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Molecular Structures of Amino Acids and Peptides.
I. The Crystal Structure and Conformation of DL-*O*-Serine Phosphate Monohydrate. Very Short Phosphate–Phosphate Hydrogen Bonds

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DL-*O*-Serine phosphate monohydrate crystallizes from aqueous solution in the space group *C*2/*c* with unit-cell dimensions *a* = 18·473 ± 0·0006, *b* = 8·327 ± 0·0002, *c* = 12·300 ± 0·0004 Å, *β* = 120·72 ± 0·0015°. For eight formula units of the monohydrate per unit cell, the calculated density of 1·661 g.cm^{-3} is in agreement with the observed density of 1·668 g.cm^{-3}. The crystal structure was determined by the heavy-atom method using 1092 observed diffractometer intensities. Isotropic and anisotropic full-matrix least-squares refinement gave an *R* index of 0·03. The molecule exists as a zwitterion, $\mathrm{H\overset{-}{O}_3POCH_2CH(\overset{+}{N}H_3)COOH}$. The amino group is protonated by a phosphate proton and the carboxyl group is not ionized. The ester C–O bond is *gauche* both to the C–N bond and the C(1)–C(2) bond. The two shortest hydrogen bonds between center-related (2·498 Å) and diad-related (2·506 Å) phosphates generate a right-handed spiral. These hydrogen bonds are symmetrical with either a single or equivalent double minima. The P–O bonds (1·530 and 1·522 Å) associated with the short hydrogen bonds are intermediate in character to the normal P–OH (1·554 Å) and the P=O (1·490 Å) bond distances. A relatively short hydrogen bond, –C–O–H···O=P–, of 2·595 Å occurs between the carboxyl and the phosphate groups.

Introduction

Detailed knowledge of the structural and hydrogen-bonding properties of biological phosphates is of considerable importance in understanding their hydrolytic behavior and their role in biological phosphorylation and related processes. The structure analysis of DL-serine phosphate monohydrate was undertaken as part of a program of studies, currently in progress in our laboratory, on the structures of amino acid derivatives and cell-membrane components. A preliminary report on the structure has already been published (Putkey & Sundaralingam, 1968). Serine phosphate is unique among the amino acid phosphates, for it occurs both in the membrane proteins and the membrane phospholipid, phosphatidylserine. It has been suggested that this versatility of serine phosphate is probably a result of its *β*-hydroxyamine chain, $\overset{+}{\mathrm{N}}$–C–C–O, which is a common structural feature of the major phospholipids, sphingolipids, anaesthetics, cholinergists and other nerve and brain amines (Sundaralingam, 1968). In batrachotoxinin A, a steroidal alkaloid from the venom of the Columbian poison arrow frog, an *N*-substituted N–C–C–O chain links the 13 and 14 positions of the steroid (Tokuyama, Daly, Witkop, Karle & Karle, 1968). Indeed, the $\overset{+}{\mathrm{N}}$–C–C– and the $\overset{+}{\mathrm{N}}$–C–C–O chains are common structural features of various alkaloids, brain amines and membrane molecules.

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Experimental

DL-Serine phosphate monohydrate, $C_3NO_6PH_8.H_2O$, purchased from Sigma Chemical Company, gave colorless rectangular prismatic crystals upon recrystallization from water at room temperature. Preliminary Weissenberg and precession photographs showed the systematic extinctions *hkl* absent for $h+k$ odd and *h0l* absent for *l* odd. The space group is therefore *C*2/*c* or *Cc*. The former space group was chosen and confirmed by the structure analysis. Precise unit-cell constants (Table 1) were determined by the method of least squares from the angular settings of eighteen independent reflections measured on a Picker four-angle diffractometer. The calculated density of 1·661 g.cm^{-3} for eight formula units per unit cell is in good agreement with that of 1·668 g.cm^{-3} measured by the method of flotation in a mixture of chloroform and bromoform.

A crystal of uniform thickness, about 0·15 mm wide and about 0·5 mm long, was used for the data collection on the Picker four-angle diffractometer which was operated on a 2θ scan mode and a scan speed of 1° per minute. Ni-filtered copper $K\alpha$ radiation was employed. Altogether, there were 1097 observed reflections significantly above background, and these were utilized in the structure analysis. Absorption corrections were not applied. The intensities were corrected only for Lorentz and polarization factors, and for the 4% fluctuations observed in the standard reflection.

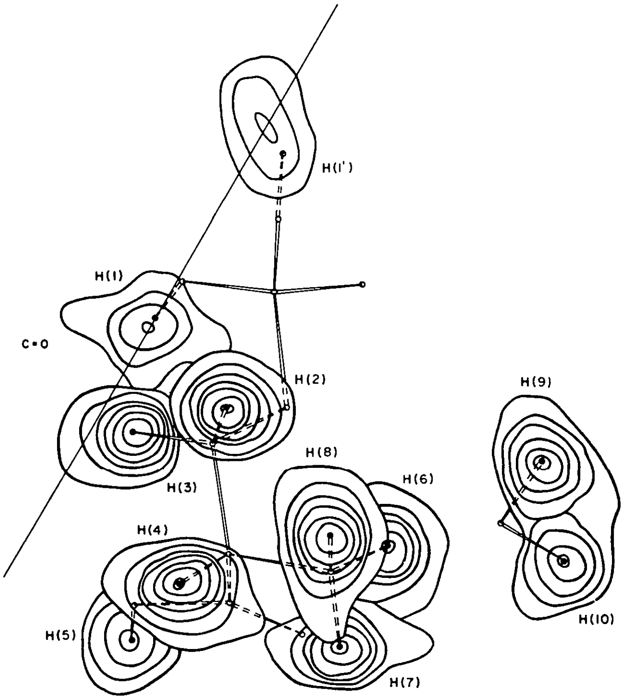


Fig. 1. Difference density distribution showing the hydrogen atoms. Contours are drawn at intervals of 0·1 e.Å^{-3}, beginning at 0·1 e.Å^{-3}.

Table 1. *Crystal data*

Crystal system	Monoclinic
Space group (by structure analysis)	*C*2/*c* *hkl*, $h+k=2n$ *h0l*, $l=2n$
a	18·473 ± 0·0006 Å
b	8·327 ± 0·0002
c	12·300 ± 0·0004
β	120·72 ± 0·0015°
V	1626·0 Å^3
Z	8
D_m	1·668 g.cm^{-3}
D_x	1·661 g.cm^{-3}
Dimensions of crystal used in data collection	0·15 × 0·15 × 0·5 mm

Determination of the crystal structure

The three-dimensional Patterson synthesis revealed distinctly the P–P interaction, which was of height 3000 relative to the origin peak of 8800, on the Harker section at $y=0$. The phosphorus *x* and *z* coordinates were obtained from this section. The *y* coordinate was calculated from the peak of height 2400 on the Harker line at $0,y,\frac{1}{2}$. A Fourier electron density calculation based on the phosphorus position alone showed the phosphate group. A second Fourier synthesis phased on the phosphate group revealed the molecule and the hydrate oxygen atom.

Refinement of the structure

Three isotropic full-matrix least-squares cycles on the non-hydrogen atom coordinates using the Oak Ridge National Laboratory least-squares program *ORFLS* (Busing, Martin & Levy, 1964) gave an *R* index of 0·09. A weighting scheme modelled on that of Hughes (1941) was used in the least-squares refinement. This weighting system placed virtually unit weights on approximately 63 per cent of the reflections, and this was justified, *a posteriori*, by the distribution of weighted residuals as a function of the magnitude of *F*. One anisotropic least-squares cycle, followed by a difference Fourier synthesis, Fig. 1, revealed eight hydrogen peaks of nearly equal density and a ninth peak of somewhat lower density. The former peaks were assigned to aliphatic, ammonium and water hydrogen atoms, while the latter was assigned to the carboxyl hydrogen atom. Two still lower hydrogen peaks appeared between phosphate groups related by a symmetry center and a diad. The phosphate oxygen atoms involved with the latter hydrogen atoms were separated by rather short distances of about 2·50 Å. The hydrogen electron density associated with the diad axis was dumb-bell-shaped with two slight maxima on either side of the axis and in the direction of the oxygen atoms, while that associated with the symmetry center at the origin had only a single maximum on the origin. In the subsequent least-squares cycles, these two hydrogen atoms were fixed on the respective symmetry elements and given half weights. The hydrogen atoms were given the

Table 2. *Calculated and observed structure factors* × 10

Reflections marked with an asterisk were suspected of secondary extinction and were not included in the least-squares refinement.

H,0,-14		
6	264	266
10	184	173
12	545	-536
14	385	-384
H,0,-12		
0	467	-450
4	91	-107
6	309	310
8	511	512
10	153	154
12	240	-236
14	782	-789
16	136	-117
18	236	247
H,0,-10		
0	666	-686
2	764	-783
4	100	101
6	101	-114
8	474	478
10	110	-123
12	330	-315
14	268	-258
16	100	-85
18	126	-122
20	113	121
H,0,-8		
0	128	-122
2	1015	-1046
4	485	-483
6	233	240
8	146	-146
10	93	-83
14	405	-416
16	562	-564
18	174	-175
20	108	194
H,0,-6		
0	258	-257
2	932	-921
8	148	-141
10	869	878
12	653	645
14	548	-552
16	1047	-1078
18	260	-249
20	235	232
H,0,-4		
0	860	-857
4	1129	-1174
6	996	1056
8	123	-95
10	590	613
12	963	937
14	769	762
16	602	-608
18	312	-302
H,0,-2		
0	115	60
2	303	307
4	1421	-1479
8	366	305
10	565	551
12	537	531
14	482	484
16	841	828
18	442	-425
20	247	-238
H,0,0		
2	215	181
4	1167	-1191
6	518	-578
8	589	593
10	407	-400
12	669	665
14	405	398
16	139	122
H,0,2		
2	2779	2867
4	149	149
6	112	98
8	89	-69
10	99	93
12	329	-332
14	690	691
16	213	205
H,0,4		
4	646	674
6	502	493
8	606	-623
10	514	-514
12	114	107
14	262	246
H,0,6		
2	848	867
4	399	390
6	558	-574
8	442	-434
10	198	-206
12	218	-234
H,0,8		
2	436	435
4	369	376
8	157	-159
H,0,10		
2	197	-172
4	336	351
6	215	212
H,1,-14		
9	169	105
13	185	-179
15	85	89
H,1,-13		
9	261	-254
11	437	-436
13	92	-93
15	511	518
17	309	312
H,1,-12		
5	96	92
7	142	-130
9	179	-177
15	201	-216
19	200	210
H,1,-11		
1	103	91
3	373	370
5	668	668
7	326	321
9	362	-365
11	680	-680
15	261	248
17	300	310
H,1,-10		
1	293	-293
3	278	274
5	177	-168
11	100	99
13	415	-414
15	232	-229
17	186	-191
21	117	127
H,1,-9		
1	272	-271
3	151	154
5	545	534
7	138	-138
9	257	255
11	313	-317
13	438	-427
17	323	319
19	149	162
21	135	127
H,1,-8		
1	649	-654
3	508	-491
5	330	325
9	151	169
13	95	87
15	596	-609
17	117	104
H,1,-7		
1	190	-205
5	198	200
7	96	-86
9	577	-566
11	140	146
13	457	-456
15	738	-753
17	123	128
19	743	743
H,1,-6		
3	545	-548
5	135	-132
7	385	-379
11	100	126
13	176	170
15	188	193
17	294	-314
H,1,-5		
1	1205	-1256
3	1229	1279
5	213	-208
7	301	300
9	253	243
11	548	-547
13	1124	-1145
15	175	-171
17	176	-170
19	149	151
21	241	247
H,1,-4		
1	289	-295
3	269	283
5	186	-204
7	256	261
9	852	-836
11	447	442
13	255	282
17	181	-177
21	108	101
H,1,-3		
1	1506	-1579
*3	1622	-1707
5	316	303
7	1106	1110
9	700	697
11	191	178
13	542	-543
15	743	-736
19	103	-106
H,1,-2		
1	637	613
3	803	-857
5	587	595
7	870	826
9	606	622
11	294	-286
13	317	313
15	124	117
17	101	-101
H,1,-1		
1	505	-429
3	2606	-2748
5	830	-855
9	1001	1008
11	319	317
13	405	409
15	387	-374
17	448	-447
19	82	-82
H,1,0		
1	343	328
7	534	518
9	264	263
11	308	311
13	146	139
15	273	257
17	115	111
H,1,1		
1	350	-348
3	1088	-1056
5	267	239
9	289	-299
11	407	412
13	530	533
17	366	-376
H,1,2		
1	1179	1208
3	497	507
5	209	-215
7	349	-338
11	94	-99
13	338	334
15	180	175
17	89	93
H,1,3		
1	478	-514
3	789	778
11	503	500
13	187	196
15	170	162
H,1,4		
1	1296	1308
3	202	226
5	175	-172
7	194	-194
11	106	-110
13	182	-180
H,1,5		
1	1331	1391
5	641	-645
7	183	-203
9	130	147
11	519	509
13	336	336
H,1,6		
1	425	-440
3	380	376
5	130	-123
7	175	176
9	127	-131
H,1,7		
1	862	879
3	217	211
5	515	-514
7	400	-395
H,1,8		
1	120	-111
5	103	97
7	132	-129
H,1,9		
1	515	523
3	136	147
5	129	121
7	195	-209
H,1,10		
1	181	-169
H,1,11		
1	114	130
3	380	385
H,1,12		
1	101	-111
H,2,-14		
12	319	317
14	325	337
H,2,-13		
4	101	96
12	184	176
14	249	265
H,2,-12		
0	121	118
4	111	123
6	453	-442
8	253	-265
12	188	189
14	273	285
16	240	266
18	290	-285
H,2,-11		
0	120	123
2	192	186
4	118	101
6	184	-190
8	133	129
10	193	-188
12	175	-174
18	260	269
H,2,-10		
0	472	446
2	285	272
4	208	208
6	115	-122
8	780	-782
12	425	449
14	177	162
18	320	321
20	254	-258
H,2,-9		
2	159	161
4	380	364
6	168	165
8	84	76
10	102	-96
12	785	-809
14	333	-346
16	139	151
18	402	425
H,2,-8		
0	218	-218
2	1149	1149
4	204	191
6	355	-352
8	553	-545
14	331	335
16	258	250
H,2,-7		
0	577	-580
2	492	483
6	390	376
8	145	-143
12	340	-347
14	285	-297
16	328	-347
H,2,-6		
0	241	221
2	96	-110
4	615	632
8	161	147
10	935	-943
12	136	-152
16	622	653
18	213	213
H,2,-5		
0	1589	-1634
2	967	-979
4	116	107
6	437	-426
8	389	-384
10	161	164
12	133	118
14	434	-450
16	178	-184
18	144	-154
20	103	110
H,2,-4		
0	434	435
2	391	-381
4	453	441
6	762	769
8	98	71
10	520	-501
12	972	-965
14	98	79
16	312	318
18	304	291
H,2,-3		
0	183	-172
2	2010	-2156
4	718	-769
6	110	-117
10	628	-628
14	453	-476
16	263	-280
18	161	155
20	259	237
H,2,-2		
0	539	-538
2	221	248
4	252	238
*6	1557	1654
8	232	-229
10	694	-686
14	162	-150
16	221	-214
18	207	196
H,2,-1		
0	734	-717
4	928	983
6	310	-330
8	222	-214
10	421	428
14	201	-199
16	271	-280
H,2,0		
*0	1899	-1988
2	586	-608
4	1001	1023
6	203	177
8	536	556
12	397	-392
14	124	-115
16	147	-157
H,2,1		
2	168	-135
4	475	-474
6	954	938
10	321	322
12	544	566
14	275	276
16	316	-304
H,2,2		
2	639	-612
4	721	-704
6	413	402
8	354	358
10	543	561
12	193	-188
14	532	-537
16	93	-86
H,2,3		
2	183	-176
4	865	-891
6	93	-65
8	508	512
10	389	390
12	129	121
14	282	291
H,2,4		
2	206	-228
4	438	-437
6	414	-402
8	740	743
10	236	228
14	319	-315
H,2,5		
2	82	-64
4	128	-110
10	189	-185
12	263	265
H,2,6		
2	303	-288
4	488	-495
6	93	-61
8	258	268
10	277	278
H,2,7		
2	737	745
4	344	351
6	242	-246
10	85	-77
H,2,8		
2	282	-269
4	318	-332
6	115	-121
8	106	-102
H,2,9		
2	226	227
H,2,10		
4	150	-141
H,2,11		
2	146	153
H,3,-13		
7	134	129
9	335	334
11	158	165
13	195	-191
15	132	-134
H,3,-12		
1	214	192
7	240	-242
9	348	344
13	260	270
15	214	220
H,3,-11		
1	156	149
3	141	-125
5	192	-194
9	303	297
11	439	439
13	90	80
15	226	-218
17	124	-111
19	107	-96
H,3,-10		
1	426	404
3	125	-116
5	128	-130
9	301	-310
11	180	178
13	374	379
15	434	436
17	153	164
H,3,-9		
1	422	428
5	909	-926
7	187	-191
9	435	438
11	314	324
13	124	131
15	89	85
17	226	-209
19	279	-266
H,3,-8		
1	506	500
3	821	821
7	390	-388
9	503	-517
11	239	-235
13	225	231
15	527	553
17	115	110
H,3,-7		
1	185	-172
3	181	-175
5	444	-436
7	675	-672
9	159	143
11	159	147
13	114	-106
15	140	118
17	80	83
19	301	-301
H,3,-6		
1	168	152
3	709	694
5	794	783
7	399	398
9	774	-785
11	291	-289
13	105	-105
15	86	93
17	156	155
19	151	142
H,3,-5		
1	342	340
3	259	-259
5	144	141
7	487	-487
9	947	-924
13	369	372
19	121	-123
H,3,-4		
1	678	-669
3	430	435
7	142	122
9	550	549
11	382	-376
13	398	-409
15	81	-82
17	354	356
H,3,-3		
1	453	-413
3	1341	1333
5	249	243
7	1162	-1156
9	918	-872
11	175	179
13	424	410
15	82	69
17	117	-102
H,3,-2		
1	765	801
3	967	-1004
5	303	338
7	760	-736
11	386	-397
13	127	-119
15	309	-296
17	228	230
19	204	211
H,3,-1		
1	158	-134
3	125	131
5	359	334
7	305	-301
9	555	-532
11	145	-131
13	192	181
15	105	102
17	127	129
H,3,0		
1	857	-886
3	576	606
5	114	-88
7	361	356
9	372	-366
11	370	-379
13	717	-707
17	170	-180
H,3,1		
3	340	343
5	457	473
7	164	161
11	306	-314
13	348	-361
15	241	239
17	379	376
H,3,2		
*1	1420	-1511
3	645	-639
5	135	131
7	977	995
9	158	145
15	408	-417
H,3,3		
1	689	670
3	84	-61
5	623	633
7	861	893
9	294	-311
11	412	-413
13	92	74
H,3,4		
1	618	-612
3	570	-566
9	526	526
11	218	204
13	91	98
H,3,5		
1	101	-102
3	137	132
5	302	300
7	417	419
9	368	374
11	278	-281
H,3,6		
3	351	-333
5	176	-167
7	104	-103
11	311	309
H,3,7		
1	530	-540
3	381	-393
5	280	280
7	313	319
9	89	97
H,3,8		
1	303	299
5	193	-204
7	93	-96
H,3,9		
3	85	-74
5	193	-188
H,3,10		
1	273	287
H,4,-13		
10	180	183
H,4,-12		
6	190	185
8	116	118
10	281	-257
H,4,-11		
4	402	-391
6	179	-171
8	299	310
10	552	549
18	345	-349
H,4,-10		
0	96	90
6	189	191
8	613	616
10	233	227
12	381	-369
H,4,-9		
0	115	112
2	190	-179
4	206	-203
6	216	-223
8	188	-194
10	193	196
12	770	785
14	138	132
16	212	-203
18	202	-205
H,4,-8		
0	158	-156
2	401	-377
4	235	-248
6	667	667
8	419	423
10	472	452
14	91	-72
18	87	-84
H,4,-7		
0	159	155
2	257	253
6	960	-987
8	226	-221
10	200	208
12	301	296
14	274	277
16	264	256
18	213	-221
H,4,-6		
0	88	76
2	220	-214
4	139	-129
6	274	-273
8	333	331
12	456	431
18	189	-175
H,4,-5		
0	1029	1031
2	483	465
6	557	-550
8	576	-612
10	147	143
12	399	402
18	233	237
H,4,-4		
0	169	178
2	533	511
4	121	-128
6	857	-837
8	421	-440
10	362	363
16	335	-324
H,4,-3		
0	80	-89
2	1115	1124
4	338	330
6	92	-97
8	563	-555
10	117	-73
12	149	-143
14	541	565
16	142	131
18	90	-85
H,4,-2		
0	120	-108
2	281	265
4	430	-409
6	627	-614
8	128	-120
10	379	367
12	154	-154
14	275	-280
16	100	-96
18	219	-212
H,4,-1		
0	425	-403
2	163	-145
4	328	315
6	798	802
8	622	-630
10	817	-785
14	305	292
16	403	396
H,4,0		
0	214	-220
2	650	-644
4	375	-355
6	416	-412
8	304	-295
12	115	117
H,4,1		
2	295	-301
4	709	710
10	702	-698
12	177	-183
16	190	195
H,4,2		
4	357	-335
6	236	-249
8	603	-596
10	397	-396
12	134	139
14	346	343
H,4,3		
2	223	203
4	566	560
6	481	483
10	234	-218
12	250	-263
14	170	-172
H,4,4		
4	575	592
6	189	-167
8	224	-229
10	267	-270
H,4,5		
2	106	-87
4	228	219
6	491	505
8	289	292
12	347	-343
H,4,6		
4	469	479
6	451	452
8	119	-112
H,4,7		
2	312	-308
4	385	-381
6	222	227
8	349	353
H,4,8		
2	392	399
6	245	245
H,4,9		
2	211	-215
4	186	-205
H,5,-12		
5	304	286
7	393	385
11	133	-136
13	175	-188
H,5,-11		
7	129	-130
11	154	-135
15	200	195
H,5,-10		
1	500	-494
5	235	227
7	466	468
9	132	142
13	218	-216
17	84	-80
H,5,-9		
3	272	274
5	197	213
7	110	106
9	307	-308
13	197	-186
H,5,-8		
1	94	102
3	445	-449
5	190	-183
7	360	359
9	763	790
15	336	-338
H,5,-7		
1	102	-83
3	318	316
5	396	405
7	293	282
9	172	153
13	128	137
15	235	-233
17	111	104
H,5,-6		
1	228	215
3	508	-497
5	656	-638
9	995	985
11	554	569
13	256	-252
15	213	-210
17	245	-246
H,5,-5		
1	123	113
3	148	-154
9	612	602
11	136	129
13	127	133
H,5,-4		
3	423	-423
5	705	-697
7	288	287
9	81	-76
11	321	312
13	248	248
17	322	-323
H,5		
11	194	200
13	196	-194
15	103	101
H,5,-2		
1	425	-420
3	207	194
5	356	-360
7	907	-908
11	241	242
13	219	208
15	111	116
17	127	-119
H,5,-1		
1	165	177
3	108	-116
5	210	215
7	548	550
9	224	-233
11	122	-131
15	125	-116
H,5,0		
1	574	580
3	220	-217
5	522	-498
7	740	-745
9	516	-517
11	486	495
13	393	394
15	152	-143
H,5,1		
1	467	-476
5	131	-137
7	128	128
9	170	158
H,5,2		
1	187	179
3	801	822
5	163	-155
7	895	-874
9	169	-154
13	169	179
H,5,3		
1	395	-389
3	397	-393
5	165	-167
7	435	-454
11	131	132
13	109	105
H,5,4		
1	389	369
3	123	100
5	521	545
7	98	-88
9	574	-575
11	210	-214
H,5,5		
1	325	346
3	255	-272
5	157	-176
7	256	-262
9	123	-122
H,5,6		
1	193	197
3	515	525
7	174	181
9	220	-220
H,5,7		
1	188	199
3	169	173
5	192	-201
7	101	84
H,5,8		
5	448	461
H,5,10		
1	155	-155
H,6,-11		
4	368	351
6	201	191
8	175	-169
10	381	-375
12	161	-157
H,6,-10		
2	142	-138
6	166	-166
8	84	82
H,6,-9		
0	139	-139
4	219	219
6	120	113
8	185	171
12	363	-364
14	99	-97
16	236	227
H,6,-8		
0	135	132
4	160	-152
10	185	-141
12	113	-94
H,6,-7		
0	124	-128
2	120	-121
6	697	695
8	225	209
10	156	-154
12	193	-202
14	130	-123
H,6,-6		
0	85	90
2	371	382
6	223	-243
8	317	321
10	189	201
12	343	-343
16	95	80
H,6,-5		
0	478	-474
2	275	-263
4	503	502
6	664	660
8	630	630
10	118	-126
12	303	-301
14	116	-106
H,6,-4		
0	161	-162
2	132	120
4	109	-104
6	202	201
8	247	-241
10	427	436
12	139	129
H,6,-3		
0	110	-102
2	524	-518
6	564	560
8	514	494
10	427	428
12	151	146
14	271	-272
16	317	-303
H,6,-2		
0	184	-179
4	161	-165
6	133	-135
8	200	182
10	195	-190
12	161	164
16	99	92
H,6,-1		
0	209	-210
2	136	-135
4	609	-615
6	441	-440
8	433	425
10	721	704
12	196	199
14	241	-230
H,6,0		
0	161	170
4	620	609
6	383	-387
14	111	-105
H,6,1		
2	307	-304
4	575	-571
6	428	-445
8	97	85
10	222	222
12	140	143
14	107	-98
H,6,2		
2	194	176
4	296	310
6	211	222
8	346	-344
10	170	160
H,6,3		
4	449	-453
6	347	-346
8	151	-142
10	130	133
H,6,4		
4	237	-254
6	146	148
H,6,5		
4	377	-375
6	342	-346
8	244	-252
H,6,6		
2	181	-191
H,6,7		
2	97	108
6	346	-348
H,6,8		
4	103	95
H,6,9		
2	307	317
H,7,-10		
9	346	-364
H,7,-9		
1	129	-121
5	122	136
7	111	135
11	191	-188
H,7,-8		
1	160	149
3	219	215
7	183	-193
9	147	-162
11	265	-299
13	194	206
H,7,-7		
1	81	67
H,7,-6		
3	187	178
5	312	299
7	204	-196
9	418	-417
11	163	-168
15	214	226
H,7,-5		
1	91	-85
5	151	156
7	219	214
11	108	93
H,7,-4		
1	136	144
3	666	656
5	182	171
9	175	-178
11	242	-245
13	296	-326
H,7,-3		
3	221	-224
5	119	-106
7	673	676
9	179	180
11	115	-111
H,7,-2		
1	119	124
3	447	449
5	556	548
7	296	266
9	212	207
11	113	-115
13	253	-263
H,7,-1		
3	109	102
7	378	-374
9	505	498
H,7,0		
1	473	-477
5	321	331
7	577	569
9	315	329
13	174	-190
H,7,1		
1	285	300
3	241	-239
5	95	-91
7	160	-156
9	139	-151
11	232	229
H,7,2		
1	505	-524
3	396	-432
5	196	194
7	318	340
9	174	191
H,7,3		
1	170	-163
5	424	-418
9	89	90
H,7,4		
1	231	-234
3	284	-282
7	125	113
9	101	110
H,7,5		
1	141	-141
7	122	-124
H,7,6		
1	239	-233
3	150	-143
5	206	-218
H,7,7		
3	157	152
H,7,8		
1	97	-104
H,8,-8		
4	109	102
6	167	-164
8	371	-353
H,8,-7		
4	161	-156
8	234	-221
10	219	216
H,8,-6		
0	112	99
4	147	139
6	150	140
10	378	-366
12	81	67
H,8,-5		
0	308	304
2	207	203
4	250	-239
6	301	-308
10	141	-153
12	208	204
H,8,-4		
0	198	-193
4	207	207
8	174	162
12	246	-241
H,8,-3		
0	421	415
2	380	363
6	424	-404
8	255	-254
10	197	-185
H,8,-2		
2	141	132
4	227	226
6	243	244
H,8,-1		
0	350	349
2	377	373
4	124	122
6	167	154
8	96	-84
10	315	-313
H,8,0		
0	123	-116
4	223	216
6	240	243
8	132	143
H,8,1		
2	145	145
4	452	465
6	182	191
H,8,2		
2	150	-147
4	161	-168
6	331	324
8	291	297
H,8,3		
2	114	100
4	195	207
6	221	237
8	137	-136
H,8,4		
2	178	-183
6	148	-150
H,8,5		
2	111	115
4	230	237
H,8,6		
2	222	-225
H,9,-6		
5	128	-122
H,9,-5		
1	309	302
5	121	-119
7	271	-258
H,9,-4		
3	214	-223
5	180	-175
H,9,-3		
1	135	135
3	260	264
5	100	-88
7	112	-128
9	147	-144
H,9,-2		
1	144	145
3	319	-332
7	159	-1 2
H,9,-1		
1	126	125
5	123	114
7	110	-103
H,9,0		
1	171	172
3	170	177
7	93	-104
H,9,1		
1	149	161
3	272	281
H,9,2		
1	259	276
3	300	314
5	107	-101
H,9,3		
3	312	330
H,9,4		
1	234	253

anisotropic temperature factors of the 'heavy' atoms to which they were bonded. Three anisotropic least-squares cycles, refining the positional parameters of all the atoms and only the thermal parameters of the non-hydrogen atoms, reduced the *R* index to the final value of 0·033.

Table 3. *Final positional coordinates and anisotropic temperature factors* for* DL-*serine phosphate*

Standard deviations are shown in parentheses. All non-hydrogen parameters are $\times 10^5$; all hydrogen parameters are $\times 10^4$.

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	7463 (3)	20739 (7)	−4296 (5)	165 (2)	688 (9)	312 (5)	−1 (3)	113 (3)	−2 (5)
O(1)	12853 (10)	27866 (21)	9602 (14)	207 (6)	1176 (26)	400 (14)	76 (10)	144 (8)	−111 (15)
O(2)	4761 (11)	35021 (21)	−13224 (17)	303 (7)	882 (24)	471 (15)	−33 (11)	197 (9)	72 (15)
O(3)	13406 (11)	9320 (22)	−5212 (15)	295 (7)	1103 (26)	543 (15)	88 (11)	231 (9)	−95 (15)
O(4)	−415 (11)	12797 (24)	−5589 (17)	224 (7)	1162 (29)	705 (17)	−50 (11)	175 (9)	241 (18)
O(5)	10387 (13)	19099 (27)	34738 (21)	315 (8)	1375 (33)	1089 (22)	18 (13)	341 (11)	353 (21)
O(6)	23506 (12)	17107 (23)	38180 (18)	327 (8)	1270 (29)	712 (18)	118 (12)	213 (10)	163 (18)
O(7)	33457 (11)	30545 (22)	24688 (19)	254 (7)	1195 (28)	707 (17)	−36 (11)	260 (10)	−14 (18)
C(1)	16987 (16)	24270 (31)	34478 (22)	262 (10)	1037 (35)	421 (20)	−8 (15)	169 (11)	−51 (22)
C(2)	15216 (15)	40833 (30)	28407 (27)	242 (9)	873 (33)	526 (20)	21 (14)	207 (11)	−62 (21)
C(3)	9162 (16)	39292 (33)	14269 (23)	280 (10)	1089 (38)	481 (21)	160 (15)	184 (12)	−58 (22)
N	23217 (14)	48345 (28)	30896 (22)	260 (8)	919 (31)	630 (20)	−32 (13)	195 (10)	−54 (20)
H(1)	0 (0)	0 (0)	0 (0)						
H(1′)	0 (0)	3502 (0)	−2500 (0)						
H(2)	852 (20)	5083 (41)	984 (30)						
H(3)	313 (22)	3515 (41)	1241 (30)						
H(4)	1273 (19)	4825 (38)	3217 (30)						
H(5)	1150 (22)	826 (51)	3807 (36)						
H(6)	2606 (21)	4154 (41)	2675 (31)						
H(7)	2688 (21)	5047 (39)	4039 (33)						
H(8)	2167 (20)	5876 (44)	2681 (33)						
H(9)	3335 (20)	3433 (40)	1689 (33)						
H(10)	3888 (24)	3317 (42)	3136 (36)						

* Anisotropic thermal parameters are in the form $\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2hl\beta_{13}+2hk\beta_{12}+2kl\beta_{23})\right]$.

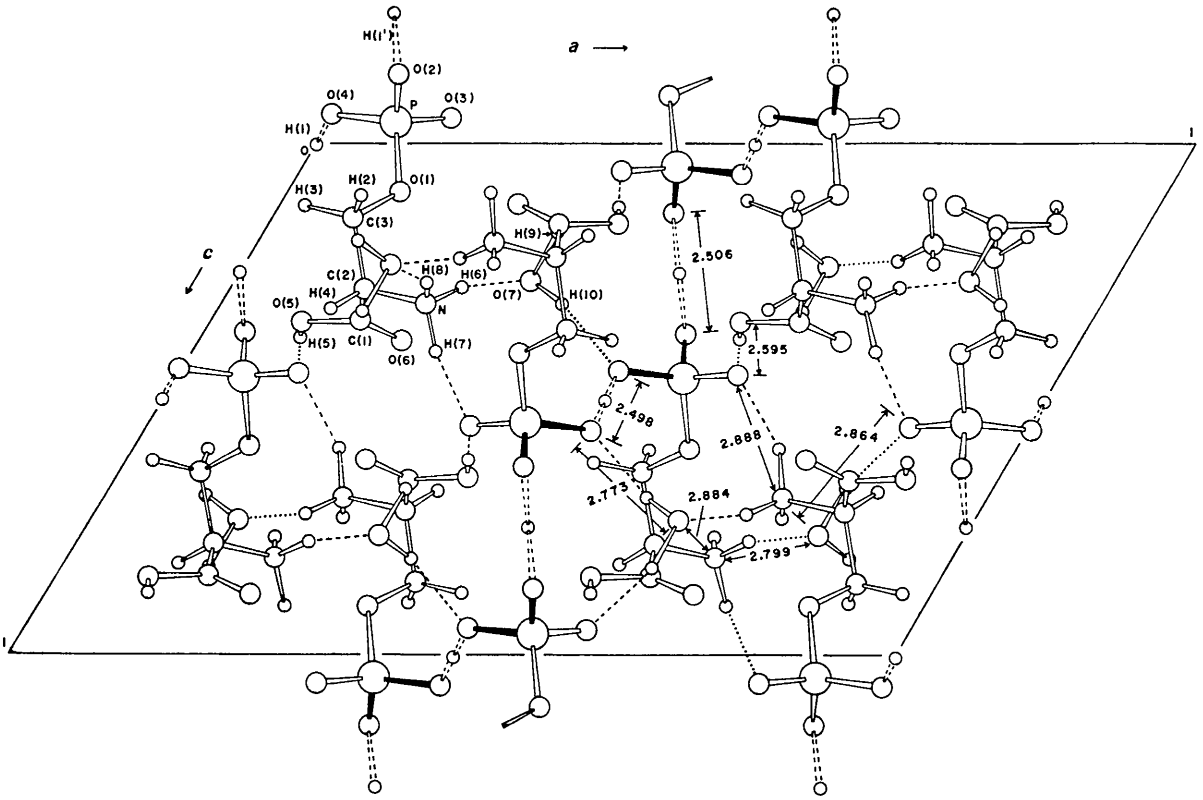


Fig. 2. Crystal packing and hydrogen bonding as viewed down the *b* axis. Solid black lines indicate the P–O bonds involved in the very short hydrogen bonds across the center of symmetry and the diad.

Table 4. *Hydrogen bonds in* DL-*serine phosphate*

Reference molecule	(1)	x	y	z
Symmetry-related molecules:	(2)	$-x$	$-y$	$-z$
	(3)	$-x$	y	$-\frac{1}{2}-z$
	(4)	x	$-y$	$\frac{1}{2}+z$
	(5)	$\frac{1}{2}+x$	$\frac{1}{2}+y$	z
	(6)	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$-z$
	(7)	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
	(8)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$

Key to notation
$A_1—A_2—H\ldots A_3—A_4$

Reference molecule			Symmetry molecule			Distances			Angles				
A_1	A_2	H	No.†	A_3	A_4	A_2H	A_3H*	A_2A_3*	$A_1A_2A_3$	A_2HA_3	HA_2A_3	$A_2A_3A_4$	HA_3A_4
P	O(4)	H(1)	2	O(4)	P	1·249 Å	1·249 (0·07) Å	2·498 (0·003)	121·57°	180·0°	0·0°	121·57°	121·57°
P	O(2)	H(1′)	3	O(2)	P	1·253	1·253 (0·05)	2·506 (0·002)	127·80	180·0	0·0	127·80	127·80
C(3)	O(5)	H(5)	4	O(3)	P	0·917	1·681 (0·04)	2·595 (0·003)	109·60	174·42	3·61	128·80	128·70
H(10)	O(7)	H(9)	6	O(3)	P	0·986	1·905 (0·04)	2·864 (0·003)	94·99	163·50	10·89	110·16	114·30
C(2)	N	H(7)	7	O(3)	P	1·019	1·949 (0·02)	2·888 (0·002)	125·58	151·74	18·64	113·27	122·73
C(2)	N	H(8)	7	O(7)	H(10) H(9)	0·929	2·046 (0·03)	2·885 (0·003)	94·77	149·13	21·35	106·53 124·42	115·23 122·58
H(9)	O(7)	H(10)	8	O(4)	P	0·901	1·873 (0·03)	2·773 (0·002)	104·65	176·24	2·54	122·97	124·02
C(2)	N	H(6)	1	O(7)	H(10) H(9)	0·967	1·846 (0·03)	2·798 (0·002)	117·43	167·67	8·10	101·16 113·62	105·39 112·14

* Standard deviations are given in parentheses.
† This number refers to the symmetry operation at the top of the Table.

An attempted refinement of the half-hydrogen atoms statistically disordered across the symmetry center and the diad did not show a significant improvement in the

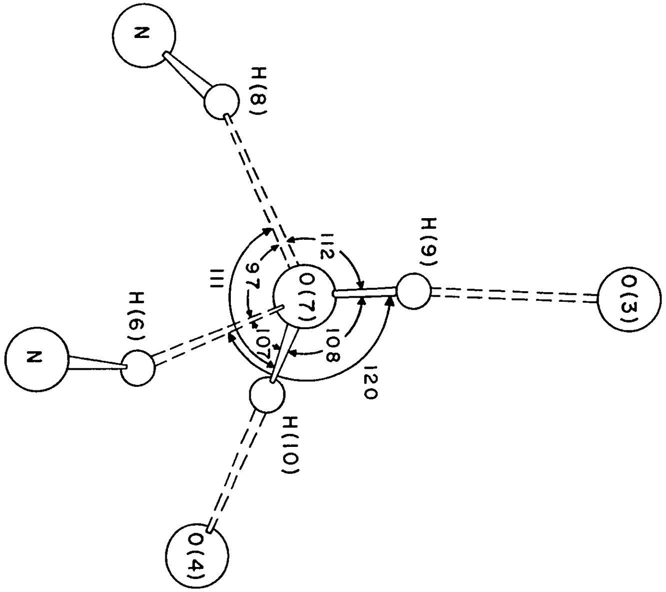


Fig. 3. The hydrogen bonding of the hydrate molecule.

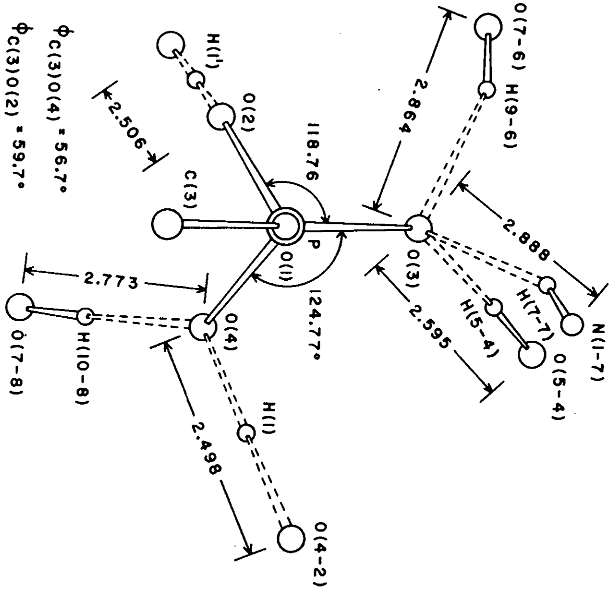


Fig. 4. The conformation of the phosphate viewed down the O(1)–P bond, and the hydrogen bonding to the phosphate group. $\varphi_{C(3)O(4)}$ and $\varphi_{C(3)O(2)}$ are the conformation angles C(3)O(1)PO(4) and C(3)O(1)PO(2) respectively.

R index. However, it is not possible with the X-ray data to decide between the models with the hydrogen atoms disordered and that with the hydrogen atoms on the symmetry elements.

The phosphorus oxygen, nitrogen and carbon scattering factors were from *International Tables for X-ray Crystallography* (1962), while those of hydrogen were from Stewart, Davidson & Simpson (1965). A listing of the observed and calculated structure factors is given in Table 2. The final atomic parameters, together with their estimated standard deviations, are given in Table 3.

Discussion of the structure

Hydrogen bonding in the crystal

One of the most interesting aspects of this crystal structure is the hydrogen-bonding pattern (Fig. 2). Altogether, there are eight different hydrogen bonds, although only seven protons are available for the hydrogen bonding. The apparent paradox comes from the fact that a phosphate proton is statistically shared by pairs of center-related and diad-related oxygen atoms of the phosphate group. These oxygen atoms are involved in the very short hydrogen bonds. The diad-related pair of oxygen atoms form a hydrogen bond of 2·506 Å, while the center-related pair form a hydrogen bond of 2·498 Å. Similar short hydrogen bonds between oxygen atoms of P–O bonds have been observed in dibenzylphosphoric acid, 2·494 ± 0·01 Å (Dunitz & Rollett, 1956); di-*p*-chlorophenyl hydrogen phosphate 2·398 ± 0·01 Å (Calleri & Speakman, 1964); dimethylphosphinic acid, 2·479 ± 0·004 Å (Giordano & Ripamonti, 1967); tetrametaphosphinic acid dihydrate, 2·46 ± 0·01 Å (Migchelsen, Olthof & Vos, 1965) and sodium phosphate, 2·47 Å (Jost, 1968). The carboxyl group of one molecule and the phosphate group of a glide-related molecule are involved in a hydrogen bond, –C–O–H···O–P–, of 2·595 Å.

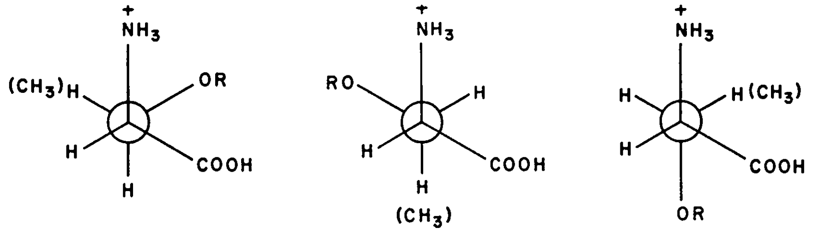
Crystalline DL-serine phosphate occurs as a zwitterion, $HOP\overset{-}{O}_2OCH_2CH(\overset{+}{N}H_3)COOH$, which differs from amino acid zwitterions in that in the amino acid phosphates the amino group is protonated by a phosphate proton, while in the amino acids it is protonated by the carboxyl proton. Therefore, in the amino acid phosphates the phosphate group is more acidic than the carboxylate group. The $P{-}\overset{-}{O}\cdots H{-}\overset{+}{N}$ hydrogen bond distance is 2·788 Å. Besides this hydrogen bond, the ammonium group is also involved in two other donor hydrogen bonds to different water molecules (Table 4). The hydrogen bonding geometry around the water molecule is shown in Fig. 3. The donor hydrogen bonds of the water molecule involve different phosphate groups. The phosphate group alone is involved in six hydrogen bonds, three to O(3), two to O(4) and one to O(2) (Fig. 4).

All of the hydrogen bond distances and angles are summarized in Table 4. Apart from the short hydrogen bonds, the remaining hydrogen bonds are nonlinear, as evidenced by the A_2HA_3 bond angles. The HA_3A_4 bond angles range from 105 to 129°.

The molecular conformation

The conformation of the molecule is shown in Figs. 4–7, and the torsion angles are given in Table 5. It is seen that the ester C(3)–O(1) bond is *gauche* both to the C(1)–C(2) and the C(2)–N⁺ bonds (Fig. 5), and staggered to the phosphate group. A similar conformation about the C(2)–C(3) bond is observed in L-serine phosphate (McCallum, Robertson & Sim, 1959; Sundaralingam & Putkey, 1970), DL-serine (Shoemaker, Barieau, Donohue & Lu, 1953) and DL-threonine phosphate (Cole, 1968). However, in L_s-threonine (Shoemaker, Donohue, Schomaker & Corey, 1950) the C(3)–O(1) bond is *trans* to the C(1)–C(2) bond and *gauche* to the C(2)–N bond.

The conformation about the ester C–O bond is *anti* with the torsion angle C(2)C(3)O(1)P of 153·2°. Similar conformations are observed for the other known primary phosphates (Sundaralingam, 1969). The ammonium group is almost perfectly staggered to the substituents on C(2); the pertinent torsion angles are shown in Fig. 6. The nitrogen atom is significantly displaced from the plane formed by the carboxyl group,



(*a*) (*b*) (*c*)

Fig. 5. The three possible staggered conformations about the C(2)–C(3) bond in serine and threonine. DL-Serine (Shoemaker *et al.*, 1953), DL-serine phosphate monohydrate (this work), L-serine phosphate (McCallum *et al.*, 1959; Sundaralingam & Putkey 1970) and DL-threonine phosphate (Cole, 1968) occur in the (*a*) conformation, while L_s-threonine (Shoemaker *et al.*, 1950) occurs in the (*b*) conformation. Therefore, the (*a*) conformation appears to be the most stable conformation for the serine derivatives, although for threonine the (*a*) and (*b*) conformations appear to be equally likely.

Table 5. *Torsion angles*

Bond sequence	
O(2)–P —O(1)–C(3)	±59·7°
O(3)–P —O(1)–C(3)	±56·7
O(4)–P —O(1)–C(3)	±178·5
P —O(1)–C(3)–C(2)	±168·1
O(5)–C(1)–C(2)–C(3)	±72·7
O(5)–C(1)–C(2)–N	±166·2
O(6)–C(1)–C(2)–C(3)	±105·91
O(6)–C(1)–C(2)–N	±15·1
C(1)–C(2)–C(3)–O(1)	±54·5
N—C(2)–C(3)–O(1)	±66·3

such that the torsion angle ψ, defined by O(6)C(1)C(2)$\overset{+}{\text{N}}$, is 15·1°.

Bond distances and angles

The bond lengths and bond angles are presented in Figs. 7 and 8 respectively. The standard deviations in the bond distances are C–C, 0·004; C–N, 0·004; C–O, 0·003; P–O, 0·002; C–H, N–H, O–H, 0·03 Å. The standard deviations in the bond angles involving the phosphorus atom are 0·10° and those involving C, N and O atoms are 0·20°.

The C(1)–C(2) bond distance of 1·525 Å involving the sp^2-hybridized carbon atom is significantly longer than the value (1·50 Å) normally associated with a Csp^2–Csp^3 single bond, and is similar to the C(2)sp^3–C(3)sp^3 bond distance of 1·518 Å. The ester C(3)–O(1) bond distance of 1·449 Å is longer than the normal C–O single bond of 1·426 Å (Kimura & Kubo, 1959). Similar 'long' C–O single bonds have been previously noticed in the nucleoside 5′-phosphates and other primary phosphates (Sundaralingam & Jensen, 1965).

The P–O(1) bond distance of 1·590 Å and the P–O(3) bond distance of 1·499 Å are close to the normal values, while the P–O(2) and P–O(4) bonds involving the short hydrogen bonds are 1·522 and 1·530 Å respectively, and intermediate in character to the P–O (1·490 Å) and P–OH (1·554 Å) bond distances found in the 'normal' phosphate monoester anions (Sundaralingam & Putkey, 1970).

The bond distances involving the hydrogen atoms are ⟨C–H⟩, 1·042, ⟨N–H⟩, 0·972 and ⟨O–H⟩, 0·937 Å, excluding those participating in the short hydrogen bonds. The above values are in good agreement with the values that are generally observed in X-ray diffraction investigations (Stewart *et al.*, 1965).

The equal sharing of a proton by two phosphate oxygen atoms has also influenced the bond angles involving the phosphorus. The two largest O–P–O angles of 115·1 and 114·3° involve the unprotonated oxygen atom O(3) and the hemi-protonated oxygen atoms O(2) and O(4). The smallest O–P–O angle of 103·7° in this structure involves the ester oxygen atom and the unprotonated oxygen atom, although as a general rule the smallest O–P–O angle involves the ester oxygen atom and the protonated oxygen atom in a phosphate monoester anion (Sundaralingam & Putkey, 1970). The bond angles involving the hydrogen atoms are within the expected values.

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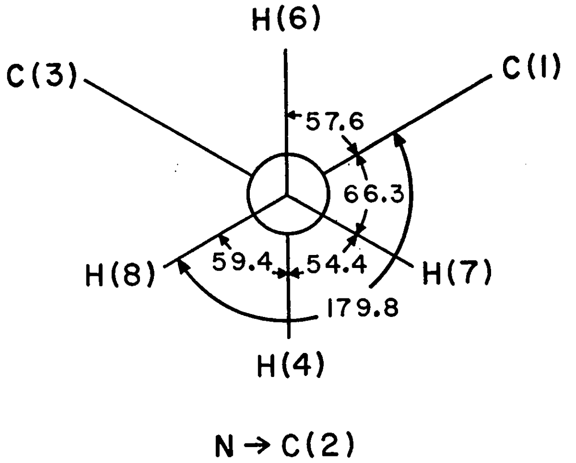

Fig. 6. The staggered conformation of the ammonium group about the N–C(2) bond.

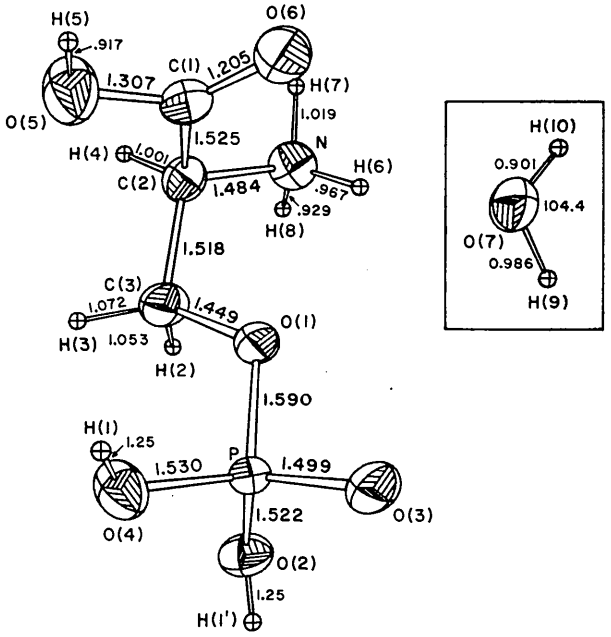

Fig. 7. Bond distances in DL-serine phosphate monohydrate.

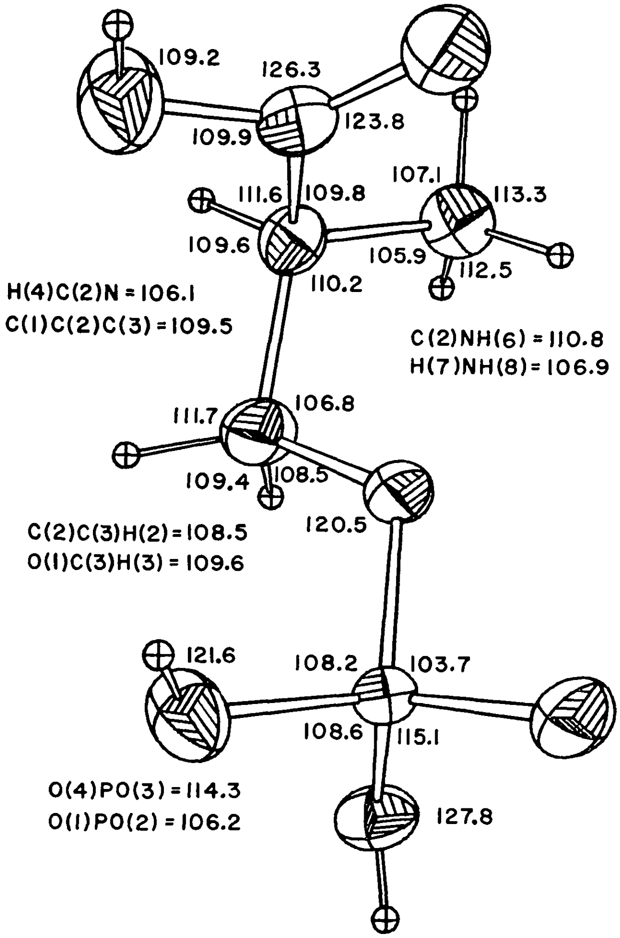

Fig. 8. Bond angles in DL-serine phosphate monohydrate.

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