
1 5 L		
0	1127	1333
1	669	664
−1	458	458
2	1097	1148
−2	1220	1075
−3	1422	1390
4	905	961
−4	1584	1532
5	704	638
−5	541	752
6	969	1008
−6	1535	1565
7	669	856
8	1569	1237
10	512	420
1 6 L		
1	595	633
2	836	745
−2	763	690
−3	349	357
4	1668	1618
−4	1402	1559
5	1727	1750
−5	1643	1795
6	1274	1319
−6	453	588
−7	969	950
1 7 L		
0	413	493
1	399	583
−1	438	497
2	408	519
−2	469	720
3	1319	1162
−3	1058	1141
4	585	602
−4	802	935
−5	600	676
6	777	843
−6	590	783
7	526	489
−7	517	284
1 8 L		
0	221	291
−1	708	791
2	1205	1223
−2	590	689
3	325	351
4	561	741
−4	389	692
5	1058	1064
8	536	679
9	630	473
2 0 L		
0	1373	1362
−1	1309	1302
−2	1255	1284
3	2814	3050
−3	708	781
4	1491	1468
−4	671	836
6	1294	1394
−6	2150	2318
7	881	793
−7	1328	1378
8	4694	365
−8	654	455
2 1 L		
0	1048	1100
1	2386	2185
−1	2199	2107
2	3331	3267
−2	2022	1764
3	1004	895
−3	359	362
4	1515	1445
−4	1565	1578
5	1068	1184
−5	871	718
6	630	547
−6	802	839
7	940	799
−7	787	772
8	640	536
−8	1122	969
2 2 L		
0	1028	998
1	1225	1178
−1	782	730
2	1727	1702
−2	1397	1269
3	1619	1666
−3	2637	2500
4	1087	1026
−4	3218	2913
−5	1491	1499
−6	1048	930
7	1358	1376
−7	699	772
−8	620	437
2 3 L		
0	787	810
−1	979	969
1	3651	3524
2	4704	4600
−2	477	492
3	1692	1328
−3	1402	1483
4	389	529
−4	1663	1777
−5	940	954
−6	886	1036
7	728	522
−7	1225	1515
8	541	738
−8	950	887
9	600	251
2 4 L		
0	1210	1345
1	699	882
−1	866	930
2	920	1025
−2	1343	1317
3	1018	937
−3	2932	2815
4	1998	1902
5	467	214
−5	640	490
6	935	1063
−6	1348	1533
7	861	1046
−7	841	900
2 5 L		
0	581	697
1	2042	2077
−1	2184	2085
2	1506	1401
−2	1747	1603
3	807	829
4	581	735
−4	891	766
5	925	857
7	1186	1207
−8	841	651
2 6 L		
0	1328	1286
1	772	687
−1	482	605
−2	728	624
3	600	611
−3	664	715
4	536	308
−4	335	377
−6	635	417
7	654	527
2 7 L		
1	689	799
−1	1466	1364
2	1117	1180
−2	1653	1407
−3	526	360
−4	725	878
5	605	578
6	502	478
7	605	619
8	807	731
9	556	293
2 8 L		
0	620	517
1	974	899
2	512	436
−2	822	872
3	630	551
−3	1319	1449
4	502	364
−4	507	597
5	428	531
−5	448	253
−6	389	288
−8	664	281
3 0 L		
1	344	272
−1	359	351
−2	1181	1199
3	561	330
−3	1476	1498
4	1028	1120
−4	1545	1579
5	2106	2268
−5	433	470
−6	428	147
−7	1461	1571
8	630	512
3 1 L		
0	1063	1157
1	413	441
−1	679	733
2	531	691
−2	571	734
3	2239	2392
−3	768	811
4	2745	2645
−4	423	422
−5	950	877
6	969	1276
−6	2155	2266
7	940	799
−7	1510	1560
3 2 L		
−1	1146	1130
2	1437	1258
−2	974	793
3	738	793
−3	831	687
4	1127	1270
−4	1314	1184
5	768	807
−5	1102	1239
−6	831	655
7	886	709
−7	1102	881
9	522	491
3 3 L		
0	1358	1457
−1	320	245
−2	925	955
3	664	793
−3	1683	1451
4	664	790
5	517	246
6	679	859
−6	846	845
7	659	906
−7	458	488
8	517	387
3 4 L		
0	379	369
1	1205	1141
−1	2396	2511
2	1353	1417
−2	1633	1555
−6	418	242
8	812	709
−8	802	783
3 5 L		
0	1653	1726
1	546	643
−1	886	973
2	497	435
−2	1412	1409
3	625	665
−3	581	665
−4	389	236
5	704	532
6	502	209
−6	438	440
3 6 L		
0	841	826
1	910	1009
−1	2273	2369
2	841	845
−2	2037	2163
4	649	403
−4	625	682
−5	477	177
6	507	423
−7	433	397
8	718	536
3 7 L		
0	600	722
1	856	803
−1	413	172
2	448	337
−3	753	691
5	428	571
9	610	500
3 8 L		
0	541	497
1	576	584
−1	787	907
2	738	851
−2	787	810
5	625	425
8	517	525
4 0 L		
−1	408	559
3	2253	2328
−3	910	742
4	1456	1590
−5	1225	1206
−6	1373	1448
7	950	1015
−7	753	813
4 1 L		
−1	659	476
2	772	765
4	1127	1095
−4	1112	1253
5	802	872
−6	467	355
4 2 L		
0	413	729
1	1122	1175
−2	556	901
3	1506	1679
−3	556	577
4	507	789
−5	802	1031
7	664	603
4 3 L		
0	551	743
1	630	478
−1	684	838
2	969	1149
−2	959	966
4	802	533
−4	1186	1304
5	989	906
−5	979	1026
4 4 L		
0	1397	1411
1	1146	1244
−1	399	361
−2	797	722
3	418	455
−3	1004	972
4	664	580
6	600	489
4 5 L		
0	689	671
1	413	102
−1	1565	1574
2	640	476
−2	1560	1616
−4	610	879
4 6 L		
0	610	746
1	807	687
−1	507	359
4	571	757
−4	477	128
−7	541	146
4 7 L		
1	708	525
−1	1117	1348
2	467	467
−2	625	853
−5	462	410
−6	482	203
−8	590	145
4 8 L		
2	595	335
−3	600	267
4	674	518
−6	526	428
−8	497	329
5 0 L		
1	462	474
−1	831	988
−4	517	580
5	546	632
−5	531	210
5 1 L		
0	1314	1225
1	861	826
−2	448	818
−3	743	717
4	699	808
6	669	481
−6	600	498
5 2 L		
0	492	411
1	831	825
3	526	397
−3	645	631
4	699	504
−4	964	934
5	590	678
−5	787	950
6	635	649
5 3 L		
0	1284	1483
1	640	794
−2	704	780
4	689	644
5	571	427
−5	551	567
−6	585	396
5 4 L		
1	600	432
−1	615	621
2	585	540
−4	1643	1246
−5	758	660
−7	610	282
5 5 L		
1	620	788
3	733	462
5 6 L		
0	615	455
1	531	356
−1	443	349
2	576	600
−3	689	300
4	748	371
−4	753	670
5 8 L		
4	551	217
6	738	217
6 0 L		
0	881	569
−3	959	1175
−6	620	205
6 1 L		
−1	566	582
−2	699	458
0	738	632
–		
6 2 L		
0	738	632
−4	576	181
6 3 L		
0	590	250
−5	507	342
6 4 L		
1	708	534
−4	600	176
−5	571	296
6 5 L		
0	600	140
1	507	398
−7	536	429
6 8 L		
−2	590	384

The first figure for reflexion 208 should read 694 instead of 4694.

Table 4. *Final bond lengths and standard deviations*

Bond	Length
P——O(1)	1·53 (2) Å
P——O(2)	1·47 (2)

Table 4 (*cont.*)

Bond	Length
P——O(3)	1·57 (2)
P——C(6)	1·82 (2)
O(1)—C(1)	1·43 (2)
O(3)—C(3)	1·46 (2)
C(1)—C(2)	1·51 (3)
C(2)—C(3)	1·55 (3)
C(2)—C(4)	1·52 (4)
C(2)—C(5)	1·55 (3)
C(6)—C(7)	1·43 (3)
C(7)—C(8)	1·34 (3)
C(8)—C(9)	1·37 (4)
C(9)—C(10)	1·40 (3)
C(10)-C(11)	1·37 (3)
C(6)—C(11)	1·33 (3)

Table 5. *Intermolecular bond angles and standard deviations*

	Angle
O(1)—P——O(2)	113·5 (0·9)°
O(1)—P——O(3)	106·2 (0·8)
O(2)—P——O(3)	111·4 (0·9)
O(1)—P——C(6)	107·6 (0·9)
O(2)—P——C(6)	111·7 (0·9)
O(3)—P——C(6)	106·5 (0·9)
O(1)—C(1)—C(2)	113·8 (1·7)
O(3)—C(3)—C(2)	111·8 (1·5)
C(1)—C(2)—C(3)	105·8 (1·8)
C(1)—C(2)—C(4)	109·8 (2·0)
C(1)—C(2)—C(5)	113·2 (1·9)
C(3)—C(2)—C(4)	109·8 (2·0)
C(3)—C(2)—C(5)	104·8 (2·0)
P——C(6)—C(7)	114·3 (1·7)
P——C(6)—C(11)	121·0 (1·6)
C(6)—C(7)—C(8)	116·2 (2·0)
C(7)—C(8)—C(9)	120·1 (2·0)
C(8)—C(9)—C(10)	122·6 (2·0)
C(10)-C(11)-C(6)	118·2 (2·0)
C(11)-C(6)—C(7)	124·7 (2·0)
P–O(1)-C(1)	120·4 (1·5)
P–O(3)-C(3)	119·3 (1·5)
C(9)-C(10)-C(11)	118·0 (2·0)
C(4)- C(2)- C(5)	113·5 (2·0)

The single-bonded phosphorus–oxygen distance (mean 1·55 Å) and double-bonded phosphorus–oxygen distance (1·47 Å) agree with those found in several structures. Kraut & Jensen (1963) allot values of 1·56 and 1·49 Å respectively to these bonds. They have also observed that oxygen–phosphorus–oxygen angles increase with decreasing oxygen–phosphorus distances, and it can be seen that this confirmed by the present results. The P–C distance of $1·82 \pm 0·02$ Å compares satisfactorily with standard P–C distances ($1·87 \pm 0·02$ Å), while, in the phosphorinane ring, the C–C distances are the expected value (mean 1·53 Å) and the C–O distances (mean 1·45 Å) are not significantly different from the usually accepted value for this bond, 1·43 Å. Large valency angles for oxygen atoms have been found in organic phosphates (Svetich & Caughlan, 1965) and this is the case in the present structure (mean value 120°). The carbon valency angles are normal except for the C–C–C angle in the heterocyclic ring which is unusually small (105°).

Bond distances in the benzene ring give an average value of 1·37 Å and bond angles an average value of 120°.

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The Crystal and Molecular Structure of Dichlorodiaquobis(dicyandiamide)copper(II)

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Crystals of $Cu(OH_2)_2(C_2N_4H_4)_2Cl_2$ are triclinic ($P\bar{1}$): $a=5·42$ (1), $b=6·45$ (1), $c=9·31$ (1) Å, $\alpha=74·5$ (0·2), $\beta=80·4$ (0·3), $\gamma=84·7$ (0·3)°, $Z=1$. The structure was solved and refined by means of three-dimensional Fourier methods (final $R=8·3$ %). The Cu^{II} atom lies on a centre of symmetry and is surrounded by a planar arrangement of two water molecules (Cu–O = 2·00 Å) and two nitrile nitrogen atoms (Cu–N = 1·92 Å) from two dicyandiamide molecules. Two chlorine atoms, in the *trans* position with respect to that plane (Cu–Cl = 2·87 Å), complete the coordination polyhedron to form an elongated octahedron.

The crystal structure of dichlorodiaquobis(dicyandiamide)copper(II) has been determined in order to study the behaviour of dicyandiamide in metal-coordination.

Dichlorodiaquobis(dicyandiamide)copper(II) occurs as blue-green triclinic platelets elongated along [100]. Cell constants, determined from Weissenberg and rota-