The Crystal and Molecular Structure of Pholanic Acid

(*P*-Oxo-*P*-hydroxo-phospholane), (CH$_2$)$_4$PO(OH)

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The crystal and molecular structure of pholanic acid (*P*-oxo-*P*-hydroxo phospholane) has been determined by X-ray diffraction methods.

The crystals are orthorhombic, space group $P2_12_12_1$ (No. 19), with cell dimensions, $a = 6.38$ Å, b 12.69 Å, $c = 7.15$ Å. There are four asymmetric molecules (CH$_2$)$_4$PO(OH) in the unit cell.

Intensities were measured by point photometry on integrated Weissenberg films. The agreement residual R_1 was 0.07 for about 640 structure amplitudes at the end of the least squares refinement process.

The molecules are bonded together to helices along the axis c by hydrogen bonds, of length 2.48 Å, between the oxo atom and the hydroxyl group of adjacent molecules.

The P−O "single bond" is 1.567 ± 0.006 Å (e.s.d.), and the "double bond", 1.473 ± 0.010 Å. The mean length of the two phosphorus-carbon bonds is 1.786 ± 0.017 Å. The amplitudes of the anisotropic thermal vibrations are large, and this may explain the abnormally low values obtained for the carbon-carbon bond lengths (down to 1.43 Å, with e.s.d. 0.03 Å).

The five-membered ring is non-planar, and asymmetrical. The angle in the ring at the phosphorus atom is 95°.

It has been found that five-membered cyclic phosphorus compounds (phospholane derivatives) are hydrolysed much faster than the six-membered analogs (phosphorinane derivatives).[1] This might be due to different sterical distribution of atoms around the phosphorus atoms in the two cases, and/or to difference in strain in the five-membered and the six-membered rings. The present paper describes the structure determination of pholanic acid, *P*-oxo *P*-hydroxo phospholane, by X-ray diffraction methods. This work was started with the purpose of obtaining information that might contribute to a better understanding of the chemistry of cyclic phosphorus compounds. It is, however, also hoped that the present work will contribute to the understanding of the structural chemistry of small ring compounds in general.

EXPERIMENTAL

The crystals are orthorhombic, space group $P2_12_12_1$ (No. 19), and there are four molecules $(CH_2)_4PO(OH)$ in the unit cell. The cell dimensions are, $a = 6.38$ Å, $b = 12.69$ Å, $c = 7.15$ Å, within ± 0.2 %.

The intensities of the reflections were measured with a point photometer on integrated equi-inclination Weissenberg films. The usual multifilm technique was employed, and in all, about 640 independent intensities of the orders $0kl$ to $4kl$ and $hk0$ to $hk5$ were recorded. On higher layers only the extended spots were measured, and an "extended spot" correction was applied. No correction for absorption has been thought necessary, as the crystals employed were small (about 0.15 mm across), and contain no element heavier than phosphorus.

DETERMINATION OF THE STRUCTURE

It was first attempted to determine the structure in the projections along a and c, by the usual heavy-atom method and by direct sign determination by the "multiplication rule". As the z coordinate for the phosphorus atom seemed ambiguous, the three-dimensional Pattersom function was computed. The x and y coordinates for the phosphorus atom were confirmed. The positions, relative to the phosphorus atom, of the two oxygen atoms and the two carbon atoms bonded to phosphorus were also indicated. As it was not known which way the non-planar ring should be twisted, the last two carbon atoms were located by $(F_o - F_c)$ synthesis. It was thus possible to solve the c projection.

The three-dimensional Patterson function did, however, indicate two possible z coordinates for the phosphorus-oxygen vectors. It was found easiest to try both sets of coordinates, and one of them at once gave reasonable agreement between observed and calculated structure factors. The least squares computations proceeded smoothly until the residual R_1 was 0.16.

Table 1. Final positional parameters of one asymmetric unit in fractions of the corresponding cell edge, with their estimated standard deviations, and B in the isotropic temperature factor exp $-B(\sin\theta/\lambda)^2$ used for the hydrogen atoms.

	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	B
P	0.3754	0.4188	0.0990	0.0003	0.0001	0.0002	
O_1	0.1973	0.4909	0.1274	0.0009	0.0003	0.0006	
O_2	0.4221	0.3954	-0.1122	0.0010	0.0006	0.0007	
C_1	0.6095	0.4576	0.2144	0.0011	0.0006	0.0013	
C_2	0.6974	0.3591	0.2954	0.0017	0.0009	0.0016	
C_3	0.5316	0.2879	0.3409	0.0017	0.0006	0.0012	
C_4	0.3631	0.2915	0.2086	0.0031	0.0012	0.0018	
H_{OH}	0.4157	0.4808	-0.176	0.017	0.008	0.014	12.1
H_{11}	0.7156	0.4944	0.132	0.017	0.007	0.015	7.6
H_{12}	0.5140	0.5047	0.285	0.012	0.005	0.011	8.2
H_{21}	0.7667	0.2788	0.168	0.019	0.008	0.014	8.8
H_{22}	0.7957	0.3745	0.405	0.019	0.008	0.013	8.0
H_{31}	0.4462	0.3525	0.476	0.016	0.009	0.014	5.2
H_{32}	0.5477	0.2227	0.350	0.022	0.012	0.018	9.0
H_{41}	0.2554	0.2973	0.232	0.024	0.008	0.015	8.5
H_{42}	0.4017	0.2322	0.119	0.021	0.010	0.016	10.7

Table 2. Anisotropic vibration parameters for the phosphorus, oxygen, and carbon atoms. The expression used is $\exp-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{23}kl+\beta_{13}hl)$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	0.0295	0.0081	0.0116	0.0044	−0.0036	0.0001
O_1	0.0488	0.0209	0.0151	0.0336	−0.0111	−0.0086
O_2	0.0595	0.0112	0.0125	0.0211	0.0041	−0.0016
C_1	0.0376	0.0098	0.0266	−0.0078	−0.0094	0.0075
C_2	0.0390	0.0095	0.0347	0.0029	−0.0344	0.0023
C_3	0.0416	0.0120	0.0439	0.0021	−0.0104	0.0215
C_4	0.0497	0.0148	0.0299	−0.0262	−0.0214	0.0130

At this stage the hydrogen atoms were included in the computations, and anisotropic temperature factors for the phosphorus, oxygen, and carbon atoms were introduced. The approximation process was interrupted when all shifts seemed insignificant. The final value of the residual R_1 was 0.07. Atomic scattering factor tables were taken from *International Tables.*[11]

The positional and thermal parameters are given in Tables 1 and 2, observed and calculated structure amplitudes in Table 3, and bond lengths and bond angles in Table 4 and in Figs. 1 and 2. The bonds involving hydrogen atoms are not included in the tables because of the inaccuracy of the hydrogen positions. However, lengths of the carbon-hydrogen bonds were found between 0.7 Å and 1.4 Å, four of them close to 1.0 Å. The oxygen-hydrogen bond was found 1.2 Å long.
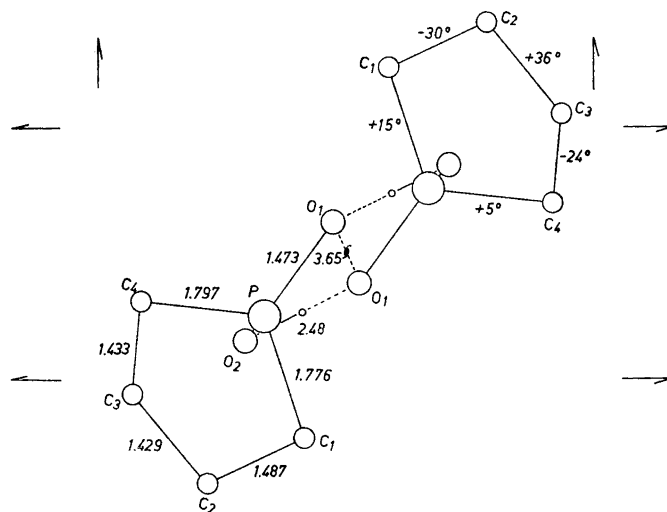

Fig. 1. Two asymmetric units projected along *c* (axis *b* horizontal) with bond lengths (Å) (left) and torsion angles around the bonds of the ring (right). The signs ± on the torsion angles indicate direction of twist (right — left screw). The length of the bond P−O₂ is indicated on Fig. 2. The indicated position of a hydrogen atom is by assumption.

Table 3. Observed and calculated structure amplitudes, multiplied by 100.0.

H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)
C	2	0	321C	3420	0	11	1	311	383	7	5	1	183	165	6	2	2	667	560	6	3	3	476	3CC
0	4	0	267	367	0	12	1	434	374	7	6	1	728	194	6	3	2	381	378	6	4	3	128	86
C	6	C	254C	2318	C	13	1	366	323	7	7	1	185	193	6	4	2	741	715	6	5	3	474	461
C	8	C	571	517	0	14	1	66	128	7	8	1	134	183	6	5	2	408	270	6	6	3	116	114
C	10	C	841	864	C	15	1	211	244	8	0	1	39	30	6	6	2	89	23	6	7	3	556	463
C	12	C	374	441	0	16	1	144	212	8	1	1	122	157	6	7	2	84	9	7	0	3	446	458
C	14	0	27C	370	1	0	1	5217	5168	8	2	1	122	145	6	8	2	425	430	7	1	3	266	211
0	16	C	135	154	1	1	1	3251	3161	8	3	1	153	241	6	9	2	199	192	7	2	3	2C4	2C7
1	1	C	4246	4160	1	2	1	3763	3927	C	C	2	3490	3480	6	10	2	263	325	7	3	3	378	363
1	2	C	642C	74C0	1	3	1	910	651	C	1	2	3583	3952	7	C	2	2C8	141	7	4	3	258	194
1	3	0	136C	1357	1	4	1	2197	2129	0	2	2	141C	1352	7	1	2	333	295	7	5	3	266	197
1	4	C	2482	2450	1	5	1	3164	3238	C	3	2	4056	4027	7	2	2	221	233	7	6	3	166	215
1	5	C	7C1	784	1	6	1	551	8C5	0	4	2	1617	1643	7	3	2	379	337	0	0	4	4451	4469
1	6	C	754	693	1	7	1	1347	1374	C	5	2	244	136	7	4	2	182	134	0	1	4	824	891
1	7	C	1677	1579	1	8	1	138F	1361	C	6	2	1173	1161	7	5	2	116	143	0	2	4	2442	2355
1	8	C	182C	1837	1	9	1	1144	11F1	C	7	2	1612	1575	7	6	2	328	343	0	3	4	248	235
1	9	C	655	6C6	1	10	1	458	48C	C	8	2	166	193	7	7	2	187	205	0	4	4	871	825
1	10	C	505	456	1	11	1	564	565	0	9	2	684	617	C	1	3	912	868	0	5	4	1141	1C89
1	11	C	1C05	1C62	1	12	1	78	48	C	10	2	54C	418	0	2	3	351	289	0	6	4	17C8	1735
1	12	C	132	81	1	13	1	325	359	C	11	2	744	690	0	3	3	2265	2180	0	7	4	524	527
1	13	C	232	361	1	14	1	321	312	0	12	2	577	527	C	4	3	2117	2062	0	8	4	288	271
1	14	C	183	223	1	15	1	169	161	C	13	2	611	605	C	5	3	1275	1403	0	9	4	59	1
1	16	C	8C	164	1	16	1	94	162	1	C	2	4810	493F	C	6	3	355	350	C	10	4	874	82C
2	C	C	89C	725	2	1	1	1344	1327	1	1	2	2220	2199	C	7	3	122	119	0	11	4	465	334
2	1	C	2782	2825	2	2	1	1554	1458	1	2	2	1763	1771	0	8	3	1125	1073	0	12	4	516	566
2	2	C	1433	1346	2	3	1	1534	1634	1	3	2	1244	1235	C	9	3	458	451	0	13	4	420	440
2	3	C	2603	2726	2	4	1	2232	22C7	1	4	2	1119	1008	C	10	3	1334	13C6	0	14	4	193	186
2	4	C	201	6C	2	5	1	775	7P5	1	5	2	1722	1713	0	11	3	141	73	1	0	4	353	358
2	5	C	553	589	2	6	1	2524	2558	1	6	2	1154	1090	0	12	3	135	139	1	1	4	3323	32C2
2	6	C	1475	1522	2	7	1	1660	1631	1	7	2	2C4	135	0	13	3	122	183	1	2	4	2397	2339
2	7	C	2C54	2159	2	8	1	643	552	1	8	2	551	575	0	15	3	74	10	1	3	4	1159	1109
2	8	C	523	532	2	9	1	75	65	1	9	2	822	767	1	0	3	199	373	1	4	4	1242	1224
2	9	C	1994	2C61	2	10	1	612	578	1	10	2	666	646	1	1	3	1296	1247	1	5	4	1124	1C11
2	1C	C	278	164	2	11	1	612	634	1	11	2	736	727	1	2	3	1851	1849	1	6	4	1024	1C56
2	11	C	374	352	2	12	1	555	523	1	12	2	577	542	1	3	3	2246	2240	1	7	4	5C3	450
2	12	C	1C6	42	2	13	1	429	412	1	13	2	138	153	1	4	3	581	604	1	8	4	1346	13C4
2	13	C	260	295	2	14	1	211	215	1	14	2	347	326	1	5	3	1607	1637	1	9	4	551	499
2	14	C	115	43	3	1	1	812	859	1	15	2	153	183	1	6	3	1070	1082	1	10	4	622	598
2	15	C	3CC	3C6	3	2	1	2025	2C36	2	0	2	934	780	1	7	3	653	527	1	11	4	409	403
3	1	C	1765	1719	3	3	1	775	789	2	1	2	23C6	2287	1	8	3	986	987	1	12	4	331	321
3	2	C	2193	2242	3	4	1	156C	201C	2	2	2	15C8	1497	1	9	3	543	509	1	13	4	2C0	248
3	3	C	1483	1568	3	5	1	997	935	2	3	2	225F	2292	1	1C	3	142	151	1	14	4	151	141
3	4	C	897	912	3	6	1	829	825	2	4	2	1174	1287	1	11	3	563	546	2	0	4	151	21
3	5	C	2465	2465	3	7	1	1097	1144	2	5	2	1019	1025	1	12	3	542	545	2	1	4	1175	1161
3	6	C	553	454	3	8	1	1155	1C59	2	6	2	469	473	1	13	3	119	96	2	2	4	1156	1134
3	7	C	1C90	1C57	3	9	1	377	337	2	7	2	344	265	1	14	3	282	285	2	3	4	2526	2482
3	8	C	6C5	574	3	1C	1	440	427	2	8	2	1294	1291	1	15	3	169	248	2	4	4	2034	2C71
3	9	C	195	152	3	11	1	444	476	2	9	2	615	581	2	1	3	1733	1827	2	5	4	810	854
3	10	C	613	565	3	12	1	216	212	2	10	2	1048	1055	2	2	3	1107	1123	2	6	4	601	568
3	11	C	418	4C0	3	13	1	191	18C	2	11	2	384	37C	2	3	3	1011	1122	2	7	4	1048	1032
3	12	C	134	129	3	14	1	184	151	2	12	2	388	111	2	4	3	1309	1291	2	8	4	446	423
3	13	C	352	379	3	15	1	105	132	2	13	2	P6	42	2	5	3	1626	1696	2	9	4	801	717
3	14	C	9C	54	4	0	1	546	861	2	14	2	317	307	2	6	3	849	814	2	10	4	616	64C
4	0	C	237C	2417	4	1	1	1198	1274	3	0	2	518	33C	2	7	3	1346	1398	2	11	4	365	319
4	1	C	177	231	4	2	1	1136	1175	3	1	2	1635	1668	2	8	3	337	398	2	12	4	138	38
4	2	C	1293	12C6	4	3	1	1623	1658	3	2	2	651	58C	2	9	3	668	630	2	13	4	168	173
4	3	C	1C33	584	4	4	1	1311	135C	3	3	2	1130	1108	2	10	3	318	330	2	14	4	95	138
4	4	C	901	955	4	5	1	872	859	3	4	2	624	590	2	11	3	413	393	3	0	4	797	777
4	5	C	95	127	4	6	1	744	726	3	5	2	1046	1110	2	12	3	180	193	3	1	4	1274	1141
4	6	C	149C	1645	4	7	1	710	655	3	6	2	1140	1201	2	13	3	486	499	3	2	4	973	994
4	7	C	224	264	4	8	1	344	320	3	7	2	274	753	2	14	3	195	184	3	3	4	1119	1143
4	8	C	744	789	4	9	1	663	625	3	8	2	957	1017	3	0	3	44C	453	3	4	4	849	847
4	10	C	272	165	4	10	1	423	425	3	9	2	1376	1252	3	1	3	249	100	3	5	4	1254	1389
4	11	C	135	141	4	11	1	234	237	3	1C	2	143	132	3	2	3	943	876	3	6	4	747	6C6
4	12	C	224	277	4	12	1	63	62	3	11	2	3C6	262	3	3	3	1188	1288	3	7	4	912	863
5	1	C	77C	760	4	13	1	164	16C	3	12	2	345	357	3	4	3	846	821	3	8	4	658	725
5	2	C	525	877	4	14	1	10C	117	3	13	2	11C	11F	3	5	3	1188	1306	3	9	4	303	227
5	3	G	196	272	5	0	1	687	647	3	14	2	274	298	3	6	3	1514	1601	3	10	4	438	340
5	4	C	1248	1285	5	1	1	1293	1267	4	C	2	2C3	239	3	7	3	9CC	910	3	11	4	321	31C
5	6	C	412	379	5	2	1	1639	1C34	4	1	2	1555	1511	3	8	3	681	661	3	12	4	184	213
5	8	C	348	388	5	3	1	531	461	4	2	2	492	571	3	9	3	503	400	3	13	4	144	179
5	10	C	195	230	5	4	1	767	757	4	3	2	104	31	3	10	3	138	279	4	0	4	1129	1018
5	11	C	172	211	5	5	1	586	557	4	4	2	61F	546	3	11	3	377	432	4	1	4	521	492
6	1	C	655	748	5	6	1	387	375	4	5	2	545	1031	3	12	3	541	491	4	2	4	516	544
6	3	C	587	614	5	7	1	450	379	4	6	2	82F	711	4	0	3	497	349	4	3	4	414	428
6	4	C	74	4C	5	8	1	424	365	4	7	2	1480	151C	4	1	3	807	746	4	4	4	930	548
6	6	C	142	12C	5	9	1	353	379	4	8	2	2F3	263	4	2	3	1250	1212	4	5	4	83C	788
6	7	C	365	325	5	10	1	66	153	4	9	2	260	263	4	3	3	808	863	4	6	4	9C5	949
6	8	C	88	1	5	11	1	182	163	4	10	2	134	8C	4	4	3	1389	1451	4	7	4	433	343
6	9	C	29C	35C	6	0	1	739	738	4	11	2	266	314	4	5	3	835	852	4	8	4	271	248
7	2	C	226	243	6	1	1	620	6C7	4	12	2	265	263	4	6	3	142	151	4	9	4	185	13C
7	4	C	211	231	6	2	1	520	524	4	13	2	294	34C	4	7	3	142	82	4	10	4	135	8C
7	5	C	251	265	6	3	1	240	163	5	C	2	109C	1042	4	8	3	579	607	4	11	4	388	394
7	6	C	91	67	6	4	1	266	7C6	5	1	2	623	57C	4	9	3	134	241	4	12	4	253	303
7	7	C	2C8	269	6	5	1	243	174	5	2	2	723	648	4	10	3	641	639	5	0	4	463	413
8	2	C	105	158	6	6	1	435	432	5	3	2	755	749	5	0	3	943	786	5	1	4	468	416
C	1	1	2435	2450	6	7	1	303	276	5	4	2	6C9	588	5	1	3	889	788	5	2	4	736	633
C	2	1	4857	5711	6	8	1	63	121	5	5	2	7P8	741	5	2	3	533	604	5	3	4	4C3	364
C	3	1	5285	5457	6	9	1	214	155	5	6	2	834	819	5	3	3	1039	970	5	4	4	5C5	545
C	4	1	17C	241	6	10	1	167	133	5	7	2	127	76	5	4	3	363	333	5	5	4	339	393
C	5	1	2374	2336	6	11	1	97	167	5	8	2	274	227	5	5	3	508	504	5	6	4	415	457
C	6	1	2455	2351	7	0	1	275	25C	5	9	2	295	280	5	6	3	366	371	5	7	4	373	352
C	7	1	1372	1324	7	1	1	347	350	5	10	2	255	279	5	7	3	267	281	5	8	4	22C	176
C	8	1	26C	268	7	2	1	257	234	5	11	2	232	272	5	8	3	126	227	5	9	4	339	413
C	9	1	1395	1372	7	3	1	64	72	5	12	2	274	253	5	9	3	447	389	5	10	4	138	237
C	10	1	24C	2C6	7	4	1	227	264	6	C	2	1C1	37	6	0	3	135	95	6	0	4	88	143
C	11	1	453	383						6	1	2	1CC	85	6	2	3	329	240	6	1	4	262	22P

Table 3. Continued.

H	K	L	F(C)	F(O)	H	K	L	F(C)	F(O)	H	K	L	F(C)	F(O)	H	K	L	F(C)	F(O)	H	K	L	F(C)	F(O)
6	2	4	511	520	2	2	5	1529	1461	0	8	6	1803	1837	3	5	6	654	595	3	2	7	346	305
6	3	4	468	507	2	3	5	243	155	0	9	6	686	606	3	6	6	278	227	3	3	7	493	486
6	4	4	379	384	2	4	5	1262	1339	0	10	6	496	456	3	7	6	511	628	3	4	7	375	381
6	5	4	114	176	2	5	5	410	777	0	11	6	1006	1062	3	8	6	482	499	3	5	7	327	385
7	1	4	157	238	2	6	5	1767	1734	0	13	6	336	361	3	9	6	339	330	3	6	7	548	655
7	2	4	231	265	2	7	5	178	118	1	0	6	577	855	3	10	6	162	285	3	7	7	145	155
7	3	4	112	155	2	8	5	647	664	1	1	6	1040	998	0	1	7	377	314	0	0	8	741	812
7	4	4	116	170	2	9	5	273	233	1	2	6	1670	1624	0	2	7	684	627	0	2	8	543	567
0	1	5	1565	1615	2	10	5	253	264	1	4	6	1228	1164	0	3	7	303	266	0	3	8	249	142
0	2	5	288	351	2	11	5	158	58	1	5	6	803	810	0	4	7	564	907	1	0	8	569	674
0	3	5	3105	2938	2	12	5	346	434	1	6	6	352	283	1	1	7	681	646	1	1	8	647	718
0	4	5	293	167	3	0	5	573	474	1	7	6	617	594	1	2	7	468	489	1	2	8	353	403
0	5	5	301	444	3	1	5	735	770	1	8	6	498	497	1	3	7	600	781	1	3	8	535	559
0	6	5	308	305	3	2	5	1544	1635	1	9	6	123	203	1	4	7	167	142	1	4	8	338	368
0	7	5	1356	1347	3	3	5	405	352	1	10	6	374	400	1	5	7	386	415	1	5	8	416	501
0	9	5	1035	930	3	4	5	1383	1342	1	11	6	403	423	1	6	7	520	453	1	6	8	308	482
1	0	5	352	558	3	5	5	1091	1058	1	12	6	141	225	1	7	7	352	340	2	0	8	156	86
1	1	5	1554	1652	3	6	5	248	234	2	1	6	1160	1209	1	8	7	432	509	2	1	8	265	253
1	2	5	1602	1557	3	7	5	466	365	2	3	6	1364	1467	1	9	7	365	446	2	2	8	613	714
1	3	5	445	442	3	8	5	356	350	2	4	6	837	796	2	0	7	598	571	2	3	8	365	420
1	4	5	1663	1758	3	9	5	217	210	2	5	6	459	465	2	1	7	720	783	2	4	8	567	659
1	5	5	1813	1791	3	11	5	252	252	2	6	6	330	252	2	2	7	238	236	2	5	8	88	111
1	7	5	824	836	3	12	5	177	67	2	7	6	395	425	2	3	7	135	76	2	6	8	238	346
1	8	5	780	699	3	13	5	64	185	2	8	6	254	193	2	4	7	131	170	3	1	8	262	326
1	9	5	141	262	0	0	6	1917	1771	2	9	6	614	672	2	5	7	618	691	3	2	8	200	157
1	10	5	530	542	0	1	6	996	871	2	10	6	410	450	2	6	7	222	243	3	3	8	445	614
1	11	5	450	438	0	2	6	1114	1041	2	11	6	196	212	2	7	7	652	750	3	4	8	177	135
1	12	5	178	75	0	4	6	588	934	3	1	6	773	873	2	8	7	193	192	3	5	8	293	389
1	13	5	206	331	0	5	6	312	155	3	2	6	700	626	2	9	7	222	254	0	1	9	435	528
2	1	5	513	600	0	6	6	1182	1084	3	3	6	501	576	3	0	7	498	553	0	2	9	324	474
					0	7	6	1635	1575	3	4	6	532	565	3	1	7	479	468					

RESULTS AND DISCUSSION

The molecules are arranged in helices around the screw axis parallel to c, as shown in Fig. 1, and are in these helices bonded together through hydrogen bonds of length 2.48 Å between the hydroxyl group of one molecule and the oxo atom of the next. Similarly short hydrogen bonds have been found in phosphoric acid and derivatives.[2,3] All other bonding between molecules seems to be due to van der Waals' forces only. The shortest such contacts are 3.65 Å between oxygen atoms, 3.60 Å between oxygen atom and carbon atom, and 3.84 Å between carbon atoms. This may explain the strong thermal vibrations at room temperature, and the low melting point (54.5°C). The crystal structure can thus be described as a packing on parallel infinite helices, the monomers being held together in the helix by one strong hydrogen bond per pholanic acid unit.

The bond lengths and valence angles are shown on Figs. 1 and 2, and in Table 4. The two phosphorus oxygen bonds show a marked difference in length, the "double bond" is 1.473±0.010 Å, while the "single bond" is 1.567±0.006 Å. Both values are in good agreement with the lengths reported in other compounds, *i.e.* 1.57 Å and 1.44 Å in methyl ethylene phosphate.[4]

The two phosphorus-carbon bonds are not significantly different, their mean length is 1.786±0.017 Å. It should be expected, as found, that these bonds are shorter than the bonds in trimethylphosphine (1.84 Å),[5] because the neighbouring phosphorus-oxygen bonds must induce a certain amount of polarity. They should, on the other hand, be longer than the phosphorus-carbon bonds in the methyl phenyl pholanium ion,[6] (mean bond length 1.77 Å) where the phosphorus atom has a net positive charge.

The carbon-carbon bonds are found as short as 1.43 Å, 1.43 Å, and 1.49 Å, respectively, with standard deviations 0.029, 0.022, and 0.019 Å.

As the phosphorus-oxygen and the phosphorus-carbon bond lengths are quite reasonable, it seems rather remarkable that the carbon-carbon bonds
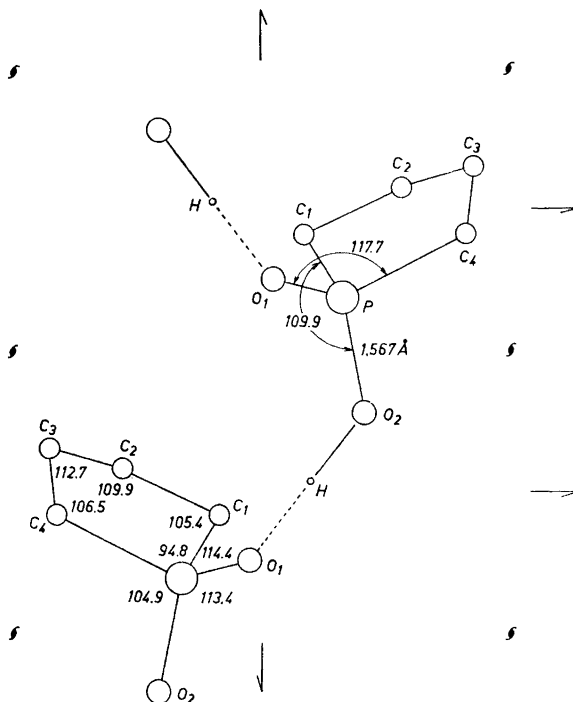
Fig. 2. The *a* projection, with valence angles (°). For clarity, two of the angles at the phosphorus atom are indicated on the molecule to the right. (Axis *b* horizontal).

show such large deviations from normal length. In similar cases it has been suggested that such "short bonds" might be due to the simplifying approximations frequently used in the least squares computations.[7] In the present case the least squares computations were first carried out with a block diagonal approximation, and then repeated with the "full matrix" method. The two resulting parameter sets were not significantly different.

Most probably the low values obtained for the lengths of these "short bonds" are due to the strong anisotropic thermal vibrations. Corrections may be estimated, but in the present case a more extensive analysis might be needed. It seems likely that the true anisotropic vibrations are far from being elliptical. A certain amount of disorder can hardly be ruled out, at a temperature only 30° below the melting point. Besides, a better approximation to the true electron density might be obtained during the computation process by moving carbon and hydrogen atoms relatively to each other, at the same time modifying the thermal parameters. It is felt that further investigations, also including a complete structure determination at low temperature, would be of interest.

Table 4. Bond distances, with standard deviation, and valence angles in the phospholanic acid molecule. The estimated standard deviations in the angles are between 0.5° (the angles at the phosphorus atom) up to 1.5° (angles at carbon atoms in the ring).

	l (Å)	$\sigma\ (l)$ (Å)	Angle	(°)
$P-O_1$	1.473	0.010	O_1-P-O_2	113.4
$P-O_2$	1.567	0.006	O_1-P-C_1	114.4
$P-C_1$	1.776	0.015	O_1-P-C_4	117.7
$P-C_4$	1.797	0.020	O_2-P-C_1	109.9
C_1-C_2	1.487	0.019	O_2-P-C_4	104.9
C_2-C_3	1.429	0.022	C_1-P-C_4	94.8
C_3-C_4	1.433	0.029	$P-C_1-C_2$	105.4
			$C_1-C_2-C_3$	109.9
			$C_2-C_3-C_2$	112.7
			C_3-C_4-P	106.5

The angle in the ring at the phosphorus atom is 94.8°, as also found in methyl phenyl phospholanium iodide.[6] The phosphorus-oxygen double bond seems to be nearer to the normal to the plane through the phosphorus atom and the two neighbouring carbon atoms than the phosphorus oxygen single bond. It seems that the angles at the carbon atoms nearest to the phosphorus atom are smaller than the two other angles in the ring, but the inaccuracy of the parameters of the carbon atoms introduces some doubt on this point.

The five-membered ring is non-planar, and asymmetrical. The torsion angles around the bonds of the ring, starting at a phosphorus-carbon bond, ($P-C_1$), are 14°, 30°, 36°, 24°, and 5°. As the angle between the normal to the plane through P, C_1, and C_4, and the normal to the plane through P, C_4, and C_3 is only 5°, the four atoms P, C_1, C_3, and C_4 are lying nearly in a plane.

In the phenyl methyl phospholanium ion the torsion angles were found to be 17°, 36°, 40°, 26°, and 5°, taken in the same order. The two rings thus do not seem significantly different. The torsion angles in methyl ethylene phosphate [4] seem somewhat smaller, 11°, 20°, 20°, 13°, and 2°, but the ring conformation is in principle the same.

In the solid state there should exist two mirror isomers of phospholanic acid, but only one of the forms is present in a single crystal of the symmetry $P2_12_12_1$.

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