

Crystal Structure of Putrescinium Di-(diethyl Phosphate)

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The crystal structure of the 1:2 complex between putrescine and diethyl phosphate has been derived from three-dimensional X-ray data collected by counter methods. The space group is $C2/c$. The structure was refined by full matrix least squares techniques to $R=0.064$ ($R_w=0.042$) for 1741 reflections. One of the carbon atoms is disordered. The conformation of the diethyl phosphate is *gauche* at both P-O ester bonds. In the putrescinium cation the conformation is *anti* at the central C-C bond, *gauche* at the others. Each NH_3^+ group is linked by three N-H \cdots O hydrogen bonds to three different phosphate groups.

In order to obtain information on the stereochemistry of interactions between nucleic acids and basic proteins we have investigated the structure of some complexes between diethyl phosphate and compounds simulating side-chains of basic amino acids. The structure of the complex with propylguanidin has been reported.¹ In the present paper the 1:2 complex with putrescine, $\text{NH}_2(\text{CH}_2)_4\text{NH}_2$, is described, whose structure may be expected to be related to that of the contact between nucleic acids and lysine or ornithine.

EXPERIMENTAL. STRUCTURE ANALYSIS

The compound was prepared by mixing equivalent amounts of diethyl phosphoric acid and putrescine in methyl alcohol. Crystals suitable for X-ray crystallographic work were grown by letting ethyl acetate vapor slowly enter the solution in a closed system. The crystals were soft and hygroscopic and had the shape of plates (010).

The X-ray diagrams showed the space group to be Cc or $C2/c$. The latter was chosen and proved to be correct by the structure analysis. Cell dimensions were measured on a diffractometer and found to be $a=27.821(4)$ Å, $b=9.067(1)$ Å, $c=8.451(1)$ Å, $\beta=91.66(2)^\circ$. By flotation the density was found to be 1.21 g/cm³, corresponding to four stoichiometric units $\text{NH}_2(\text{CH}_2)_4\text{NH}_2 \cdot 2(\text{C}_2\text{H}_5\text{O})_2\text{PO}(\text{OH})$ in the unit cell. The asymmetric unit consists of one molecule of diethyl phosphoric acid and half a molecule of putrescine. The calculated density is 1.23 g/cm³.

A crystal was given a roughly spherical shape (radius 0.17 mm) by being partly dissolved on a sheet of paper soaked in ethyl alcohol, and kept in a stream of dry air. It was then sealed off in a capillary for the intensity measurements, which were carried out on a Picker automatic diffractometer using graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) and $\omega/2\theta$ scan technique. Of 2312 reflections with $2\theta < 55^\circ$, 1741 had intensities above a 2σ cut-off limit and were used in the structure analysis. The intensities of three standard reflections did not change significantly during the measurements. The standard deviations of the intensities were based on counter statistics and an assumed 2 % instrumental instability. Corrections for absorption and secondary extinction were not applied. The atomic scattering factors were those of Hanson *et al.*² for non-hydrogen atoms and of Stewart *et al.*³ for hydrogen atoms. All programs used are described in Ref. 4.

Table 1. Positional ($\times 10^5$) and thermal parameters ($\times 10^4$) with estimated standard derivatives. The temperature factor is
 $[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	15747	24916	37440	12	107	109	-5	3	11
	3	10	9	0	1	1	0	1	2
O1	12326	22871	52006	20	147	167	-20	39	-19
	10	26	29	1	4	4	2	2	2
O2	12308	26904	22444	22	193	184	0	-35	26
	11	31	32	1	5	4	3	3	8
O3	18454	38730	41116	18	117	145	-17	1	14
	9	25	25	0	3	4	2	2	6
O4	18410	11252	34266	18	128	242	1	35	-14
	10	27	33	0	4	5	2	2	7
N	22095	38145	73053	15	94	110	6	-4	-20
	12	32	34	1	5	4	2	3	7
C1	9970	8988	54579	25	204	275	-51	66	31
	18	52	58	1	8	10	5	5	14
C2	5598	10877	62154	24	350	621	-39	92	221
	21	76	84	1	14	21	7	8	28
C3	9639	39546	19750	28	240	359	33	-59	78
	20	64	66	1	10	13	6	6	18
C4	5786	37789	8581	40	401	674	15	-211	237
	25	88	97	2	16	24	9	11	33
C5	20801	24211	81096	16	112	131	-11	-10	33
	15	45	43	1	5	5	3	3	9
C61	22194	24917	98906	10	97	81	1	5	10
	24	99	80	1	9	9	6	5	18
C62	24421	19700	94218	36	129	154	-44	-34	50
	58	108	115	3	14	16	11	12	23
H1 N	20337	38853	63322	4.1					
	120	371	393	.8					
H2 N	25706	39527	72349	7.1					
	167	489	462	1.1					
H3 N	21192	45519	78010	2.3					
	100	323	318	.6					

The Patterson map showed the positions of the phosphorus and oxygen atoms, while those of the other non-hydrogen atoms were revealed by the corresponding weighted Fourier synthesis. The structure was refined by full matrix least squares techniques, applying anisotropic temperature factors for the non-hydrogen atoms. The parameters of one of the atoms, C6, gave unreasonable values for the corresponding bond lengths and angles. Its maximum B -value was also very large (19 \AA^2). It was therefore substituted by two half-atoms about 1 \AA apart and then refined. This disorder represents two different ways of placing identical putrescinium ions in the crystal. The two arrangements were given equal statistical weights. The positions of the hydrogen atoms were postulated ($C-H$ 1.05 \AA) and assigned an isotropic temperature factor ($B=5 \text{ \AA}^2$ for hydrogens at N, $B=10 \text{ \AA}^2$ at C1, C3 and C5, and $B=15 \text{ \AA}^2$ at C2 and C4). These parameters were refined only for hydrogen atoms attached to the nitrogen atom. The contribution from hydrogen atoms bonded to the disordered carbon atom was neglected.

The final value of R is 0.064 ($R_w=0.042$) for the observed reflections. The positional and thermal parameters are given in Table 1. In Table 3 observed and calculated structure factors are listed.

Table 2. Distances (\AA) and angles ($^\circ$). Estimated standard deviations in parenthesis.

P-O1	1.588(2)	O1-P-O2	105.9(2)
P-O2	1.576(3)	O1-P-O3	104.3(1)
P-O3	1.490(2)	O1-P-O4	111.0(1)
P-O4	1.472(3)	O2-P-O3	111.3(2)
O1-C1	1.439(4)	O2-P-O4	104.3(2)
C1-C2	1.401(6)	O3-P-O4	119.4(2)
O2-C3	1.381(6)	P-O1-C1	120.3(2)
C3-C4	1.417(8)	O1-C1-C2	111.6(5)
N-C5	1.484(5)	P-O2-C3	122.6(3)
C5-C61	1.545(8)	O2-C3-C4	114.2(5)
C5-C62	1.532(13)	N-C5-C61	110.7(4)
C61-C61	1.567(13)	N-C5-C62	113.3(5)
C62-C62	1.402(19)	C5-C61-C61	109.7(6)
N-H1N	0.95 (3)	C5-C62-C62	117.0(13)
N-H2N	1.02 (4)	C5-N-H1N	109.2(20)
N-H3N	0.83 (3)	C5-N-H2N	112.7(25)
		C5-N-H3N	111.9(18)
N-O3	2.856(4)	C5-N-O3	111.4(2)
N-O4'	2.731(4)	C5-N-O4'	111.7(2)
N-O3'	2.801(4)	C5-N-O3'	106.9(2)
H1N-O3	1.93 (3)		
H2N-O4'	1.75 (5)		
H3N-O3'	1.97 (3)		
		Dihedral angles	
		C3-O2-P-O1	71.8
		C3-O2-P-O4	171.0
		C4-C3-O2-P	162.3
		C1-O1-P-O2	77.1
		C1-O1-P-O3	165.4
		C2-C1-O1-P	150.9

Table 3. Observed and calculated structure factors ($\times 10$).

h	k	l	P _o	P _c	h	k	l	P _o	P _c	h	k	l	P _o	P _c	h	k	l	P _o	P _c	h	k	l	P _o	P _c		
7	0	0	1517	-1511	-14	0	10	135	-147	-9	1	10	40	32	0	2	0	298	-222	4	2	4	268	-222		
8	0	0	1376	-1445	-12	0	10	126	89	-5	1	1	10	41	32	0	2	0	276	-276	4	2	4	268	-276	
9	0	0	939	-1486	-10	0	10	107	140	-4	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
10	0	0	154	103	-4	0	10	74	-70	-1	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
11	0	0	469	-116	-4	0	10	96	72	-1	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
14	0	0	163	-165	-4	0	10	64	41	0	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
16	0	0	30	-43	-2	0	10	72	-74	5	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
18	0	0	916	-185	0	0	10	52	30	7	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
20	0	0	132	-142	0	0	10	163	152	11	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
24	0	0	352	-164	10	0	10	31	-71	13	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
30	0	0	145	-147	12	0	10	120	-123	13	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
32	0	0	244	288	1	0	10	321	-22	21	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
34	0	0	72	60	3	0	10	282	244	15	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-34	0	2	131	-135	5	0	10	321	-323	21	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-30	0	2	110	137	7	1	0	301	343	25	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-20	0	2	107	226	9	1	0	264	243	25	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-28	0	2	243	237	11	1	0	131	124	-29	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-22	0	2	67	-59	13	1	0	142	-159	-29	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-16	0	2	65	100	17	1	0	35	77	-29	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-10	0	2	150	153	19	1	0	36	-1	-21	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-4	0	2	959	827	21	1	0	90	-74	-17	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-2	0	2	202	76	23	1	0	30	-74	-17	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
2	0	2	202	2202	25	1	0	44	29	-17	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
4	0	2	353	34	20	1	0	37	-54	-11	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
6	0	2	110	76	-33	1	0	149	40	-7	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
8	0	2	244	338	-29	1	0	223	224	-5	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
10	0	2	949	1172	-27	1	0	223	231	-5	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
12	0	2	258	-2726	-25	1	0	111	-9	-1	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
14	0	2	302	114	-23	1	0	126	282	-1	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
16	0	2	956	638	-21	1	0	132	-174	5	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
18	0	2	126	-1274	-19	1	0	154	-174	5	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
20	0	2	384	401	-15	1	0	117	421	9	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
22	0	2	287	237	-11	1	0	225	-232	13	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
24	0	2	270	281	-9	1	0	217	-232	13	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
26	0	2	234	-244	-9	1	0	116	613	15	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
28	0	2	113	118	-5	1	0	117	-171	15	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
22	0	2	70	91	-5	1	0	2143	-225	17	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
24	0	2	381	-344	-3	1	0	159	249	21	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
26	0	2	118	123	-3	1	0	172	-149	21	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
30	0	2	146	142	1	1	0	30	132	25	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
32	0	2	59	-96	1	1	0	1768	1712	-29	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
34	0	2	18	135	7	1	0	94	-8	27	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-32	0	2	86	-98	7	1	0	653	-732	-29	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-30	0	2	56	60	11	1	0	968	808	-25	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-28	0	2	91	72	13	1	0	63	-24	-23	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-26	0	2	416	-137	13	1	0	354	211	-23	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-24	0	2	41	81	13	1	0	138	124	-19	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-22	0	2	221	-234	17	1	0	117	-234	-19	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-20	0	2	335	-338	21	1	0	207	105	-11	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-18	0	2	113	-116	21	1	0	75	-78	-11	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-16	0	2	236	229	25	1	0	1049	-922	-9	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-14	0	2	67	49	27	1	0	148	178	-5	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-12	0	2	647	-636	27	1	0	116	116	-21	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-10	0	2	549	544	31	1	0	152	-108	-3	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-8	0	2	983	821	31	1	0	141	101	1	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-6	0	2	113	-1052	-31	1	0	3	31	1	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
-4	0	2	164	200	-23	1	0	2	66	0	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476	
4	0	2	164	159	-23	1	0	2	111	-126	3	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476
6	0	2	91	82	-17	1	0	2	111	-126	3	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476
8	0	2	163	142	-15	1	0	2	259	-256	3	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476
10	0	2	116	-123	-11	1	0	2	258	-256	3	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476
14	0	2	638	780	-9	1	0	2	748	708	15	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476
16	0	2	632	639	-9	1	0	2	120	-119	15	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476
18	0	2	751	-691	-9	1	0	2	186	-188	17	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476
20	0	2	294	281	-3	1	0	2	64	78	23	1	0	10	77	-57	0	2	0	304	-370	4	2	4	376	-476
22	0	2	88	92	-3	1	0	2	191	181	23	1	0	10	77	-57	0	2	0	304	-370	4	2			

Table 3. Continued.

Table with multiple columns of numerical data, organized in groups of four columns each. Each group contains two columns of values (left and right) and two columns of headers (h, k, l and P, F). The data represents crystallographic parameters for Putrescinium di-(diethyl phosphate).

Table 3. Continued.

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
-10	0	3	20	42	6	0	0	143	120	-21	7	5	62	67	-22	0	4	121	50	3	0	3	120	120
-8	0	3	46	96	10	0	0	140	129	-19	7	5	62	60	-20	0	4	122	121	0	0	3	66	90
0	0	3	256	270	12	0	0	66	70	-17	7	4	120	122	-16	0	4	120	100	7	0	3	122	122
8	0	3	271	278	14	0	0	70	74	-15	7	5	60	60	-12	0	4	281	90	11	0	3	140	150
0	0	3	43	94	-4	0	0	70	71	-13	7	4	150	105	-10	0	4	151	101	13	0	3	150	154
0	0	3	156	156	-6	0	0	77	75	-11	7	5	110	127	-8	0	4	152	130	17	0	3	150	100
10	0	3	120	122	0	0	0	46	44	-7	7	4	237	240	-6	0	4	153	128	-17	0	3	57	8
12	0	3	160	162	1	0	0	93	81	-5	7	5	91	90	-2	0	4	154	102	-13	0	4	42	27
14	0	3	99	102	3	0	0	145	144	0	7	4	60	60	0	0	4	155	150	-12	0	4	77	77
18	0	3	97	40	5	0	0	45	45	-1	7	5	372	277	2	0	4	152	61	-9	0	4	65	66
20	0	3	91	64	7	0	0	111	92	1	7	4	166	126	0	0	4	165	156	-7	0	4	68	74
-26	0	4	26	50	11	7	0	87	87	5	7	5	265	244	0	0	4	164	100	-1	0	4	162	147
-22	0	4	102	110	-8	7	0	30	26	7	7	4	66	50	0	0	4	160	161	-3	0	4	151	149
-22	0	4	156	122	-8	7	0	95	104	9	7	4	66	80	12	0	4	205	206	3	0	4	41	31
-18	0	4	105	107	-20	7	1	99	36	11	7	5	63	98	16	0	4	62	60	13	0	4	41	30
-18	0	4	204	212	-20	7	1	346	307	13	7	5	163	107	16	0	4	67	60	10	0	4	111	69
-14	0	4	64	70	-21	7	1	153	171	13	7	5	165	109	20	0	4	105	149	-11	0	4	92	93
-12	0	4	209	200	-15	7	1	156	121	17	7	5	46	48	-10	0	4	69	52	-9	0	4	92	93
-8	0	4	101	101	-12	7	1	92	81	19	7	5	218	218	-16	0	4	87	60	-8	0	4	102	102
-6	0	4	183	183	-11	7	1	32	1	21	7	5	113	102	-12	0	4	52	47	-7	0	4	102	102
-6	0	4	203	200	-7	7	1	316	327	-19	7	6	27	19	-8	0	4	26	22	-5	0	4	66	36
-4	0	4	154	150	-5	7	1	154	144	-17	7	4	47	16	-6	0	4	167	160	-3	0	4	128	141
-2	0	4	140	143	-5	7	1	356	255	-7	7	4	64	94	-6	0	4	69	60	-1	0	4	100	104
0	0	4	102	92	-6	7	1	215	273	-5	7	4	64	94	-2	0	4	102	110	1	0	4	106	88
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0	0	6	70	70	-11	7	3	267	270	-16	0	0	236	247	3	0	4	165	160	-2	10	0	120	127
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0	0	6	170	171	-7	7	3	223	240	-10	0	2	63	87	11	0	4	121	112	6	10	0	43	34
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10	0	6	96	96	-1	7	3	221	230	-8	0	2	225	230	-11	0	4	197	182	10	10	0	70	70
12	0	6	120	120	-1	7	3	117	112	-8	0	2	222	216	13	0	4	112	112	12	10	0	42	42
14	0	6	132	126	1	7	3	316	320	-7	0	2	226	231	15	0	4	117	118	-12	10	0	90	90
16	0	6	69	28	-2	7	3	438	450	-2	0	2	137	114	-10	0	4	162	161	-13	10	0	131	124
18	0	6	67	87	0	7	3	350	330	-2	0	2	469	417	19	0	4	77	60	-8	10	0	40	30
20	0	6	67	87	7	7	3	306	307	6	0	2	433	433	-11	0	4	66	60	-8	10	0	40	30
22	0	6	63	70	11	7	3	247	242	6	0	2	235	231	-8	0	4	66	60	-8	10	0	40	30
-16	0	7	73	71	11	7	3																	

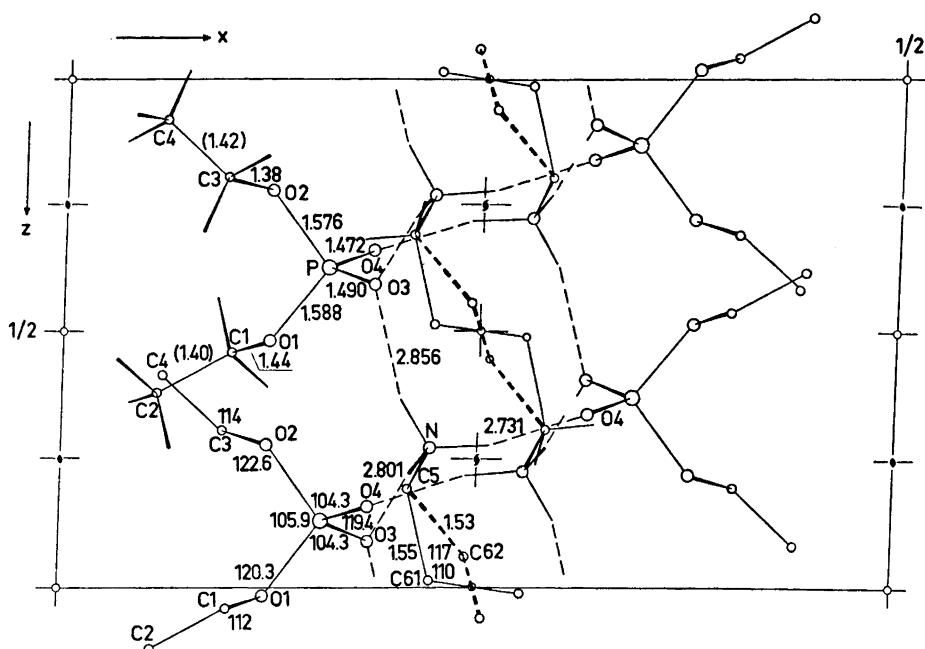


Fig. 1. The structure viewed along b . One of the positions of the putrescinium ion is shown by broken lines.

caused by crystal forces. The bond lengths and angles at the phosphorus atom are normal. The difference in bond length between P–O3 (1.490 Å) and P–O4 (1.472 Å) is probably significant and may be explained by the fact that O3 receives two hydrogen bonds, O4 one. The C–C bonds are found much too short (1.40 Å and 1.42 Å), due to the large vibrations of these atoms, the maximum values of B for the terminal carbon atoms being 20 Å² and 28 Å². Similar effects are observed in related crystal structures.^{1,5} "Riding motion" correction gives the values 1.46 Å and 1.53 Å for the C1–C2 and C3–C4 bonds, respectively.

The putrescinium cation ($\text{NH}_3^+\text{CH}_2\text{CH}_2$)₂ is disordered and centrosymmetric in the crystal. It does not have the extended all-*anti* conformation usually found in crystal structures of normal hydrocarbons and related compounds, the conformation being *anti* at the central C–C, *gauche* at the others. In a related compound, spermine, the conformation is *anti* at all bonds in the phosphate salt⁶ but *gauche* at two bonds in the tetrahydrochloride salt.⁷ The energy difference between such conformations is evidently small.

The crystal structure (Fig. 1) is built up of layers of complexes parallel to the (y,z)-plane of thickness 13.9 Å. Within the layers there is a central sheet of putrescinium cations hydrogen bonded on each side to equivalent sheets of diethyl phosphate anions. The surface of the layers is formed by a nearly planar and regular hexagonal array of terminal methyl groups, the carbon atoms of

each such group being surrounded by six others at distances of about 4.6 Å. This distance is roughly the expected van der Waals diameter of methyl groups with r.m.s. amplitudes of vibration of about 0.5 Å. The distance between the layers (defined by the plane through the terminal carbon atoms) is about 3.2 Å.

The NH_3^+ groups are engaged in three N—H...O hydrogen bonds of lengths 2.731 Å, 2.801 Å, and 2.856 Å to three different phosphate groups. They are nearly tetrahedrally arranged and approximately linear, the angles at the hydrogen atoms being 164.0°, 162.1°, and 172.5° for H1N, H2N, and H3N, respectively. In the phosphate groups O3 receives two hydrogen bonds and O4 one, the latter being the shortest one.

REFERENCES

1. Furberg, S. and Solbakk, J. *Acta Chem. Scand.* To be published.
2. Hanson, H. P., Herman, F., Lea, J. D. and Skillman, L. *Acta Cryst.* **17** (1964) 1040.
3. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* **42** (1965) 3175.
4. Dahl, T., Gram, F., Groth, P., Klewe, B. and Rømming, C. *Acta Chem. Scand.* **24** (1970) 2232.
5. Kyogoku, Y. and Iitaka, Y. *Acta Cryst.* **21** (1966) 49.
6. Iitaka, Y. and Huse, Y. *Acta Cryst.* **18** (1965) 110.
7. Giglio, E., Liquori, A. M., Puliti, R. and Ripamonti, A. *Acta Cryst.* **20** (1966) 652.

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