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The Crystal Structure of Spermine Phosphate Hexahydrate

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Spermine phosphate hexahydrate, $C_{10}H_{26}N_4.2H_3PO_4.6H_2O$, is found to have a monoclinic unit cell with dimensions $a=7{\cdot}95_5$, $b=23{\cdot}21_6$, $c=6{\cdot}87_0$ Å, $\beta=113°\ 39'$. The space group is $P2_1/a$. There are two formula units in a cell. The spermine molecules are thus required to be centrosymmetric. The structure was solved by analysis of the three-dimensional Patterson function and was refined by Fourier and least-squares methods.

The molecules have a normal extended zigzag chain configuration and are almost planar except for the terminal nitrogen atoms which lie 0·19 Å out of the best plane formed by the remaining 12 atoms. Both the amino and the imino nitrogen atoms are protonated and the phosphate group has one un-ionized OH group. The chemical formula of spermine phosphate hexahydrate may therefore be written $[NH_3^+(CH_2)_3NH_2^+(CH_2)_2]_2.2[HPO_4]^{2-}.6H_2O$.

The structure consists of parallel sheets of spermine molecules separated by a sheet of phosphate ions and water molecules. The latter sheet has the composition $HPO_4^{2-}.3H_2O$ containing chains of monohydrogen phosphate ions running along the *a*-axis. The chains are arranged antiparallel and separated by water molecules forming a hexagonal network of hydrogen bonds. The two kinds of sheet are stacked alternately parallel to the (001) plane and are held together by N–H · · · O hydrogen bonds. The arrangement of phosphate ions and the binding of water and basic amino and imino groups to the phosphate ions are discussed in comparison with the structure of deoxyribonucleic acid.

Introduction

Spermine is an aliphatic polyamine and is widely distributed in biological materials — animals and microorganisms. It occurs at particularly high concentrations in mammalian pancreas and prostate and in human semen.

Recently, considerable information has been accumulated on a variety of its physiological and pharmacological effects. Many interesting phenomena have been reported on the effect of spermine on various enzyme activities and on the relationship of this amine to nucleic acids and to problems of membrane stability (Tabor, Tabor & Rosenthal, 1961). Although mechanisms of these biological phenomena remain unexplained, a number of papers have been published on the binding of spermine to nucleic acids (Razin & Rozansky, 1959; Kaiser, 1963). Much of the evidence, however, is indirect, but the data definitely indicate that spermine and nucleic acids have a strong affinity for each other.

Spermine is a strong base and is very soluble in water. The addition of phosphoric acid to its aqueous solution results in the immediate precipitation of the salt, spermine phosphate. The analysis of the structure of spermine phosphate hexahydrate was therefore undertaken, to provide information on the binding relation of this amine to phosphoric acid and water, which in turn should be of interest to biochemists studying the mechanism of its biological effect.

Experimental

Commercial spermine phosphate (L. Light & Co. Ltd. England) was recrystallized as very thin flaky crystals from a hot aqueous solution by slow cooling. The crystals are elongated along the *c* axis and flattened on the (010) face. Rather thick crystals used for X-ray specimens were grown by very slow cooling with the rate *ca.* 0·2 °C per hr.

Oscillation and Weissenberg photographs were taken about the three crystallographic axes. The systematic absences (*h0l* when *h* is odd and *0k0* when *k* is odd) indicated the space group $P2_1/a$. The unit-cell dimensions were found to be

$$a=7{\cdot}95_5,\ b=23{\cdot}21_6,\ c=6{\cdot}87_0\ \text{Å};\ \beta=113°\ 39'.$$

The density, measured by flotation in a mixture of carbon disulphide and carbon tetrachloride, is 1·443 g.cm^{-3} and the calculated density is 1·445 g.cm^{-3}, assuming that two units of $C_{10}H_{26}N_4.2H_3PO_4.6H_2O$ are contained in a cell.

Complete three-dimensional intensity data for Cu $K\alpha$ radiation were obtained from equi-inclination Weissenberg photographs about the *b* axis (up to the 2nd layer), the *c* axis (up to the 5th layer) and the *a* axis (zero layer). Multiple-film techniques were employed

and the relative intensities were estimated visually with the aid of a calibrated intensity scale.

The X-ray specimen for the c axis was a thin flake with approximate dimensions of $0{\cdot}35\times0{\cdot}07\times1$ mm, the longer side being the oscillation axis. For the a and b axes a similar crystal was cut parallel to the (001) face. Intensities were corrected for Lorentz and polarization factors in the usual way, but no absorption correction was applied. Sets of intensities for various axes and layer lines were correlated by common spots. A total of 2163 independent observed structure factors were then obtained and they were put on an absolute scale by Wilson's statistical method. At the same time, an overall temperature factor of 1·82 Å^2 was obtained.

The following calculations were carried out on the parametron computer PC 2. The atomic scattering factors were computed by the three-term Gaussian expansion. The coefficients of the formula were taken from the paper by Forsyth & Wells (1959). For oxygen, nitrogen and carbon they evaluated the coefficients from the tabulated values of atomic scattering factors by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) and for phosphorus, the values of Viervoll & Øgrim (1949) were used.

Determination and refinement of the structure

Since the space group $P2_1/a$ has four general positions, an asymmetric unit contains one half of the spermine molecule, one phosphate group and three water molecules. The centers of the spermine molecules are then constrained to lie on centers of symmetry. An analysis of the two-dimensional Patterson maps was first contemplated. A long b axis suggested that the extended long chain molecules are likely to pack parallel to the b axis and we tried to interpret the ($h0l$) Patterson map (Fig. 1) based on the structure which consists of alternate layers of molecules and phosphate–water groups packed parallel to (001). Several possible structures were tested but none could be refined beyond $R=0{\cdot}30$ ($h0l$) and 0·60 ($hk0$).

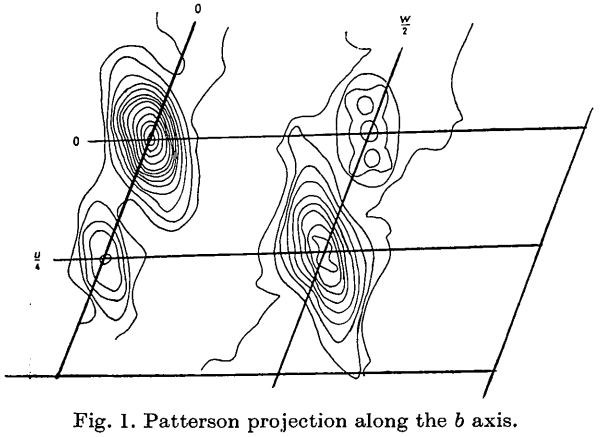

Fig. 1. Patterson projection along the b axis.

Later, it turned out that the spermine molecules are not parallel but inclined at about 57° to the b axis and that the phosphorus atom deviates significantly from the postulated position.

Next, a three-dimensional sharpened Patterson function was computed. The coefficients were modified to correspond roughly to those from atoms at rest. The approximate coordinates of the phosphorus atom were determined by inspection of rather high peaks originating from the symmetry-equivalent phosphorus atoms. The vector convergence method (Robertson & Beevers, 1951) was then applied and the approximate

Table 1. *Refinement process*

R for 743 reflections	
Start	0·163
After 4th cycle	0·121
R for 1004 reflections	
Start	0·146
After 4th cycle	0·130
R for 1747 reflections	
Start	0·130
After 1st cycle	0·128
After 2nd cycle	0·127

Table 2. *Positional parameters of atoms in fractional coordinates*

	x/a	y/b	z/c	B
P	−0·0010	0·1967	0·3665	1·28 Å^2
O(1)	−0·0691	0·2110	0·1318	2·44
O(2)	−0·0205	0·2463	0·4995	2·31
O(3)	−0·0941	0·1420	0·3983	2·21
O(4)	0·2100	0·1804	0·4485	2·09
$W(1)(H_2O)$	0·1170	0·0465	0·5452	3·39
$W(2)$	0·4185	0·0536	0·4424	4·47
$W(3)$	0·6706	0·1470	0·5961	3·02
N(1)	0·7135	0·0942	−0·0075	1·83
N(2)	0·1676	0·2115	−0·0657	1·96
C(1)	0·9650	0·0313	−0·0110	2·17
C(2)	0·7806	0·0340	0·0015	2·12
C(3)	0·5231	0·0950	−0·0097	2·29
C(4)	0·4482	0·1560	−0·0293	2·11
C(5)	0·2585	0·1535	−0·0291	2·36

Table 3. *Standard deviations of the atomic parameters*

	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)	$\sigma(B)$ (Å^2)
P	0·0015	0·0012	0·0017	0·02
O(1)	0·0054	0·0049	0·0056	0·09
O(2)	0·0049	0·0044	0·0054	0·08
O(3)	0·0049	0·0044	0·0054	0·08
O(4)	0·0049	0·0044	0·0053	0·08
$W(1)(H_2O)$	0·0060	0·0058	0·0063	0·11
$W(2)$	0·0072	0·0072	0·0076	0·14
$W(3)$	0·0059	0·0051	0·0062	0·10
N(1)	0·0055	0·0051	0·0062	0·09
N(2)	0·0058	0·0056	0·0063	0·09
C(1)	0·0068	0·0063	0·0078	0·12
C(2)	0·0068	0·0065	0·0078	0·11
C(3)	0·0072	0·0067	0·0081	0·12
C(4)	0·0069	0·0065	0·0078	0·11
C(5)	0·0073	0·0072	0·0080	0·12

Table 4. *Observed and calculated structure factors*

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
0	0	1	3.92	-5.28	7	1	2	0.00	1.29	7	2	3	0.00	0.65	7	3	0	2.39	-2.55	-2	4	1	7.72	-7.21
0	0	2	44.69	50.31	7	1	3	0.00	-0.10	8	2	0	1.91	-1.74	7	3	1	2.88	-0.84	-2	4	2	3.90	-3.45
0	0	3	8.56	12.02	8	1	0	0.00	-0.33	8	2	1	2.35	2.06	7	3	2	0.00	-1.80	-2	4	3	3.30	-3.01
0	0	4	1.31	1.28	8	1	1	3.51	-3.60	8	2	2	0.00	0.74	7	3	3	3.89	-3.94	-2	4	4	2.46	-1.36
0	0	5	8.80	10.68	8	1	2	4.07	4.02	9	2	0	0.00	-0.52	8	3	0	0.00	-1.05	-2	4	5	2.93	-2.57
0	0	6	4.14	4.28	9	1	0	2.53	2.40	-1	2	1	12.13	-15.00	8	3	1	3.52	3.75	-3	4	1	2.30	-2.34
0	0	7	0.00	1.02	-1	1	1	4.76	-5.13	-1	2	2	9.51	10.75	8	3	2	2.62	-2.57	-3	4	2	12.14	12.28
0	0	8	4.65	5.22	-1	1	2	6.17	-5.19	-1	2	3	12.93	-14.72	9	3	0	3.64	-3.10	-3	4	3	3.44	-2.98
2	0	0	12.77	14.15	-1	1	3	0.00	0.44	-1	2	4	2.81	2.17	-1	3	1	15.25	17.32	-3	4	4	7.61	8.28
2	0	1	1.73	1.48	-1	1	4	6.00	-6.14	-1	2	5	0.00	-0.11	-1	3	2	16.60	18.14	-3	4	5	6.56	-5.48
2	0	2	6.10	-6.11	-1	1	5	0.00	0.40	-1	2	6	5.92	-6.24	-1	3	3	0.00	0.92	-4	4	1	11.19	-10.92
2	0	3	10.52	11.37	-2	1	1	11.87	-14.71	-1	2	7	0.00	0.46	-1	3	4	18.25	20.20	-4	4	2	1.85	-1.23
2	0	4	9.06	-9.46	-2	1	2	8.78	8.86	-1	2	8	2.91	-3.75	-1	3	5	1.39	-1.00	-4	4	3	2.33	-2.45
2	0	5	2.05	1.15	-2	1	3	7.11	-6.72	-2	2	1	7.12	7.82	-2	3	1	4.20	4.28	-4	4	4	1.78	-1.64
2	0	6	2.92	2.60	-2	1	4	0.00	-0.90	-2	2	2	10.58	11.54	-2	3	2	3.60	2.96	-4	4	5	2.32	1.23
2	0	7	4.69	-4.99	-2	1	5	5.66	7.55	-2	2	3	1.94	-1.28	-2	3	3	2.68	-2.08	-5	4	1	0.00	1.43
4	0	0	13.33	11.83	-2	1	6	7.57	-8.03	-2	2	4	10.93	10.45	-2	3	4	4.98	4.98	-5	4	2	12.51	-13.84
4	0	1	5.75	6.57	-2	1	7	2.60	2.60	-2	2	5	3.70	-3.70	-2	3	5	5.96	-5.35	-5	4	3	4.56	-4.55
4	0	2	2.49	2.97	-3	1	1	4.34	-3.59	-2	2	6	3.29	-2.63	-3	3	1	18.50	18.25	-5	4	4	4.80	-4.77
4	0	3	8.66	9.46	-3	1	2	1.21	-1.30	-2	2	7	1.80	1.88	-3	3	2	2.00	0.32	-5	4	5	11.14	-10.35
4	0	4	3.35	-2.52	-3	1	3	1.41	1.05	-2	2	8	3.91	-4.28	-3	3	3	3.96	4.38	-6	4	1	2.29	-1.84
4	0	5	1.98	2.24	-3	1	4	2.29	-2.21	-3	2	1	0.00	-0.12	-3	3	4	5.96	4.92	-6	4	2	2.29	2.21
4	0	6	2.03	2.03	-3	1	5	3.16	2.51	-3	2	2	0.92	-0.82	-3	3	5	5.69	-3.28	-6	4	3	0.00	0.95
6	0	0	3.89	3.84	-4	1	1	4.45	-2.85	-3	2	3	1.25	0.94	-4	3	1	7.77	7.37	-6	4	4	0.00	0.86
6	0	1	4.53	-4.71	-4	1	2	0.00	-1.68	-3	2	4	0.00	-0.40	-4	3	2	3.72	-3.54	-6	4	5	0.00	0.33
6	0	2	2.13	1.32	-4	1	3	2.57	-2.35	-3	2	5	3.47	2.82	-4	3	3	0.00	-0.40	-7	4	1	0.00	1.04
6	0	3	2.01	1.43	-4	1	4	4.21	2.87	-3	2	6	1.89	-1.88	-4	3	4	2.65	2.61	-7	4	2	8.28	-9.11
6	0	4	1.44	-1.69	-4	1	5	3.47	3.18	-4	2	1	17.13	18.82	-4	3	5	7.22	-6.42	-7	4	3	0.71	-1.06
8	0	0	2.74	2.45	-5	1	1	2.52	-1.49	-4	2	2	1.04	-0.26	-5	3	1	10.48	9.93	-7	4	4	0.00	0.35
8	0	1	3.77	-3.64	-5	1	2	2.37	-1.89	-4	2	3	3.03	3.61	-5	3	2	0.00	0.52	-7	4	5	5.35	-6.28
8	0	2	0.00	-0.31	-5	1	3	0.55	0.82	-4	2	4	1.89	1.74	-5	3	3	4.03	4.71	-8	4	1	2.82	-3.12
-2	0	1	24.29	-27.50	-5	1	4	2.03	-2.14	-4	2	5	2.72	-1.29	-5	3	4	2.50	2.35	-8	4	2	0.00	0.81
-2	0	2	7.48	6.79	-5	1	5	0.00	1.03	-4	2	6	4.09	-3.03	-5	3	5	3.08	3.25	-8	4	3	0.69	-0.05
-2	0	3	14.69	-17.71	-6	1	1	2.46	-2.17	-4	2	7	4.07	4.46	-6	3	1	3.95	3.50	-8	4	4	0.00	-0.83
-2	0	4	0.00	-1.25	-6	1	2	5.61	4.99	-4	2	8	1.43	-1.35	-6	3	2	5.46	-7.28	-8	4	5	0.00	0.79
-2	0	5	0.00	-1.94	-6	1	3	3.85	3.56	-5	2	1	6.74	-6.74	-6	3	3	2.27	2.42	-9	4	1	0.00	1.12
-2	0	6	5.10	5.04	-6	1	4	3.30	-3.54	-5	2	2	7.44	7.43	-6	3	4	1.68	-1.70	-9	4	2	5.62	-5.26
-2	0	7	3.05	-3.11	-6	1	5	6.16	6.53	-5	2	3	3.75	-4.41	-6	3	5	2.45	-2.25	-9	4	3	1.43	2.21
-2	0	8	3.97	4.68	-6	1	6	6.92	-6.61	-5	2	4	0.86	1.60	-7	3	1	2.75	-2.85	-9	4	4	0.00	0.07
-4	0	1	5.20	2.96	-7	1	1	0.00	0.10	-5	2	5	0.75	0.49	-7	3	2	2.70	3.21	-9	4	5	2.33	-2.44
-4	0	2	14.16	11.57	-7	1	2	1.90	-1.44	-5	2	6	4.10	-2.91	-7	3	3	8.07	-9.03	-10	4	3	1.56	0.26
-4	0	3	9.66	9.25	-7	1	3	4.05	3.73	-5	2	1	7.33	7.33	-7	3	4	3.65	3.36	-10	4	4	1.40	1.29
-4	0	4	12.31	13.51	-7	1	4	2.32	-1.85	-6	2	2	1.75	-2.21	-7	3	5	1.57	-2.02	0	5	1	0.70	-0.38
-4	0	5	5.93	6.30	-7	1	5	1.57	1.51	-6	2	3	3.26	-2.60	-8	3	1	1.74	-1.76	0	5	2	4.76	-5.03
-4	0	6	14.62	15.25	-7	1	8	1.60	1.35	-6	2	4	2.84	1.80	-8	3	2	2.82	-2.22	0	5	3	0.00	0.34
-4	0	7	2.25	-1.87	-8	1	1	0.00	-0.96	-6	2	5	2.17	-2.03	-8	3	3	0.69	0.68	0	5	4	1.62	-2.14
-4	0	8	5.41	7.90	-8	1	2	4.06	4.09	-6	2	6	0.00	-1.21	-8	3	4	0.00	0.92	0	5	5	0.00	0.00
-6	0	1	4.07	-3.90	-8	1	3	0.35	-0.47	-6	2	7	5.07	4.50	-8	3	5	0.00	0.03	0	5	6	0.00	-0.99
-6	0	2	3.77	-4.21	-8	1	4	5.58	-5.34	-7	2	1	0.62	-1.23	-9	3	1	3.80	4.00	0	5	7	0.00	-0.52
-6	0	3	7.39	8.84	-8	1	5	3.95	4.53	-7	2	2	2.60	2.14	-9	3	2	0.00	0.38	0	5	8	0.92	-1.46
-6	0	4	6.03	-6.78	-8	1	6	7.91	-8.00	-7	2	3	0.00	0.00	-9	3	3	1.45	-2.78	1	5	0	21.53	29.60
0	1	0	0.00	0.00	-8	1	7	2.03	1.84	-7	2	4	2.17	-2.39	-9	3	4	4.46	4.70	1	5	1	5.90	5.71
-6	0	6	0.00	0.68	-9	1	1	2.57	-2.76	-7	2	5	1.78	2.87	-9	3	5	1.52	-1.66	1	5	2	13.62	13.54
-6	0	7	4.96	-4.80	-9	1	2	0.00	1.03	-7	2	6	4.21	-3.92	-10	3	3	2.32	1.00	1	5	3	8.57	7.96
-6	0	8	2.37	2.52	-9	1	3	1.03	0.10	-8	2	1	4.34	3.87	-10	3	4	1.97	2.23	1	5	4	1.55	-1.17
-8	0	1	4.05	-4.35	-9	1	4	0.00	-0.92	-8	2	2	0.00	0.00	-10	3	5	0.97	-1.18	1	5	5	3.28	3.00
-8	0	2	0.00	-0.79	-9	1	5	0.00	0.28	-8	2	3	0.35	-1.38	0	4	0	1.08	-0.71	2	5	0	1.17	1.02
-8	0	3	4.13	3.31	-10	1	2	2.92	3.14	-8	2	4	1.61	1.70	0	4	1	4.34	-4.03	2	5	1	2.00	-1.17
-8	0	4	2.28	-2.75	-10	1	3	3.99	-3.87	-8	2	5	0.00	0.60	0	4	2	0.00	-0.42	2	5	2	3.18	-2.64
-8	0	5	0.00	0.57	-10	1	4	1.11	-1.17	-8	2	6	0.00	-1.91	0	4	3	11.46	-10.70	2	5	3	2.13	-1.23
-8	0	6	2.47	2.75	-10	1	5	1.07	1.56	-8	2	7	4.74	4.64	0	4	4	1.85	1.39	2	5	4	1.02	0.98
-8	0	7	4.56	-4.82	0	2	0	13.34	-17.07	-9	2	1	0.31	-1.24	0	4	5	6.07	-7.28	2	5	5	1.02	-1.23
-10	0	3	3.73	3.70	0	2	1	10.19	10.96	-9	2	2	2.45	2.42	0	4	6	1.53	2.33	3	5	0	5.11	4.07
-10	0	4	3.77	-3.63	0	2	2	3.44	3.56	-9	2	3	0.00	-1.16	0	4	7	1.57	-2.85	3	5	1	2.64	-2.06
-10	0	5	2.33	2.57	0	2	3	2.57	3.90	-9	2	4	1.46	-1.85	0	4	8	0.00	0.72	3	5	2	2.75	-1.62
0	1	1	10.96	-12.50	0	2	4	10.17	10.94	-9	2	5	1.48	1.92	1	4	0	8.32	9.30	3	5	3	6.67	6.80
0	1	2	13.81	14.25	0	2	5	2.75	3.44	-9	2	6	2.94	-2.74	1	4	1	30.49	33.72	3	5	4	6.78	-6.74
0	1	3	5.43	-4.48	0	2	6	0.00	0.68	-10	2	3	3.14	-2.85	1	4	2	4.93	-4.00	3	5	5	1.85	2.28
0	1	4	6.00	6.76	0	2	7	4.80	5.93	-10	2	4	2.32	2.52	1	4	3	18.70	18.99	4	5	0	3.35	-2.71
0	1	5	8.61	8.87	0	2	8	1.71	-1.53	-10	2	5	1.32	-1.70	1	4	4	2.03	2.58	4	5	1	2.03	1.90
0	1	6	0.00	0.59	1	2	0	0.82	1.29	0	3	1	7.86	7.69	1	4	5	2.45	-1.62	4	5	2	1.25	-1.13
0	1	7	3.74	3.50	1	2	1	8.85	-8.54	0	3	2	2.08	-1.60	2	4	0	12.67	12.47	4	5	3	3.76	-3.38
0	1	8	1.79	2.51	1	2	2	4.41	4.31	0	3	3	4.61	3.96	2	4	1	7.93	-8.00	4	5	4	0.00	0.64
1	1	0	5.92	6.27	1	2	3	2.67	-1.97	0	3	4	1.09	-0.25	2	4	2	12.54	12.11	4	5	5	2.89	-3.49
1	1	1	4.46	-4.57	1	2	4	3.89	-3.67	0	3	5	3.15	-2.87	2	4	3	4.40	-3.15	5	5	0	13.10	12.97
1	1	2	3.10	2.77	1	2	5	6.90	7.22	0	3	6	0.00	1.46	2	4	4	1.65	2.07	5	5	1	2.62	-1.95
1	1	3	0.00	0.14	1	2	6	3.48	-3.75	0	3	7	0.00	0.49	2	4	5	0.00	0.29	5	5	2	5.96	5.03
1	1	4	1.74	-1.53	1	2	7	2.51	2.72	0	3	8	0.00	0.07	3	4	0	21.24	-18.69	5	5	3	6.03	6.11
1	1	5	0.00	0.36	2	2	0	8.64	-8.96	1	3	0	8.72	-9.96	3	4	1	11.71	11.00	5	5	4	1.67	-1.67
2	1	0	0.00	0.72	2	2	1	0.64	1.91	1	3	1	14.10	14.28	3	4	2	8.78	-7.66	5	5	5	1.89	2.31
2	1	1	10.23	-10.44	2	2	2	5.44	-5.74	1	3	2	4.13	-3.27	3	4	3	6.03	5.22	6	5	0	5.74	5.17
2	1	2	3.02	2.72	2	2	3	2.26	-1.82	1	3	3	0.78	1.09	3	4	4	5.35	5.11	6	5	1	3.32	-3.71
2	1	3	8.85	-8.14	2	2	4	0.80	0.67	1	3	4	5.67	5.35	3	4	5	4.35	-4.85	6	5	2	4.74	5.09
2	1	4	4.69	-3.95	2	2	5	1.78	1.84	1	3	5	0.00	0.58	4	4	0	2.78	2.73	6	5	3	0.85	-1.38
2	1	5	5.21	5.49	2	2	6	3.82	-4.33	2	3	0	1.96	-1.51	4	4	1	6.47	-6.37	6	5	4	1.71	2.25
2	1	6	3.53	-3.42	2	2	7	2.95	3.94	2	3	1	5.64	4.71	4	4	2	0.00	0.14	7	5	0	2.71	2.25
2	1	7	2.79	2.88	3	2	0	3.28	3.16	2	3	2	1.35	1.36	4	4	3	0.00	-0.39	7	5	1	3.82	-2.71
3	1	0	0.00	0.22	3	2	1	4.58	-3.58	2	3	3	5.42	4.39	4	4	4	2.03	-2.43	7	5	2	0.00	-1.02
3	1	1	1.96	1.61	3	2	2	1.52	-1.94	2	3	4	2.52	2.30	4	4	5	0.00	-0.39	7	5	3	3.79	3.82
3	1	2	4.10	-4.03	3	2	3	1.35	-1.22	2	3	5	2.12	-2.30	5	4	0	3.58	3.33	8	5	0	0.00	1.28
3	1	3	5.02	4.68	3	2	4	5.75	-6.06	3	3	0	5.50	-6.08	5	4	1	4.84	4.52	8	5	1	0.93	-0.87
3	1	4	4.03	-4.16	3	2	5	2.17	2.66	3	3	1	3.82	3.80	5	4	2	3.39	-2.46	8	5	2	0.00	-0.35
3	1	5	1.02	1.28	3	2	6	3.09	-3.37	3	3	2	5.25	5.10	5	4	3	4.20	4.64	9	5	0	3.98	3.63
4	1	0	15.91	18.45	4	2	0	8.78	-8.48	3	3	3	8.42	-7.84	5	4	4	3.36	3.53	-1	5	1	2.39	1.53
4	1	1	6.99	-6.67	4	2	1	12.42	12.78	3	3	4	7.68	8.13	5	4	5	0.00	-0.38	-1	5	2	1.03	0.14
4	1	2	12.15	13.00	4	2	2	3.42	-2.25	3	3	5	2.04	-2.43	5	4	0	3.59	3.23	-1	5	3	5.44	5.47
4	1	3	4.66	-4.23	4	2	3	0.00	1.57	4	3	0	1.71	-1.70	6	4	1	0.00	-0.23	-1	5	4	9.28	-10.00
4	1	4	0.00	-0.98	4	2	4	4.10	4.07	4	3	1	1.65	1.12	5	4	2	2.01	1.75	-1	5	5	4.58	3.87
4	1	5	2.64	3.25	4	2	5	1.68	1.83	4	3	2	3.82	-3.17	6	4	3	2.23	1.71	-2	5	1	4.70	3.76
4	1	6	2.02	-2.32	5	2	0	0.00	-0.22	4	3	3	5.74	5.32	6	4	4	0.00	0.12	-2	5	2	4.03	-3.54
5	1	0	1.14	-0.34	5	2	1	0.00	-0.53	4	3	4	2.03	1.89	7	4	0	3.28	3.08	-2	5	3	3.33	2.94
5	1	1	0.00	-0.50	5	2	2	4.77	4.40	4	3	5	0.00	1.16	7	4	1	2.85	2.48	-2	5	4	1.74	1.52
5	1	2	0.00	-0.43	5	2	3	2.78	-2.74	5	3	0	2.84	-2.07	7	4	2	2.21	-2.09	-2	5	5	1.60	-1.42
5	1	3	0.00	0.64	5	2	4	0.00	0.50	5	3	1	4.47	3.52	7	4	3	0.00	0.67	-3	5	1	9.60	-9.13
5	1	4	0.00	-0.32	5	2	5	0.00	-0.00	5	3	2	0.00	1.52	8	4	0	0.00	1.22	-3	5	2	6.99	-7.39
5	1	5	0.00	-0.82	6	2	0	6.75	-6.87	5	3	3	2.84	-2.76	8	4	1	2.00	-2.03	-3	5	3	3.41	2.53
6	1	0	0.00	0.69	6	2	1	5.24	4.83	5	3	4	2.50	2.73	8	4	2	0.00	0.21	-3	5	4	5.57	-4.82
6	1	1	0.00	0.22	6	2	2	2.17	-2.10	5	3	5	0.00	0.39	9	4	0	1.21	1.09	-3	5	5	5.02	3.86
6	1	2	4.56	4.34	6	2	3	2.42	-2.12	6	3	0	2.69	-1.57	-1	4	1	2.94	-1.60	-4	5	1	4.13	-3.61
6	1	3	0.00	-0.28	6	2	4	1.50	1.64	6	3	1	0.00	0.94	-1	4	2	20.14	-26.13	-4	5	2	0.77	0.28
6	1	4	1.53	-0.96	7	2	0	0.76	1.50	6	3	2	5.98	-5.80	-1	4	3	5.48	6.21	-4	5	3	2.40	2.40
7	1	0	1.31	1.54	7	2	1	0.00	-0.68	6	3	3	0.00	0.95	-1	4	4	12.24	-12.32	-4	5	4	3.52	-3.11
7	1	1	1.77	-1.55	7	2	2	3.61	3.73	6	3	4	0.00	-0.93	-1	4	5	6.50	-5.32	-4	5	5	3.56	2.81

Table 4 (*cont.*)

-5	5	1	4.64	-3.48	-8	6	3	0.67	1.40	1	8	4	4.20	-4.17	5	9	0	2.29	-1.50	-2	10	3	11.65	14.32
-5	5	2	5.01	4.99	-8	6	4	0.00	-1.06	1	8	5	2.78	-2.42	5	9	1	1.99	-1.68	-2	10	4	17.46	-18.45
-5	5	3	8.34	10.92	-8	6	5	0.00	0.03	2	8	0	6.42	-1.96	5	9	2	2.47	-2.08	-2	10	5	7.07	6.53
-5	5	4	0.00	-0.81	-9	6	1	1.84	-1.48	2	8	1	3.08	-0.66	5	9	3	0.00	-0.59	-3	10	1	2.92	-2.67
-5	5	5	9.71	9.07	-9	6	2	0.58	1.71	2	8	2	4.71	2.44	5	9	4	3.30	-3.35	-3	10	2	1.42	-1.46
-6	5	1	4.57	4.49	-9	6	3	3.30	-3.80	2	8	3	7.70	-7.29	6	9	0	6.53	6.28	-3	10	3	1.73	-1.85
-6	5	2	0.00	-0.38	-9	6	4	2.46	-2.53	2	8	4	8.29	7.02	6	9	1	5.94	6.35	-3	10	4	3.53	3.42
-6	5	3	2.32	2.57	-9	6	5	0.00	-0.15	2	8	5	3.27	-3.78	6	9	2	2.16	-1.93	-3	10	5	3.28	-2.82
-6	5	4	2.36	1.50	0	7	1	6.72	-6.11	3	8	0	2.65	-2.41	6	9	3	3.40	4.24	-4	10	1	11.43	-10.77
-6	5	5	0.99	1.28	0	7	2	8.15	8.34	3	8	1	6.70	5.25	6	9	4	2.28	3.09	-4	10	2	2.34	-1.82
-7	5	1	4.95	-4.93	0	7	3	4.51	-4.22	3	8	2	3.58	-3.07	7	9	0	0.00	0.38	-4	10	3	6.03	6.03
-7	5	2	2.47	-2.78	0	7	4	1.54	1.85	3	8	3	8.06	8.12	7	9	1	0.00	-0.14	-4	10	4	9.00	-8.28
-7	5	3	3.20	3.73	0	7	5	3.81	3.26	3	8	4	1.71	1.38	7	9	2	0.00	0.35	-4	10	5	7.46	8.12
-7	5	4	7.07	-6.66	0	7	6	1.07	-1.32	3	8	5	0.00	0.75	8	9	0	1.00	-0.97	-5	10	1	0.00	0.37
-7	5	5	0.00	1.39	0	7	7	0.00	1.11	4	8	0	4.11	-3.72	8	9	1	3.61	3.24	-5	10	2	6.84	-5.84
-8	5	1	2.80	3.31	1	7	0	12.63	-12.25	4	8	1	2.45	1.17	-1	9	1	2.71	-2.21	-5	10	3	3.92	3.88
-8	5	2	2.10	-2.11	1	7	1	6.14	-5.09	4	8	2	5.03	4.21	-1	9	2	0.83	1.31	-5	10	4	1.93	-2.29
-8	5	3	0.68	1.86	1	7	2	2.67	-1.85	4	8	3	6.71	-7.37	-1	9	3	4.85	-5.62	-5	10	5	0.00	0.34
-8	5	4	0.00	-0.90	1	7	3	4.25	-3.14	4	8	4	6.80	7.57	-1	9	4	1.96	-1.44	-6	10	1	3.32	-2.78
-8	5	5	1.50	-0.78	1	7	4	5.69	5.50	4	8	5	2.81	-3.70	-1	9	5	0.00	-1.55	-6	10	2	1.09	1.53
-9	5	1	2.84	-2.73	1	7	5	0.00	1.34	5	8	0	7.64	-6.96	-2	9	1	1.77	0.82	-6	10	3	4.49	5.63
-9	5	2	2.82	2.18	2	7	0	1.29	0.24	5	8	1	3.25	-2.55	-2	9	2	6.72	-7.64	-6	10	4	4.32	-4.24
-9	5	3	3.06	3.78	2	7	1	7.25	6.34	5	8	2	5.97	-5.58	-2	9	3	3.92	-3.62	-6	10	5	3.38	3.42
-9	5	4	0.00	-0.88	2	7	2	5.00	4.35	5	8	3	0.00	-1.05	-2	9	4	1.07	1.20	-7	10	1	0.00	1.57
-9	5	5	2.47	2.72	2	7	3	3.23	3.32	5	8	4	1.39	1.14	-2	9	5	9.09	-8.87	-7	10	2	1.33	-0.17
-10	5	4	1.75	-1.82	2	7	4	1.36	-0.72	5	8	5	1.47	-1.88	-3	9	1	7.13	-6.43	-7	10	3	0.71	1.10
0	6	0	9.68	9.48	2	7	5	5.79	6.49	6	8	0	3.23	-2.78	-3	9	2	1.92	-1.93	-7	10	4	0.00	-0.12
0	6	1	5.28	-4.60	3	7	0	0.00	-0.36	6	8	1	1.85	1.19	-3	9	3	2.56	-3.03	-7	10	5	2.32	-2.42
0	6	2	2.22	-1.43	3	7	1	3.07	2.43	6	8	2	0.00	0.66	-3	9	4	0.00	0.26	-8	10	1	3.74	-3.55
0	6	3	8.69	7.46	3	7	2	3.50	-2.98	6	8	3	3.38	-3.54	-3	9	5	2.17	1.88	-8	10	2	0.00	-0.50
0	6	4	8.11	-7.71	3	7	3	2.01	-1.58	6	8	4	1.85	2.45	-4	9	1	11.97	11.63	-8	10	3	2.57	3.05
0	6	5	4.85	5.37	3	7	4	2.33	1.99	7	8	0	0.00	1.32	-4	9	2	8.14	-8.39	-8	10	4	3.88	-4.06
0	6	6	1.52	-2.71	3	7	5	0.00	-0.39	7	8	1	0.00	1.25	-4	9	3	4.50	4.37	-8	10	5	1.62	2.04
0	6	7	0.00	-0.35	4	7	0	4.46	3.61	7	8	2	2.10	-2.05	-4	9	4	3.08	2.50	-9	10	1	0.00	-0.43
1	6	0	12.97	-12.82	4	7	1	8.81	-8.77	8	8	0	2.62	-2.35	-4	9	5	6.35	-6.36	-9	10	2	1.65	-1.38
1	6	1	11.92	11.75	4	7	2	7.26	6.94	8	8	1	1.54	1.59	-5	9	1	3.05	-2.71	-9	10	3	0.84	-0.39
1	6	2	9.78	-7.53	4	7	3	3.79	-3.57	-1	8	1	7.06	6.65	-5	9	2	0.00	-0.84	-9	10	4	2.60	-2.54
1	6	3	5.37	4.85	4	7	4	0.00	0.03	-1	8	2	4.66	4.97	-5	9	3	1.58	0.67	-9	10	5	0.74	-0.87
1	6	4	1.92	-1.05	4	7	5	1.75	1.98	-1	8	3	1.91	-1.35	-5	9	4	1.78	2.22	0	11	1	7.74	-7.28
1	6	5	8.42	8.36	5	7	0	7.18	-7.11	-1	8	4	3.46	3.33	-5	9	5	1.60	0.74	0	11	2	4.87	3.76
2	6	0	9.46	-6.96	5	7	1	7.95	8.12	-1	8	5	5.40	-4.07	-6	9	1	2.26	2.07	0	11	3	3.71	-3.93
2	6	1	9.60	8.33	5	7	2	0.00	-1.39	-2	8	1	9.80	-0.74	-6	9	2	15.28	-18.60	0	11	4	0.00	-1.09
2	6	2	9.21	-9.54	5	7	3	0.00	-0.25	-2	8	2	7.40	10.69	-6	9	3	1.71	1.54	0	11	5	5.43	5.33
2	6	3	7.56	6.61	5	7	4	4.22	5.10	-2	8	3	7.06	-8.19	-6	9	4	9.39	-9.39	0	11	6	2.00	-3.43
2	6	4	4.67	-5.01	5	7	5	0.92	0.70	-2	8	4	12.25	9.97	-6	9	5	6.82	-7.56	0	11	7	0.00	1.07
2	6	5	0.59	0.41	5	7	0	4.09	3.67	-2	8	5	2.95	-3.17	-7	9	1	2.37	-2.08	1	11	0	7.39	-4.65
3	6	0	4.99	-4.12	6	7	1	3.89	3.75	-3	8	1	7.46	7.41	-7	9	2	1.55	0.83	1	11	1	10.32	-9.40
3	6	1	1.59	-0.87	5	7	2	5.15	5.52	-3	8	2	3.93	-3.74	-7	9	3	0.71	-0.57	1	11	2	4.40	-4.85
3	6	2	3.98	3.17	6	7	3	2.55	2.76	-3	8	3	2.32	2.27	-7	9	4	0.00	0.89	1	11	3	2.12	-3.00
3	6	3	8.28	-7.84	6	7	4	0.00	0.97	-3	8	4	0.00	0.28	-7	9	5	0.00	-0.31	1	11	4	3.36	-3.53
3	6	4	2.23	-2.06	7	7	0	4.69	-4.09	-3	8	5	4.90	-4.28	-8	9	1	0.00	0.90	1	11	5	1.89	-2.67
3	6	5	0.00	1.36	7	7	1	1.68	2.37	-4	8	1	5.54	4.87	-8	9	2	4.40	-4.06	2	11	0	2.85	-1.60
4	6	0	0.00	0.92	7	7	2	0.00	0.35	-4	8	2	2.34	1.96	-8	9	3	2.63	3.40	2	11	1	5.86	-5.20
4	6	1	0.00	-0.08	7	7	3	3.33	-4.15	-4	8	3	5.00	-5.15	-8	9	4	0.00	-0.21	2	11	2	0.00	-0.22
4	6	2	2.64	-1.94	8	7	0	0.00	-0.14	-4	8	4	5.71	5.01	-8	9	5	0.00	0.34	2	11	3	4.22	-4.10
4	6	3	2.76	2.14	8	7	1	2.22	-1.87	-4	8	5	4.47	-3.91	-9	9	1	0.00	-0.46	2	11	4	3.28	-3.31
4	6	4	3.17	-3.04	-1	7	1	0.00	0.35	-5	8	1	5.09	4.57	-9	9	2	2.79	-2.28	2	11	5	3.79	4.21
4	6	5	1.32	0.83	-1	7	2	3.10	2.52	-5	8	2	0.00	0.42	-9	9	3	0.50	1.28	3	11	0	1.51	1.79
5	6	0	7.41	7.32	-1	7	3	1.82	1.60	-5	8	3	0.00	0.28	-9	9	4	1.31	-1.48	3	11	1	0.00	-1.03
5	6	1	0.00	-0.32	-1	7	4	6.03	5.96	-5	8	4	1.30	1.60	-9	9	5	0.00	0.50	3	11	2	0.00	-0.74
5	6	2	11.61	11.82	-1	7	5	0.00	0.35	-5	8	5	2.83	-2.85	0	10	0	8.61	-7.40	3	11	3	3.62	2.42
5	6	3	2.21	-2.29	-2	7	1	16.17	-16.62	-6	8	1	0.00	0.64	0	10	1	16.16	15.07	3	11	4	2.13	-2.02
5	6	4	1.65	1.76	-2	7	2	4.67	3.92	-6	8	2	3.21	4.11	0	10	2	10.44	-11.03	3	11	5	1.67	1.85
5	6	5	1.77	2.17	-2	7	3	7.78	-8.41	-6	8	3	7.61	-8.76	0	10	3	8.32	7.35	4	11	0	1.53	-1.24
6	6	0	0.00	-0.16	-2	7	4	5.39	-3.78	-6	8	4	8.18	8.44	0	10	4	8.17	-7.96	4	11	1	0.00	0.57
6	6	1	3.05	-3.50	-2	7	5	2.76	2.85	-6	8	5	5.74	-6.05	0	10	5	0.00	0.14	4	11	2	3.39	2.53
6	6	2	2.37	-2.26	-3	7	1	3.60	2.57	-7	8	1	0.00	0.63	0	10	6	1.45	2.00	4	11	3	4.03	-3.79
6	6	3	0.00	-0.85	-3	7	2	13.02	13.03	-7	8	2	5.25	-5.50	0	10	7	2.31	-2.93	4	11	4	2.93	-2.96
6	6	4	2.17	-2.78	-3	7	3	5.14	-4.71	-7	8	3	0.00	1.10	1	10	0	7.52	7.76	4	11	5	0.00	0.65
7	6	0	0.00	0.91	-3	7	4	5.36	5.71	-7	8	4	0.00	0.02	1	10	1	4.07	-4.54	5	11	0	4.09	4.14
7	6	1	2.80	-3.89	-3	7	5	3.39	-2.76	-7	8	5	0.00	0.10	1	10	2	2.76	2.57	5	11	1	9.23	-9.09
7	6	2	4.27	4.88	-4	7	1	3.16	-3.03	-8	8	1	2.90	2.97	1	10	3	0.00	-0.04	5	11	2	0.00	-1.30
7	6	3	1.67	-1.35	-4	7	2	5.56	5.78	-8	8	2	0.00	0.53	1	10	4	1.89	2.35	5	11	3	1.11	-1.54
8	6	0	0.00	0.42	-4	7	3	4.50	-4.91	-8	8	3	2.67	-3.06	1	10	5	2.85	2.91	5	11	4	3.44	-4.24
8	6	1	0.91	0.17	-4	7	4	3.13	3.22	-8	8	4	3.77	3.93	2	10	0	3.02	2.60	6	11	0	0.00	-0.07
8	6	2	1.32	-1.38	-4	7	5	0.84	0.61	-8	8	5	1.71	-2.16	2	10	1	1.79	-1.47	6	11	1	1.64	-1.76
9	6	0	1.55	1.45	-5	7	1	7.67	7.35	-9	8	1	1.32	0.86	2	10	2	6.27	5.09	6	11	2	5.09	5.67
-1	6	1	16.69	-19.88	-5	7	2	2.69	2.00	-9	8	2	0.54	-0.94	2	10	3	4.69	3.61	6	11	3	0.00	-0.69
-1	6	2	5.97	4.31	-5	7	3	8.72	-9.45	-9	8	3	2.92	3.04	2	10	4	2.30	-2.26	7	11	0	2.19	2.14
-1	6	3	1.63	1.37	-5	7	4	6.49	5.90	-9	8	4	1.74	1.60	2	10	5	2.51	2.46	7	11	1	1.51	1.55
-1	6	4	4.91	-5.42	-5	7	5	9.71	-8.77	-9	8	5	1.11	1.32	3	10	0	1.88	2.00	7	11	2	2.18	-2.04
-1	6	5	10.82	10.85	-6	7	1	9.66	-10.00						3	10	1	2.30	2.12	8	11	0	1.06	-0.72
-2	6	1	8.47	8.09	-6	7	2	0.00	-0.32	0	9	1	11.08	9.54	3	10	2	3.10	-2.53	8	11	1	2.59	-2.34
-2	6	2	4.73	-4.33	-6	7	3	7.51	-8.67	0	9	2	8.29	-8.03	3	10	3	0.00	-0.60	-1	11	1	6.08	-4.53
-2	6	3	8.79	9.92	-6	7	4	5.77	-5.48	0	9	3	8.05	7.35	3	10	4	0.00	-0.80	-1	11	2	5.85	-5.59
-2	6	4	4.56	-4.86	-6	7	5	2.34	-2.03	0	9	4	1.19	-1.21	3	10	5	0.00	-1.46	-1	11	3	4.88	5.43
-2	6	5	7.24	6.25	-7	7	1	7.26	7.02	0	9	5	3.76	-3.35	4	10	0	10.28	9.05	-1	11	4	5.75	-5.71
-3	6	1	17.94	-20.32	-7	7	2	1.56	-2.28	0	9	6	0.94	2.45	4	10	1	8.58	-7.30	-1	11	5	2.78	2.96
-3	6	2	13.24	13.35	-7	7	3	2.27	-0.33	0	9	7	0.00	-0.05	4	10	2	0.00	0.75	-2	11	1	5.59	-5.92
-3	6	3	7.50	-8.34	-7	7	4	3.11	3.03	1	9	0	7.07	7.14	4	10	3	4.96	4.48	-2	11	2	5.40	5.34
-3	6	4	0.00	0.78	-7	7	5	2.66	-2.42	1	9	1	6.33	4.55	4	10	4	4.67	-5.50	-2	11	3	1.73	-2.00
-3	6	5	7.80	7.11	-8	7	1	0.00	-1.43	1	9	2	0.00	-0.18	4	10	5	2.46	2.75	-2	11	4	0.00	0.10
-4	6	1	1.39	0.86	-8	7	2	2.31	2.75	1	9	3	1.70	1.95	5	10	0	5.89	5.17	-2	11	5	5.15	4.69
-4	6	2	1.79	-0.96	-8	7	3	0.67	-1.03	1	9	4	4.55	-4.37	5	10	1	5.37	4.78	-3	11	1	2.53	2.50
-4	6	3	3.67	3.32	-8	7	4	0.00	-1.33	1	9	5	1.01	-0.72	5	10	2	0.00	1.27	-3	11	2	2.52	-1.53
-4	6	4	3.00	-2.25	-8	7	5	2.06	2.82	2	9	0	7.69	6.72	5	10	3	2.66	3.12	-3	11	3	4.47	4.77
-5	6	1	10.71	-10.35	-9	7	1	3.19	3.12	2	9	1	9.53	8.10	5	10	4	0.00	0.37	-3	11	4	3.26	-3.07
-5	6	2	9.09	8.50	-9	7	2	0.57	-0.16	2	9	2	4.89	3.53	6	10	0	7.53	7.30	-3	11	5	0.94	-1.64
-5	6	3	6.32	-7.62	-9	7	3	0.54	-0.61	2	9	3	6.97	5.59	6	10	1	0.00	-0.02	-4	11	1	11.39	-11.09
-5	6	4	4.47	4.12	-9	7	4	0.00	0.39	2	9	4	6.76	6.33	6	10	2	2.11	1.86	-4	11	2	7.37	7.92
-5	6	5	2.11	1.40	-9	7	5	0.00	0.07	2	9	5	2.85	-3.01	6	10	3	5.84	6.47	-4	11	3	3.70	-4.07
-6	6	1	2.21	-2.00	0	8	0	17.45	-14.58	3	9	0	3.59	2.92	7	10	0	0.00	0.12	-4	11	4	0.00	-0.26
-6	6	2	4.07	-3.50	0	8	1	7.08	5.56	3	9	1	3.65	-2.76	7	10	1	0.00	0.78	-4	11	5	5.13	4.82
-6	6	3	3.89	4.00	0	8	2	2.50	-2.28	3	9	2	4.90	4.07	7	10	2	0.00	0.48	-5	11	1	9.45	-9.10
-6	6	4	6.75	-5.32	0	8	3	2.82	-2.42	3	9	3	2.07	-1.35	8	10	0	2.24	2.23	-5	11	2	3.29	-1.92
-6	6	5	4.67	4.12	0	8	4	6.50	5.67	3	9	4	0.00	1.15	8	10	1	1.91	-1.67	-5	11	3	1.17	-0.92
-7	6	1	0.00	0.03	0	8	5	2.50	-1.91	3	9	5	0.00	-1.06	-1	10	1	4.47	3.47	-5	11	4	7.53	-8.00
-7	6	2	6.56	6.06	0	8	6	1.05	-0.00	4	9	0	1.12	0.91	-1	10	2	5.50	-5.13	-5	11	5	0.00	-0.07
-7	6	3	0.71	-0.60	0	8	7	0.00	1.37	4	9	1	2.19	1.53	-1	10	3	1.45	1.28	-6	11	1	3.66	-3.65
-7	6	4	1.12	-1.53	1	8	0	2.07	-2.91	4	9	2	6.18	-5.67	-1	10	4	2.25	1.76	-6	11	2	10.03	10.60
-7	6	5	2.35	2.62	1	8	1	0.00	0.30	4	9	3	5.48	5.10	-1	10	5	0.00	-0.35	-6	11	3	1.89	-2.55
-8	6	1	0.00	-0.16	1	8	2	2.81	-2.69	4	9	4	0.00	1.13	-2	10	1	4.28	4.86	-6	11	4	4.35	4.42
-8	6	2	0.00	-0.64	1	8	3	2.98	2.55	4	9	5	1.44	-1.37	-2	10	2	16.60	-21.31	-6	11	5	3.27	3.09

Table 4 (*cont.*)

-7	11	1	0.00	0.24	1	13	5	2.37	-2.60	6	14	3	1.39	1.42	-6	15	1	0.00	1.38	3	17	1	3.32	2.74
-7	11	2	1.87	1.22	2	13	0	2.96	-2.89	7	14	0	0.00	0.78	-6	15	2	1.08	-0.95	3	17	2	0.00	0.32
-7	11	3	2.23	2.89	2	13	1	6.76	6.76	7	14	1	4.25	3.71	-6	15	3	2.54	3.05	3	17	3	2.73	-2.71
-7	11	4	1.09	-1.50	2	13	2	2.46	-2.31	7	14	2	2.52	-2.40	-6	15	4	1.08	0.71	3	17	4	3.18	3.17
-7	11	5	2.67	2.93	2	13	3	5.80	6.09	8	14	0	1.80	-1.49	-6	15	5	1.67	-2.01	3	17	5	0.00	-0.73
-8	11	1	0.00	-1.07	2	13	4	0.00	0.80	-1	14	1	7.96	6.82	-7	15	1	2.60	-2.56	4	17	0	0.00	-0.54
-8	11	2	4.99	4.78	2	13	5	0.00	-1.26	-1	14	2	10.13	-8.82	-7	15	2	0.00	-1.36	4	17	1	5.47	-6.12
-8	11	3	2.34	-2.98	3	13	0	2.91	-2.63	-1	14	3	0.89	0.75	-7	15	3	2.32	3.34	4	17	2	3.32	2.85
-8	11	4	0.00	0.00	3	13	1	0.00	-0.14	-1	14	4	0.00	0.61	-7	15	4	3.82	-3.94	4	17	3	2.64	-2.41
-8	11	5	0.00	-0.45	3	13	2	2.63	1.90	-1	14	5	8.07	-8.21	-7	15	5	0.00	1.00	5	17	0	2.10	1.62
-9	11	1	2.23	-1.73	3	13	3	5.75	-5.34	-2	14	1	5.44	-4.68	-8	15	1	1.42	-1.35	5	17	1	2.11	-2.20
-9	11	3	1.12	-0.77	3	13	4	4.05	4.39	-2	14	2	0.65	-0.73	-8	15	2	1.87	2.00	5	17	2	2.89	2.67
-9	11	4	1.97	-2.14	3	13	5	2.28	-2.21	-2	14	3	5.39	-6.37	-8	15	3	1.53	-1.78	5	17	3	3.28	-3.18
-9	11	5	1.26	-0.94	4	13	0	3.24	-3.21	-2	14	4	1.49	-1.45	-8	15	4	0.00	0.39	5	17	0	0.00	-1.19
0	12	0	10.72	-9.71	4	13	1	0.00	-0.17	-2	14	5	1.76	1.31	-8	15	5	0.00	-3.10	6	17	1	2.36	-2.47
0	12	1	1.31	1.08	4	13	2	0.00	0.46	-3	14	1	10.40	9.95	0	16	0	5.77	-5.99	6	17	2	1.89	1.51
0	12	2	1.92	2.06	4	13	3	0.00	0.85	-3	14	2	9.21	-9.17	0	16	1	19.65	-19.42	7	17	0	1.84	-1.53
0	12	3	1.89	-2.00	4	13	4	4.07	4.65	-3	14	3	6.56	6.92	0	16	2	6.64	-6.53	7	17	1	1.61	1.21
0	12	4	8.63	8.64	4	13	5	0.00	-0.35	-3	14	4	0.00	-0.42	0	16	3	7.60	-7.37	-1	17	1	3.14	2.85
0	12	5	1.27	-1.21	5	13	0	9.67	-8.74	-3	14	5	4.26	-3.65	0	16	4	6.10	-5.58	-1	17	2	2.85	2.22
0	12	6	0.97	1.39	5	13	1	4.31	3.74	-4	14	1	0.00	0.50	0	16	5	3.73	-4.39	-1	17	3	0.00	0.74
0	12	7	0.67	1.34	5	13	2	0.00	-1.72	-4	14	2	7.01	-7.14	0	16	6	1.97	-1.67	-1	17	4	5.87	5.49
1	12	0	3.35	0.50	5	13	3	2.91	-2.88	-4	14	3	0.00	0.99	1	16	0	6.87	5.47	-1	17	5	0.00	0.51
1	12	1	11.14	9.07	5	13	4	2.96	3.07	-4	14	4	1.90	-1.75	1	16	1	16.14	-14.44	-2	17	1	1.75	-0.89
1	12	2	8.92	7.71	6	13	0	2.35	-2.00	-4	14	5	1.88	1.86	1	16	2	10.71	9.13	-2	17	2	4.71	4.17
1	12	3	2.29	2.52	6	13	1	1.21	-1.77	-5	14	1	5.26	4.91	1	16	3	9.45	-8.08	-2	17	3	2.32	-1.67
1	12	4	3.71	4.28	6	13	2	2.54	-2.44	-5	14	2	7.36	-7.11	1	16	4	0.00	0.03	-2	17	4	0.64	-1.64
1	12	5	2.86	2.96	6	13	3	1.89	-1.65	-5	14	3	3.57	4.10	1	16	5	3.60	3.94	-2	17	5	3.50	3.67
2	12	0	5.03	-5.79	7	13	0	2.06	-2.22	-5	14	4	2.42	-2.15	2	16	0	6.38	5.78	-3	17	1	7.57	7.04
2	12	1	2.48	-1.68	7	13	1	4.08	3.39	-5	14	5	2.85	-3.24	2	16	1	5.20	-5.31	-3	17	2	1.07	-0.01
2	12	2	1.53	1.35	7	13	2	2.45	2.53	-6	14	1	0.00	-0.39	2	16	2	0.00	1.13	-3	17	3	0.70	-0.24
2	12	3	8.82	-7.87	8	13	0	4.21	3.65	-6	14	2	1.55	-0.15	2	16	3	1.89	0.94	-3	17	4	3.03	2.98
2	12	4	6.39	6.33	-1	13	1	0.00	0.37	-6	14	3	0.71	-0.10	2	16	4	1.07	-0.86	-3	17	5	4.87	-4.60
2	12	5	3.85	-4.05	-1	13	2	5.39	-4.86	-6	14	4	1.42	1.77	2	16	5	0.00	0.83	-4	17	1	0.00	0.68
3	12	0	0.00	-0.10	-1	13	3	7.14	-8.64	-6	14	5	0.00	-0.68	3	16	0	5.87	5.25	-4	17	2	3.66	3.31
3	12	1	7.30	-7.30	-1	13	4	2.72	1.82	-7	14	1	0.00	1.53	3	16	1	4.87	-4.11	-4	17	3	1.60	-1.07
3	12	2	7.45	7.22	-1	13	5	5.68	-5.75	-7	14	2	3.94	-5.23	3	16	2	4.64	3.43	-4	17	4	2.59	-2.43
3	12	3	4.05	-4.39	-2	13	1	5.18	5.03	-7	14	3	0.65	1.42	3	16	3	2.42	-2.05	-4	17	5	2.60	2.99
3	12	4	0.00	0.55	-2	13	2	3.63	-3.38	-7	14	4	0.00	0.59	3	16	4	3.00	-2.92	-5	17	1	1.07	0.24
3	12	5	2.39	2.67	-2	13	3	6.20	6.50	-7	14	5	2.99	-3.36	3	16	5	2.28	2.81	-5	17	2	1.34	1.44
4	12	0	4.58	3.47	-2	13	4	4.07	-3.38	-8	14	1	0.00	0.23	4	16	0	1.69	1.48	-5	17	3	0.00	-1.07
4	12	1	1.27	-1.27	-2	13	5	1.82	1.85	-8	14	2	1.42	-1.89	4	16	1	7.00	-7.41	-5	17	4	0.00	-0.30
4	12	2	4.82	4.41	-3	13	1	1.12	-1.29	-8	14	3	1.34	1.37	4	16	2	4.03	-3.67	-5	17	5	0.00	0.27
4	12	3	4.41	-4.21	-3	13	2	3.72	3.51	-8	14	4	0.00	-1.15	4	16	3	0.00	-0.21	-6	17	1	2.62	-2.99
4	12	4	4.22	4.68	-3	13	3	6.31	-7.11	-8	14	5	0.00	0.38	4	16	4	3.39	-3.96	-6	17	2	3.28	3.19
4	12	5	0.00	-0.46	-3	13	4	5.52	4.39	-9	14	3	2.71	2.47	5	16	0	0.00	0.35	-6	17	3	1.89	-2.33
5	12	0	4.71	4.14	-3	13	5	1.83	-1.45	0	15	1	2.87	2.53	5	16	1	0.00	-0.08	-6	17	4	0.83	-1.49
5	12	1	0.00	-0.67	-4	13	1	3.07	2.50	0	15	2	3.48	-3.39	5	16	2	1.92	1.82	-6	17	5	3.33	3.67
5	12	2	7.09	6.99	-4	13	2	1.42	-1.28	0	15	3	4.86	5.04	5	16	3	0.00	0.05	-7	17	1	0.00	0.45
5	12	3	0.00	0.32	-4	13	3	0.66	0.82	0	15	4	1.90	1.83	6	16	0	3.09	3.32	-7	17	2	0.00	1.21
5	12	4	1.14	1.35	-4	13	4	3.17	-2.73	0	15	5	2.96	3.48	6	16	1	1.39	-1.40	-7	17	3	3.19	-3.30
6	12	0	0.00	-1.39	-4	13	5	0.00	-0.25	0	15	6	2.98	3.16	6	16	2	0.00	0.49	-7	17	4	1.43	1.53
6	12	1	0.00	-0.96	-5	13	1	1.67	1.53	0	15	7	1.07	1.82	7	16	0	1.75	-1.28	-7	17	5	0.00	-0.83
6	12	2	0.00	-0.10	-5	13	2	1.71	-1.03	1	15	0	9.19	8.31	7	16	1	1.07	-0.95	-8	17	1	1.85	-2.02
6	12	3	3.50	-3.73	-5	13	3	8.34	-10.57	1	15	1	0.00	-0.04	-1	16	1	0.67	0.27	-8	17	2	0.00	1.92
7	12	0	0.00	0.46	-5	13	4	3.81	4.80	1	15	2	1.00	-0.52	-1	16	2	6.75	6.18	-8	17	3	0.41	-1.14
7	12	1	1.32	-0.67	-5	13	5	7.15	-8.51	1	15	3	7.10	6.92	-1	16	3	3.97	-4.23	-8	17	4	0.94	-0.53
7	12	2	2.22	2.17	-6	13	1	0.00	-0.37	1	15	4	5.99	-6.00	-1	16	4	4.45	4.03	0	18	0	11.89	-10.35
8	12	0	1.22	-1.24	-6	13	2	1.91	-0.36	1	15	5	2.57	2.87	-1	16	5	1.88	2.11	0	18	1	5.18	4.40
8	12	1	2.78	2.46	-6	13	3	2.27	-3.01	2	15	0	1.89	1.43	-2	16	1	2.07	-1.75	0	18	2	3.36	-2.57
-1	12	1	16.35	-14.71	-6	13	4	1.82	1.32	2	15	1	2.78	-2.12	-2	16	2	3.21	2.65	0	18	3	6.46	-6.89
-1	12	2	1.30	1.16	-6	13	5	0.00	-0.85	2	15	2	1.50	-1.52	-2	16	3	5.29	5.45	0	18	4	2.07	2.77
-1	12	3	5.13	-5.00	-7	13	1	5.04	5.39	2	15	3	3.43	-3.54	-2	16	4	2.21	-1.61	0	18	5	3.50	-4.50
-1	12	4	5.82	-5.78	-7	13	2	0.00	1.32	2	15	4	0.00	0.65	-2	16	5	0.00	0.79	0	18	6	2.32	-2.67
-1	12	5	2.14	1.92	-7	13	3	0.67	-1.37	2	15	5	1.28	-1.67	-3	16	1	2.28	-2.08	1	18	0	3.63	-3.05
-2	12	1	8.88	7.87	-7	13	4	4.64	5.98	3	15	0	5.85	5.94	-3	16	2	1.04	-0.10	1	18	1	4.78	4.26
-2	12	2	4.25	2.89	-7	13	5	1.62	-2.04	3	15	1	4.17	-3.17	-3	16	3	1.96	-2.06	1	18	2	1.09	-1.17
-2	12	3	2.58	3.53	-8	13	1	1.65	1.66	3	15	2	0.00	-0.64	-3	16	4	0.00	-0.79	1	18	3	0.00	1.25
-2	12	4	5.94	5.35	-8	13	2	5.32	-4.78	3	15	3	4.78	4.40	-3	16	5	1.88	1.53	1	18	4	0.00	0.90
-2	12	5	1.68	-1.00	-8	13	3	1.15	1.23	3	15	4	3.50	-4.07	-4	16	1	9.78	-10.08	1	18	5	3.50	-3.78
-3	12	1	0.00	-1.21	-8	13	4	1.14	0.67	3	15	5	1.21	1.28	-4	16	2	0.00	-1.19	2	18	0	7.17	-6.50
-3	12	2	7.22	6.68	-8	13	5	0.00	-0.60	4	15	0	3.18	3.35	-4	16	3	5.96	-6.55	2	18	1	5.28	4.57
-3	12	3	0.00	-0.09	-9	13	3	1.79	-1.84	4	15	1	6.53	6.33	-4	16	4	7.08	-6.40	2	18	2	0.00	1.36
-3	12	4	2.30	-1.80	0	14	0	0.00	-0.07	4	15	2	2.79	-1.90	-4	16	5	6.58	-6.52	2	18	3	3.38	-3.20
-3	12	5	6.48	6.99	0	14	1	2.80	3.07	4	15	3	4.58	4.19	-5	16	1	2.75	-2.35	2	18	4	3.30	3.32
-4	12	1	2.05	1.38	0	14	2	6.76	-6.53	4	15	4	1.84	-1.88	-5	16	2	3.13	3.28	2	18	5	0.00	-0.25
-4	12	2	6.60	7.13	0	14	3	1.39	1.32	5	15	0	3.89	3.76	-5	16	3	1.24	1.83	3	18	0	2.14	1.50
-4	12	3	5.01	-4.87	0	14	4	8.98	-9.44	5	15	1	0.00	-0.98	-5	16	4	1.82	-1.54	3	18	1	0.00	-0.51
-4	12	4	4.36	4.25	0	14	5	0.00	0.24	5	15	2	0.00	-0.85	-5	16	5	5.60	5.68	3	18	2	3.36	2.62
-4	12	5	5.12	-4.75	0	14	6	3.51	-4.38	5	15	3	3.79	3.60	-6	15	1	1.02	-0.80	3	18	3	2.64	2.27
-5	12	1	8.67	-7.85	0	14	7	0.53	-1.25	5	15	4	2.22	-2.83	-6	16	2	2.39	-0.11	3	18	4	2.98	2.77
-5	12	2	1.29	1.13	1	14	0	8.06	5.25	6	15	0	0.00	-0.25	-6	16	3	1.82	2.03	3	18	5	1.11	1.14
-5	12	3	8.20	-9.02	1	14	1	0.00	1.54	6	15	1	3.72	3.63	-6	16	4	2.67	-3.03	4	18	0	7.50	-7.65
-5	12	4	3.48	-3.17	1	14	2	1.68	-1.43	6	15	2	1.39	-1.58	-6	16	5	0.00	0.93	4	18	1	3.25	2.45
-5	12	5	0.00	-1.16	1	14	3	1.17	0.80	6	15	3	1.53	1.96	-7	16	1	2.46	-2.37	4	18	2	2.59	-2.10
-6	12	1	0.00	-0.28	1	14	4	2.58	2.70	7	15	0	3.02	2.96	-7	16	2	4.60	5.34	4	18	3	2.90	-2.76
-6	12	2	2.47	2.01	1	14	5	4.58	-5.30	7	15	1	2.34	-2.14	-7	16	3	1.37	-1.86	5	18	0	2.04	-1.68
-6	12	3	3.93	-5.43	2	14	0	0.00	0.01	-1	15	0	3.06	8.31	-7	16	4	0.00	0.29	5	18	1	0.00	-1.22
-6	12	4	3.11	2.99	2	14	1	4.85	4.79	-1	15	1	2.57	-1.97	-7	16	5	0.00	1.28	5	18	2	2.10	-1.88
-6	12	5	2.37	-2.50	2	14	2	3.19	-2.45	-1	15	2	1.92	-1.94	-8	16	1	0.71	-0.89	6	18	0	4.44	-4.76
-7	12	1	4.06	-4.64	2	14	3	4.75	4.25	-1	15	3	5.14	5.25	-8	16	2	0.00	0.46	6	18	1	2.95	3.17
-7	12	2	2.38	2.10	2	14	4	2.89	-2.55	-1	15	4	7.88	-7.37	-8	16	3	0.46	1.31	6	18	2	0.00	-0.22
-7	12	3	2.69	-3.77	2	14	5	0.00	1.01	-1	15	5	3.78	3.11	-8	16	4	1.79	-1.80	7	18	0	0.00	-0.82
-7	12	4	2.71	-2.70	3	14	0	1.82	1.50	-2	15	1	0.00	-0.62	-8	16	5	2.13	0.39	-1	18	1	2.05	0.78
-7	12	5	2.42	2.55	3	14	1	2.88	1.99	-2	15	2	1.38	-1.53	0	17	1	6.03	-5.34	-1	18	2	0.75	1.29
-8	12	1	2.10	2.42	3	14	2	5.46	-4.91	-2	15	3	0.92	-1.19	0	17	2	6.21	6.35	-1	18	3	2.25	1.84
-8	12	2	1.57	1.49	3	14	3	3.44	2.53	-2	15	4	2.65	2.22	0	17	3	6.53	-6.21	-1	18	4	0.00	0.78
-8	12	3	2.42	-3.25	3	14	4	0.00	1.02	-2	15	5	2.07	-2.35	0	17	4	1.78	-1.56	-1	18	5	0.00	0.09
-8	12	4	3.37	3.67	3	14	5	2.72	-3.39	-3	15	1	6.80	-6.17	0	17	5	0.00	-0.21	-2	18	1	6.77	5.77
-8	12	5	2.00	-2.37	4	14	0	7.28	-6.71	-3	15	2	1.43	-1.44	0	17	6	4.09	-4.32	-2	18	2	2.42	-2.46
-9	12	3	4.06	-3.71	4	14	1	0.00	0.65	-3	15	3	3.03	3.65	1	17	0	6.76	-5.62	-2	18	3	2.57	-2.99
0	13	1	4.17	3.96	4	14	2	2.82	-2.33	-3	15	4	5.84	-5.93	1	17	1	0.00	-0.63	-2	18	4	4.10	3.54
0	13	2	1.52	-0.74	4	14	3	1.92	-1.78	-3	15	5	4.42	4.59	1	17	2	0.00	0.02	-2	18	5	1.64	-1.90
0	13	3	1.39	1.33	4	14	4	0.00	-0.99	-4	15	1	3.22	-2.54	1	17	3	5.17	-4.75	-3	18	1	4.90	4.46
0	13	4	0.00	0.39	4	14	5	2.43	-2.78	-4	15	2	3.39	-3.00	1	17	4	4.43	4.65	-3	18	2	3.47	-2.78
0	13	5	4.70	-4.11	5	14	0	0.00	-1.05	-4	15	3	0.00	0.08	1	17	5	2.56	-2.76	-3	18	3	2.78	2.57
0	13	6	0.00	1.92	5	14	1	3.02	3.08	-4	15	4	2.32	2.17	2	17	0	2.39	1.81	-3	18	4	2.82	-2.29
0	13	7	0.87	-1.27	5	14	2	5.33	-5.50	-4	15	5	1.68	-1.32	2	17	1	5.18	-4.99	-3	18	5	0.81	0.42
1	13	0	13.48	-12.08	5	14	3	2.08	2.24	-5	15	1	2.75	-2.29	2	17	2	7.10	6.49	-4	18	1	3.32	2.42
1	13	1	0.00	0.53	5	14	4	0.00	0.38	-5	15	2	0.00	0.07	2	17	3	1.89	-1.65	-4	18	2	3.03	-2.82
1	13	2	2.09	-1.86	6	14	0	1.26	-1.31	-5	15	3	3.93	4.42	2	17	4	0.00	-0.78	-4	18	3	3.36	-3.75
1	13	3	6.95	-6.63	6	14	1	0.00	0.97	-5	15	4	2.33	-2.16	2	17	5	2.63	2.87	-4	18	4	2.30	1.96
1	13	4	3.78	3.72	6	14	2	0.00	-0.56	-5	15	5	2.82	2.70	3	17	0	5.81	-4.54	-4	18	5	1.78	-1.59

Table 4 (*cont.*)

-5	18	1	1.28	1.71	1	20	2	8.06	-7.71	-2	21	1	3.05	-2.85	2	23	1	0.00	-0.71	2	25	1	0.00	-0.92
-5	18	2	0.00	-1.08	1	20	3	2.42	-2.07	-2	21	2	3.66	3.20	2	23	2	1.35	-1.07	2	25	2	4.51	-4.74
-5	18	3	0.00	-0.77	1	20	4	1.52	-1.60	-2	21	3	2.33	-2.58	2	23	3	0.00	0.35	2	25	3	1.20	-1.29
-5	18	4	2.61	0.35	1	20	5	2.87	-2.60	-2	21	4	0.00	-0.16	2	23	4	1.22	-1.46	3	25	0	3.53	4.02
-5	18	5	0.00	-1.22	2	20	0	7.25	7.14	-2	21	5	2.29	1.83	3	23	0	5.92	-6.83	3	25	1	3.80	-3.68
-6	18	1	3.80	3.67	2	20	1	4.95	-4.36	-3	21	1	2.13	-2.21	3	23	1	4.64	4.72	3	25	2	0.00	0.98
-6	18	2	0.99	-0.75	2	20	2	2.17	-1.51	-3	21	2	2.67	3.04	3	23	2	0.00	-0.88	4	25	0	1.01	1.09
-6	18	3	1.57	-1.81	2	20	3	3.92	3.65	-3	21	3	1.54	1.96	3	23	3	1.67	-1.48	4	25	1	1.91	2.16
-6	18	4	2.71	2.75	2	20	4	4.44	-4.60	-3	21	4	2.86	-2.22	4	23	0	0.00	0.35	5	25	0	3.75	3.86
-6	18	5	0.00	-0.54	2	20	5	1.31	1.25	-3	21	5	0.00	-0.11	4	23	1	2.27	-1.98	-1	25	1	2.87	-3.03
-7	18	1	0.00	-0.27	3	20	0	0.00	-0.22	-4	21	1	3.15	-3.16	5	23	0	3.64	-3.78	-1	25	2	1.33	1.05
-7	18	2	2.19	-2.07	3	20	1	3.26	3.29	-4	21	2	2.88	2.25	5	23	1	1.32	1.28	-1	25	3	1.25	1.14
-7	18	3	0.76	0.42	3	20	2	2.92	-2.77	-4	21	3	1.49	-1.32	-1	23	1	3.32	3.32	-1	25	4	0.00	-0.78
-7	18	4	0.00	-0.83	3	20	3	0.00	-1.16	-4	21	4	0.30	-0.89	-1	23	2	1.05	0.95	-2	25	1	3.72	3.11
-7	18	5	1.48	1.13	3	20	4	0.00	-0.15	-4	21	5	3.18	3.46	-1	23	3	3.46	-3.89	-2	25	2	0.65	-1.36
-8	18	2	1.11	-0.07	4	20	0	3.88	3.98	-5	21	1	3.35	-3.10	-1	23	4	3.26	3.10	-2	25	3	3.07	2.65
-8	18	3	2.03	-2.42	4	20	1	0.00	-0.30	-5	21	2	1.67	-2.17	-1	23	5	0.00	-0.97	-2	25	4	1.87	1.70
-8	18	4	1.71	2.31	4	20	2	0.00	0.49	-5	21	3	1.74	-1.39	-2	23	1	2.31	2.20	-3	25	1	2.46	-2.58
0	19	1	4.25	3.55	4	20	3	3.09	2.85	-5	21	4	3.90	-4.31	-2	23	2	2.56	2.10	-3	25	2	0.61	-0.57
0	19	2	5.17	-5.35	5	20	0	1.32	-1.17	-5	21	5	2.82	-2.23	-2	23	3	1.29	0.65	-3	25	3	2.77	2.71
0	19	3	1.24	1.15	5	20	1	0.00	0.76	-6	21	1	0.00	-0.03	-2	23	4	2.14	1.65	-3	25	4	3.51	-3.25
0	19	4	1.32	1.25	5	20	2	2.20	-2.19	-6	21	2	1.29	1.50	-2	23	5	0.00	0.07	-4	25	2	2.22	-2.60
0	19	5	4.71	-5.35	6	20	0	2.95	2.98	-6	21	3	0.52	0.31	-3	23	1	3.86	3.80	-4	25	3	0.47	1.35
0	19	6	2.77	3.14	6	20	1	3.07	-2.64	-6	21	4	1.59	-1.38	-3	23	2	1.42	-1.85	-5	25	2	0.00	-0.04
1	19	0	3.72	-3.30	-1	20	1	5.64	5.63	-6	21	5	2.20	2.52	-3	23	3	4.10	-3.77	-5	25	3	3.26	3.35
1	19	1	3.01	2.58	-1	20	2	0.78	-1.53	-7	21	3	3.39	3.26	-3	23	4	3.78	3.98	0	26	1	0.61	-1.40
1	19	2	2.34	-1.74	-1	20	3	5.36	6.36	-7	21	4	1.16	-1.60	-3	23	5	2.15	-2.05	0	26	2	1.13	-1.39
1	19	3	0.00	-0.22	-1	20	4	1.87	1.54	0	22	1	2.96	-2.25	-4	23	1	3.57	3.59	0	26	3	3.35	3.83
1	19	4	2.09	-1.86	-1	20	5	1.87	1.75	0	22	2	1.42	1.22	-4	23	2	0.94	-1.07	0	26	4	1.25	-1.89
1	19	5	0.00	-0.32	-2	20	1	9.72	-8.96	0	22	3	1.82	-1.20	-4	23	3	0.00	0.11	1	26	0	1.99	-1.10
2	19	0	0.00	-0.10	-2	20	2	5.26	4.36	0	22	4	1.54	1.74	-4	23	4	1.19	0.93	1	26	1	0.00	-0.97
2	19	1	5.34	4.97	-2	20	3	3.20	-2.64	0	22	5	1.32	1.40	-4	23	5	2.65	-2.55	1	26	2	0.00	0.25
2	19	2	7.12	-6.42	-2	20	4	0.00	-0.48	1	22	0	0.00	0.48	-5	23	1	2.68	2.65	2	26	0	1.19	1.57
2	19	3	3.89	3.62	-2	20	5	0.00	-0.84	1	22	1	6.44	-5.60	-5	23	2	0.00	-0.35	2	26	1	2.44	-2.23
2	19	4	0.00	0.26	-3	20	1	3.05	-3.44	1	22	2	4.25	4.65	-5	23	3	1.16	-0.81	2	26	2	2.15	-2.14
2	19	5	2.22	-2.61	-3	20	2	1.35	-2.08	1	22	3	3.53	-3.37	-5	23	4	3.14	3.22	2	26	3	0.82	1.36
3	19	0	2.16	-2.13	-3	20	3	1.00	-1.16	1	22	4	3.60	-2.97	-6	23	1	2.85	2.25	3	26	0	2.57	-2.26
3	19	1	1.31	-1.38	-3	20	4	0.00	-0.42	1	22	5	1.53	1.44	-6	23	2	1.42	0.98	3	26	1	0.00	-1.19
3	19	2	0.00	0.66	-3	20	5	2.12	-1.93	2	22	0	4.75	-4.84	-6	23	3	3.49	2.74	3	26	2	1.55	1.71
3	19	3	0.89	-1.49	-4	20	1	0.00	0.04	2	22	1	3.21	2.72	-6	23	4	1.40	1.27	4	26	0	2.56	2.68
3	19	4	0.00	-0.03	-4	20	2	0.00	-0.13	2	22	2	3.80	-3.28	0	24	1	2.39	2.64	4	26	1	1.14	-0.97
4	19	0	2.37	-2.16	-4	20	3	4.39	5.03	2	22	3	0.00	0.35	0	24	2	0.00	0.72	-1	26	1	0.88	-1.25
4	19	1	4.53	4.13	-4	20	4	1.47	-1.75	2	22	4	0.00	-0.07	0	24	3	2.36	-2.47	-1	26	2	1.50	1.03
4	19	2	5.00	-5.00	-4	20	5	1.61	2.03	3	22	0	0.00	-0.35	0	24	4	2.04	1.60	-1	26	3	0.70	0.78
4	19	3	0.74	0.86	-5	20	1	2.77	2.65	3	22	1	2.08	-2.16	1	24	0	0.00	-0.63	-1	26	4	2.64	-2.35
5	19	0	3.11	-3.07	-5	20	2	1.76	2.00	3	22	2	4.39	3.56	1	24	1	5.58	5.55	-2	26	1	0.00	-0.34
5	19	1	0.00	0.68	-5	20	3	3.32	4.43	3	22	3	0.00	0.44	1	24	2	1.51	-4.53	-2	26	2	0.59	0.55
5	19	2	0.78	-1.03	-5	20	4	3.90	3.85	4	22	0	3.35	-3.06	1	24	3	3.71	3.88	-2	26	3	3.75	4.44
6	19	0	0.00	-0.92	-5	20	5	1.88	1.84	4	22	1	4.16	3.60	1	24	4	1.64	0.97	-2	26	4	1.77	-1.51
6	19	1	3.68	3.12	-6	20	1	3.25	-3.35	4	22	2	1.53	-1.36	2	24	0	0.00	0.80	-3	26	1	4.13	-4.01
6	19	2	2.47	-2.59	-6	20	2	0.89	-0.34	4	22	3	0.00	0.89	2	24	1	1.15	-0.90	-3	26	2	6.57	5.04
7	19	0	2.29	1.50	-6	20	3	1.62	2.00	5	22	0	3.14	-2.85	2	24	2	3.32	3.00	-3	26	3	3.13	-2.85
-1	19	1	2.35	-0.28	-6	20	4	2.78	-2.81	5	22	1	4.87	-4.79	2	24	3	2.09	-1.85	-4	25	1	0.00	0.44
-1	19	2	5.42	-5.57	-6	20	5	1.18	0.89	6	22	0	2.22	-2.08	3	24	0	0.00	0.14	-4	26	2	0.00	-0.72
-1	19	3	5.08	-5.78	-7	20	1	2.89	2.60	-1	22	1	1.31	-1.32	3	24	1	2.42	2.60	-4	26	3	3.75	3.79
-1	19	4	3.51	-3.57	-7	20	2	2.52	2.01	-1	22	2	5.34	5.53	3	24	2	4.39	-4.46	-5	26	2	2.37	2.39
-1	19	5	4.73	-4.79	-7	20	3	1.64	1.47	-1	22	3	2.26	-3.03	3	24	3	1.46	1.53	0	27	1	0.97	-1.38
-2	19	1	5.94	5.19	-7	20	4	3.10	2.87	-1	22	4	0.00	-0.18	4	24	0	0.00	-0.56	0	27	2	1.96	2.50
-2	19	2	7.39	-7.42						-1	22	5	2.24	1.80	4	24	1	1.00	-0.68	1	27	0	0.00	-0.50
-2	19	3	4.54	4.85	0	21	1	2.30	-2.10	-2	22	1	2.71	2.45	5	24	0	1.25	1.17	1	27	1	0.93	1.46
-2	19	4	0.00	-0.44	0	21	2	3.20	2.90	-2	22	2	0.76	0.08	5	24	1	3.26	4.04	1	27	2	1.95	1.60
-2	19	5	3.31	-3.24	0	21	3	0.00	0.08	-2	22	3	1.92	-0.96	-1	24	1	0.71	0.44	2	27	0	0.00	-0.49
-3	19	1	2.01	-2.22	0	21	4	0.00	-0.21	-2	22	4	1.52	1.10	-1	24	2	4.40	-3.82	2	27	1	0.00	-0.62
-3	19	2	4.64	-4.99	0	21	5	4.03	4.28	-2	22	5	0.00	-1.05	-1	24	3	1.05	0.78	2	27	2	3.19	3.93
-3	19	3	1.01	-0.82	1	21	0	2.16	1.71	-3	22	1	2.20	-1.66	-1	24	4	0.00	0.74	3	27	0	1.28	-1.47
-3	19	4	2.78	-2.50	1	21	1	8.19	-8.25	-3	22	2	3.17	3.64	-1	24	5	2.60	-2.72	3	27	1	1.51	1.46
-3	19	5	1.36	1.87	1	21	2	3.36	-2.50	-3	22	3	1.76	-2.15	-2	24	1	0.00	-1.26	4	27	0	2.10	-2.23
-4	19	1	1.69	1.94	1	21	3	0.00	-0.37	-3	22	4	1.96	-1.14	-2	24	2	1.40	-1.53	-1	27	1	2.47	2.23
-4	19	2	4.92	-4.12	1	21	4	3.91	-3.71	-3	22	5	2.36	1.91	-2	24	3	2.36	-2.71	-1	27	2	0.76	0.51
-4	19	3	2.45	2.89	1	21	5	0.00	-0.03	-4	22	1	3.32	2.96	-2	24	4	0.00	0.03	-1	27	3	0.83	1.02
-4	19	4	0.00	-0.57	2	21	0	0.00	1.25	-4	22	2	0.00	0.62	-2	24	5	1.83	-1.68	-2	27	1	3.33	-3.32
-4	19	5	2.60	-2.60	2	21	1	5.45	-4.85	-4	22	3	2.45	-2.39	-3	24	1	2.89	2.96	-2	27	2	3.54	3.72
-5	19	1	1.01	-0.43	2	21	2	5.03	4.51	-4	22	4	1.85	1.91	-3	24	2	3.69	-4.13	-2	27	3	2.28	-2.36
-5	19	2	2.99	-3.35	2	21	3	4.92	-4.70	-4	22	5	2.42	-2.53	-3	24	3	1.43	2.24	-3	27	1	0.82	1.07
-5	19	3	0.00	-0.28	2	21	4	0.00	0.48	-5	22	1	0.00	-0.69	-3	24	4	1.83	1.15	-3	27	3	0.83	-0.82
-5	19	4	2.14	-1.70	3	21	0	5.02	4.27	-5	22	2	4.30	4.42	-3	24	5	2.79	-2.86	-4	27	1	2.89	-2.78
-5	19	5	0.00	-0.32	3	21	1	1.78	-1.75	-5	22	3	1.61	-1.48	-4	24	1	1.03	-1.15	-4	27	2	4.32	4.70
-6	19	1	0.00	0.78	3	21	2	1.96	-2.03	-5	22	4	0.82	-0.99	-4	24	2	1.07	-0.45	0	28	1	0.70	1.00
-6	19	2	1.50	-1.25	3	21	3	3.01	3.05	-5	22	5	3.60	3.02	-4	24	3	0.53	-0.28	0	28	2	1.82	1.67
-6	19	3	0.00	-0.25	3	21	4	2.46	-2.89	-6	22	1	3.98	3.59	-4	24	5	1.12	1.25	1	28	0	2.68	-2.09
-6	19	4	3.00	2.76	4	21	0	2.00	1.82	-6	22	2	1.03	-1.64	-5	24	2	3.51	-3.75	1	28	1	1.31	-0.92
-6	19	5	3.92	-3.85	4	21	1	0.00	-1.06	-6	22	3	0.46	0.39	-5	24	3	0.45	0.34	1	28	2	2.51	-1.96
-7	19	1	0.00	-0.33	4	21	2	3.89	3.46	-6	22	4	0.00	-0.57	-5	24	4	1.73	1.32	2	28	0	3.58	-3.78
-7	19	2	2.52	1.73	4	21	3	0.00	-0.57	0	23	1	0.00	-0.05	-6	24	2	1.29	0.85	2	28	1	3.02	3.04
-7	19	3	0.85	0.25	5	21	0	0.00	-0.25	0	23	2	0.00	0.90	0	25	1	0.60	0.80	-1	28	1	1.47	1.48
-7	19	4	1.03	1.16	5	21	1	3.13	-2.71	0	23	3	1.02	-1.52	0	25	2	1.96	-2.35	-1	28	2	2.86	1.76
0	20	0	15.39	13.91	5	21	2	2.37	-2.63	0	23	4	0.00	0.23	0	25	3	0.00	0.67	-2	28	1	0.91	1.21
0	20	1	5.98	-4.69	5	21	3	0.90	1.35	0	23	5	1.46	-2.25	0	25	4	0.00	0.74	-2	28	3	3.46	-4.34
0	20	2	5.02	4.70	6	21	1	2.67	-2.70	1	23	0	3.57	-3.02	1	25	0	4.14	3.89	0	29	1	2.10	2.00
0	20	3	4.20	4.42	-1	21	1	6.17	-6.59	1	23	1	4.15	4.21	1	25	1	2.64	-2.22	1	29	0	2.27	2.17
0	20	4	2.16	-2.53	-1	21	2	0.00	0.04	1	23	2	0.00	0.85	1	25	2	0.00	-0.10	1	29	1	1.70	1.89
0	20	5	2.92	3.02	-1	21	3	2.11	2.36	1	23	3	3.07	-2.94	1	25	3	3.12	3.06	-1	29	1	1.10	1.16
1	20	0	4.49	-3.97	-1	21	4	2.89	-2.35	1	23	4	2.49	2.35	1	25	4	1.53	-1.99	-1	29	2	2.46	2.07
1	20	1	2.28	-2.08	-1	21	5	0.47	1.12	2	23	0	2.62	-1.79	2	25	0	1.72	-1.30	-2	29	1	0.96	1.01

coordinates of six oxygen atoms were determined. A subsequent structure factor calculation gave the R index 0·59, but there appeared to be no serious discrepancy between the observed and calculated structure factors. The signs of about 967 reflections were adequately determined and a three-dimensional Fourier synthesis was computed. In the Fourier map, electron-density peaks corresponding to all seven atoms of the spermine molecule clearly showed up together with the atoms of the phosphate group and the three water oxygen atoms and no spurious peak was present. A subsequent structure factor calculation with coordinates derived from this synthesis gave an R index of 0·38.

Two cycles of refinement by the three-dimensional F_o synthesis followed by a three-dimensional difference synthesis reduced R to 0·16. Next, the structure was refined by the three-dimensional least-squares method. Throughout the calculation, 416 reflections which are too weak to be observed were omitted. For computational convenience, the whole reflection data were, at first, divided into two groups.

The program refines the structure using diagonal approximations but the interaction between an overall temperature factor and a scale factor was taken into account. It includes a temperature factor for each atom. The weighting system was:

$$\begin{aligned} w(hkl) &= 0 && \text{if } F_o(hkl) \leq 1 , \\ w(hkl) &= 1/F_o^2(hkl) && \text{if } F_o(hkl) > 4 , \\ w(hkl) &= 1/16 && \text{if } F_o(hkl) \leq 4 . \end{aligned}$$

Finally, two cycles of least-squares refinement with full three-dimensional data were carried out, and gave an R of 0·127 (omitting $F_o=0$ terms). The process of the refinement is outlined in Table 1. The hydrogen atom contribution was not included.

The final refined parameters and their standard deviations calculated from the diagonal element of the normal equations for the last least-squares cycle are given in Tables 2 and 3. The bond lengths and angles and their standard deviations are listed in the subsequent tables. Darlow's equation (Darlow, 1960) was used to obtain the standard deviations of the bond angles. The final structure factors are listed in Table 4.

Discussion of the structure

The spermine molecule

As shown in Fig. 2, the molecule has a normal extended zigzag chain configuration with the full length of N(2)–N(2) 16·23 Å. It is centrosymmetric and all atoms are almost coplanar except the terminal nitrogen N(2) atoms. The N(2) atoms lie 0·19 Å out of the best plane formed by the remaining 12 atoms. The deviations of the individual atoms from this least-squares plane are given in Table 5. The bond lengths and angles of the spermine molecule are listed in Table 6 together with their standard deviations. In general, the values are in good agreement with those found in analogous compounds. The three C–N

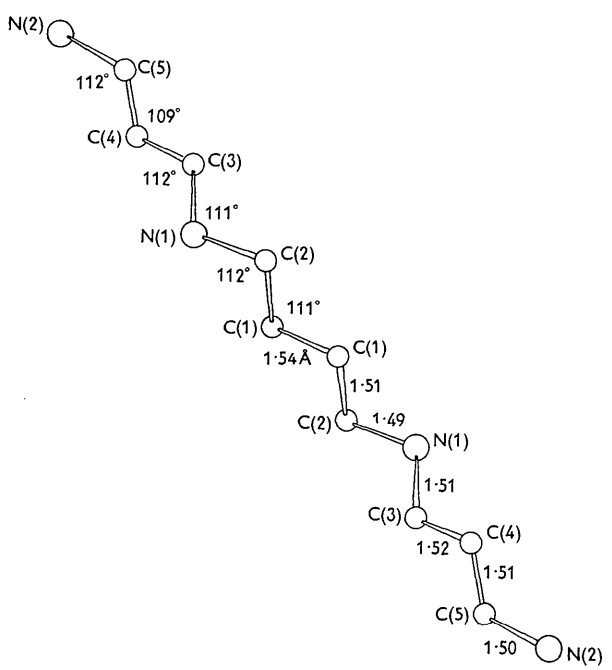

Fig. 2. Bond lengths and angles of the spermine molecule.

Table 5. *Deviations of atoms from the best molecular plane*

C(1)	0·03 Å
C(2)	−0·04
N(1)	−0·05
C(3)	−0·03
C(4)	0·02
C(5)	0·03
N(2)	−0·19 Å

Table 6. *Bond lengths and angles of the spermine molecule with their standard deviations*

N(2)–C(5)	1·503 ± 0·009 Å	N(2)–C(5)–C(4)	112·3 ± 0·6°
N(1)–C(2)	1·488	C(5)–C(4)–C(3)	108·7
N(1)–C(3)	1·510	C(4)–C(3)–N(1)	111·6
		C(3)–N(1)–C(2)	110·8
C(5)–C(4)	1·512 ± 0·010 Å	N(1)–C(2)–C(1)	112·4
C(4)–C(3)	1·522	C(2)–C(1)–C(1)	110·9
C(2)–C(1)	1·506		
C(1)–C(1)	1·541		

bond lengths found in the spermine molecule are $1{\cdot}50_3$ (N(2)–C(5)), $1{\cdot}48_8$ (N(1)–C(2)) and $1{\cdot}51_0$ Å (N(1)–C(3)). The average value $1{\cdot}50_0$ Å is a typical single-bond length between carbon and quarternary nitrogen atoms. It is not clear whether the differences in these three C–N bond lengths are actually significant or not, since they are almost within the limit of experimental error.

As will be discussed later, the hydrogen bond directions from the imino and amino nitrogen atoms, N(1) and N(2), suggest that the configuration of the bonds about the nitrogen atoms is tetrahedral. Both of these nitrogen atoms are, therefore, protonated and exist as NH_2^+ and NH_3^+ ions respectively.

The phosphate group

In Table 7, bond lengths and angles of the phosphate group are listed which may be compared with those of 2-aminoethanol phosphate (2-AE) determined by Kraut (1961) and of adenosine-5′-phosphate (A-5′-P) by Kraut & Jensen (1963). The values found in spermine phosphate fall within the expected range.

Three of the four P–O bonds have nearly the same rather short lengths: P–O(1), P–O(2) and P–O(3) of $1{\cdot}51_8$, $1{\cdot}51_7$ and $1{\cdot}52_9$ Å respectively, and seems to have each a double bond character. These values agree well with those of P–O(2) and P–O(3) in 2-AE and A–5′–P as shown in Table 8. The P–O(4) bond $1{\cdot}58_9$ Å is much the longest of the four and it seems to be that the O(4) atom belongs to the un-ionized OH group. The P–OH distance in spermine phosphate is appreciably longer than the corresponding distances (P–O(4)) in 2-AE and A–5′–P but it is still much less

Table 7. *Bond lengths and angles of the phosphate group with their standard deviations*

P–O(1)	1·518 ± 0·005 Å	O(1)–P–O(2)	113·2 ± 0·3°
P–O(2)	1·517	O(1)–P–O(3)	110·3
P–O(3)	1·529	O(1)–P–O(4)	107·8
P–O(4)	1·589	O(2)–P–O(3)	111·8
		O(2)–P–O(4)	108·4
O(1)–O(2)	2·534 ± 0·007 Å	O(3)–P–O(4)	104·9
O(1)–O(3)	2·501		
O(1)–O(4)	2·510		
O(2)–O(3)	2·523		
O(2)–O(4)	2·519		
O(3)–O(4)	2·472		

Table 8. *Comparison of* P–O *bond lengths in different compounds*

Spermine phosphate		2-Aminoethanol phosphate		Adenosine-5′-phosphate	
P–O(4)	1·589 Å	P–O(4)	1·557 Å	P–O(4)	1·566 Å
P–O(1)	1·518	P–O(2)	1·493	P–O(2)	1·514
P–O(2)	1·517	P–O(3)	1·503	P–O(3)	1·495
P–O(3)	1·529				

than the expected P–O single bond length of 1·73 Å (Pauling, 1960).

It is of interest to compare the P–O bond lengths with those found in KH_2PO_4 below the Curie point

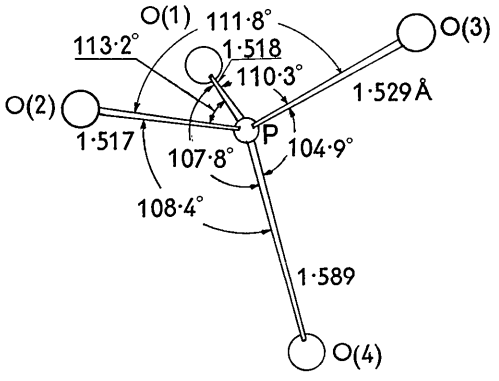

Fig. 3. Bond lengths and angles of the phosphate group.

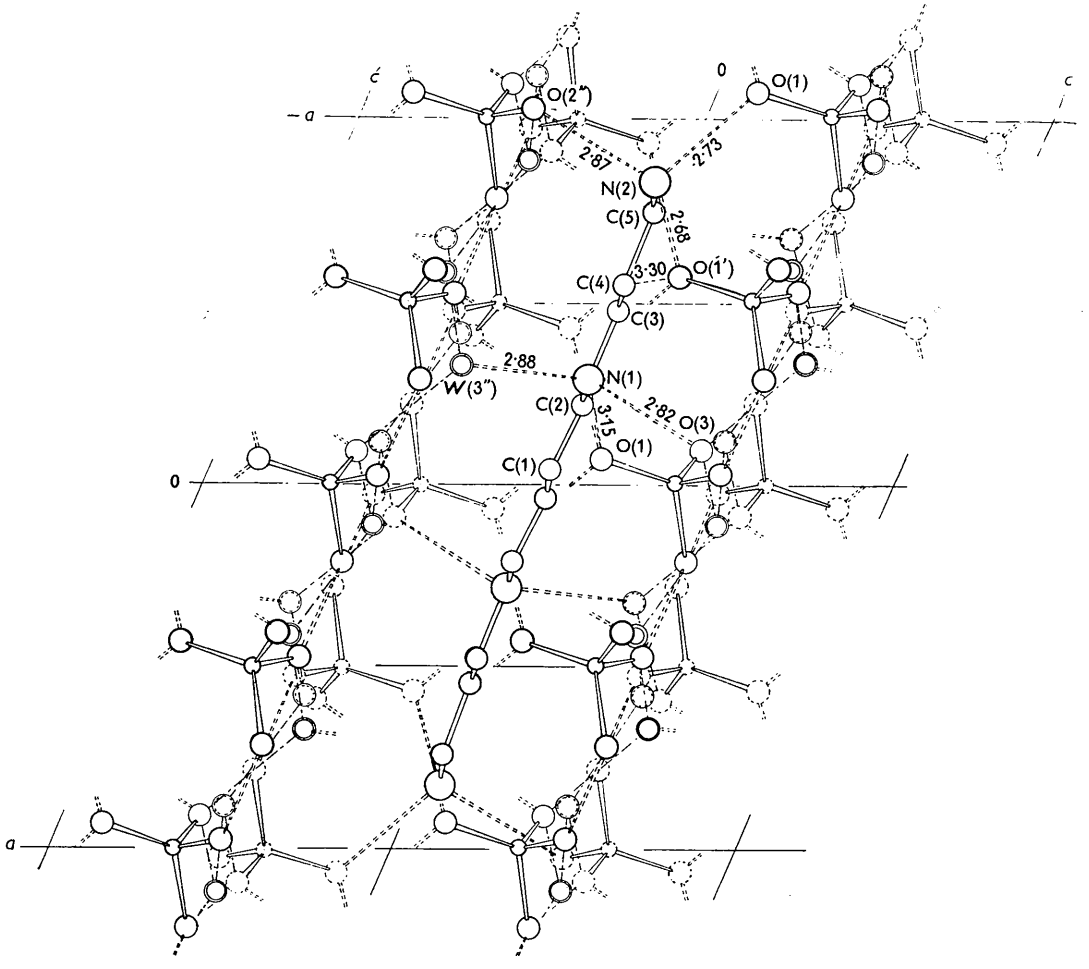

Fig. 4. Projection of the structure along the *b* axis. Hydrogen bonds are indicated by double broken lines and single chain lines. The atoms of the lower phosphate chains are indicated by broken circles. Only one spermine molecule is shown. Some shortest intermolecular contacts are also shown by single broken lines.

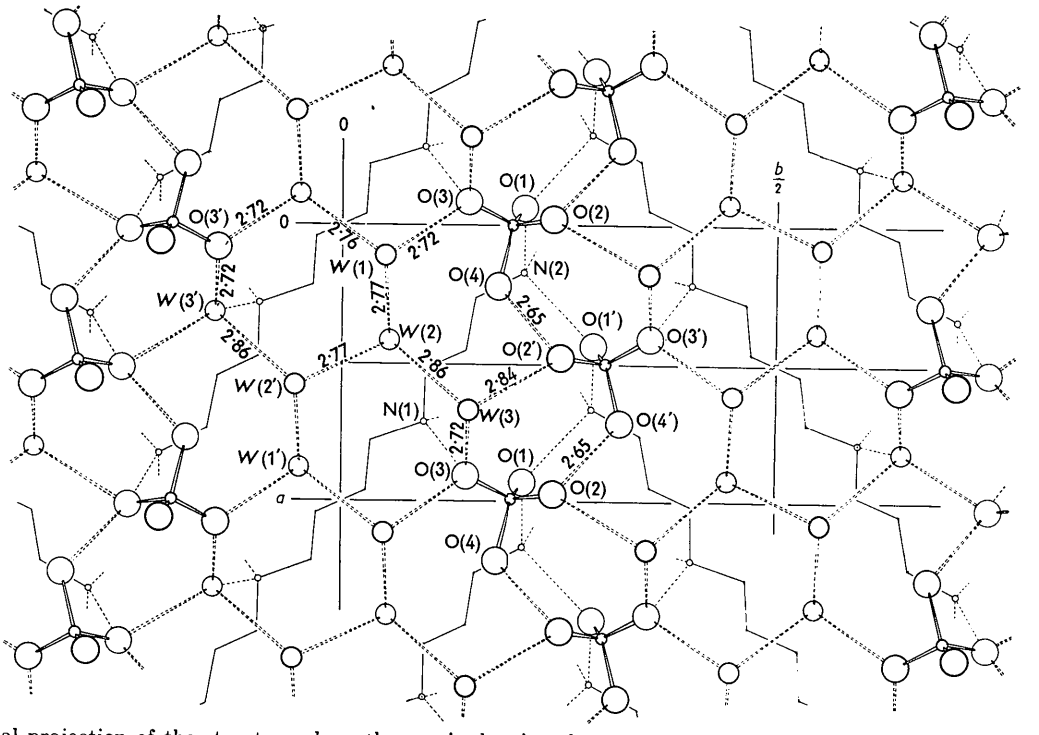

Fig. 5. Partial projection of the structure along the *c* axis showing the networks of hydrogen bonding within the phosphate–water sheet by double broken lines. Hydrogen bonds from the spermine molecules are also shown by single broken lines.

(Frazer & Pepinsky, 1953). The phosphate groups in KH_2PO_4 were found to be regular, but on passing through the Curie temperature, the central phosphorus atoms were displaced by 0·03 Å within the tetrahedra, accompanied by the ordering of hydrogen atoms. The P–O bond lengths were found to be 1·57 Å at 126 °K just above the Curie temperature. Below the transition temperature, however, the high symmetry of the phosphate group was destroyed and two kinds of P–O bond lengths, 1·58 and 1·53 Å, were observed. It was then assumed that the hydrogen atoms belong to the oxygen atoms associated with the longer P–O distance, and have been lost by the oxygen atoms of another kind.

From the considerations of hydrogen bonding and the protonation of the spermine molecules, it is suggested that the phosphate group should have two negative formal charges which are distributed mainly among the three oxygen atoms O(1), O(2) and O(3). The chemical formula of spermine phosphate hexahydrate may then be written as

$$NH_3^+(CH_2)_3NH_2^+(CH_2)_4NH_2^+(CH_2)_3NH_3^+ . \\ 2[HPO_4]^{2-} . 6H_2O .$$

The existence of NH_3^+ and HPO_4^{2-} groups in the structure is also indicated by infrared studies of the crystals (Kyogoku & Huse, unpublished).

As in the case of adenosine-5′-phosphate (Kraut & Jensen, 1963), we shall consider the hydrogen bond distribution about the phosphate group. Atom O(1) is the acceptor of two hydrogen bonds which are in a roughly planar trigonal arrangement with its covalent bond to the phosphorus atom. Atoms O(2) and O(3), on the other hand, are acceptors of three hydrogen bonds having an approximately tetrahedral arrangement. However, there seems to be no significant difference in the three P–O bond lengths and hence in the bond nature.

Hydrogen bonds and framework features

The crystal structure of spermine phosphate viewed along the *b* axis is illustrated in Fig. 4. Figs. 5 and 7 are the partial projections of the structure along the *c* axis. In these figures, presumed hydrogen bonds are indicated by broken lines.

The outstanding structural feature is the presence of two kinds of sheet. As shown in Fig. 4, the structure consists of parallel sheets of spermine molecules separated by phosphate ions and water molecules which form a sheet of composition $HPO_4^{2-} . 3H_2O$ by O–H · · · O hydrogen bonds. These two kinds of sheet are stacked alternately parallel to the (001) plane, being held together by N–H · · · O hydrogen bonds. In discussing the structure, we shall consider these two kinds of sheet separately.

The phosphate–water sheets: Fig. 5 is a partial projection of the structure along the *c* axis showing the linkage of phosphate ions and water molecules within the sheet. The sheet contains parallel chains of phosphate ions running along the *a* axis. The

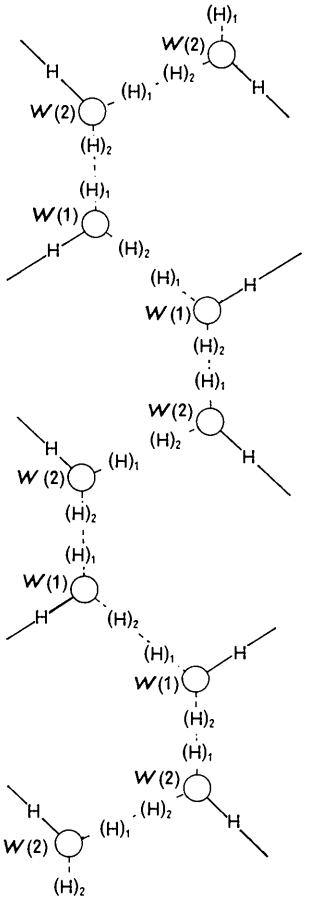

Fig. 6. Schematic representation of the hydrogen bonding between the water molecules. Two alternative hydrogen positions are indicated.

hydrogen bonds between the two phosphate ions related by an *a*-glide operation hold the ions to give a chain of composition,

$$\cdots O_2\text{–}P\text{–}O_4\text{–}H \cdots O_2\text{–}P\text{–}O_4\text{–}H \cdots O_2\text{–}P\text{–}O_4\text{–}H \cdots .$$

The belief that the atom O(4) belongs to the unionized OH group is supported by the considerations on the P–O bond lengths described above. Adjoining chains in the sheet are arranged antiparallel with the distances $b/2 = 11{\cdot}6$ Å. These chains are separated by the water molecules which form a hexagonal network of hydrogen bonds.

In Table 9 are listed the shortest O · · · O distances found within the sheet which suggest the presence of hydrogen bonding. Bonds of this sort have been observed to vary in length from 2·64 to 2·91 Å, with the average of twenty values 2·75 Å (Fuller, 1959). Angles of O · · · O · · · O subtended at each oxygen atom of the water molecules are listed in Table 10. Some of O · · · O · · · N angles are also involved in the Table for *W*(3). It is clearly shown that each water oxygen atom forms strong hydrogen bonds approximately in three of the four tetrahedral directions. The fourth direction turns to the adjoining layer of the spermine molecules. Only the *W*(3) atom accepts a hydrogen bond from the NH_2^+ group and completes a tetrahedral arrangement.

Table 9. *Hydrogen bond lengths and their standard deviations*

O–H · · · O hydrogen bonds	
W(1)–H · · · *W*(1)	2·757 ± 0·009 Å
W(1)–H · · · *W*(2)	2·766
W(2)–H · · · *W*(2)	2·772
W(2)–H · · · *W*(3)	2·855
W(3)–H · · · O(2′)	2·843 ± 0·008
W(3)–H · · · O(3)	2·723
W(1)–H · · · O(3)	2·719
O(4)–H · · · O(2′)	2·649 ± 0·007
N–H · · · O hydrogen bonds	
N(2)–H · · · O(1)	2·729 ± 0·008 Å
N(2)–H · · · O(2″)	2·869
N(2)–H · · · O(1′)	2·682
N(1)–H · · · O(3)	2·816
N(1)–H · · · *W*(3″)	2·881

Table 10. *Angles of* O · · · O · · · O *subtended at each oxygen atom of the water molecules*

O(3) · · · *W*(1) · · · *W*(2)	109·1 ± 0·3°
O(3) · · · *W*(1) · · · *W*(1′)	107·1
W(1′) · · · *W*(1) · · · *W*(2)	124·5
W(1) · · · *W*(2) · · · *W*(3)	120·3
W(1) · · · *W*(2) · · · *W*(2′)	103·2
W(2′) · · · *W*(2) · · · *W*(3)	113·4
W(2) · · · *W*(3) · · · O(3)	107·8
O(2′) · · · *W*(3) · · · O(3)	109·4
O(2′) · · · *W*(3) · · · *W*(2)	110·2
N(1) · · · *W*(3) · · · O(3)	127·5
N(1) · · · *W*(3) · · · O(2′)	116·2
N(1) · · · *W*(3) · · · *W*(2)	79·9

As to the hydrogen bonding between the water molecules, we should like to point out the following interesting features. From the discussions described above, it may be concluded that the locations of the hydrogen atoms on the water molecules would be as shown schematically in Fig. 6. Two possible positions of hydrogen atoms along each of the hydrogen bonds *W*(1)–*W*(2), *W*(1)–*W*(1) and *W*(2)–*W*(2) are suggested based on the geometrical considerations. These hydrogen bonds link the water molecules *W*(1) and *W*(2) to form a chain along the *a* axis. If we assume that each water molecule has two closest hydrogen atoms, we get two alternative ways of hydrogen arrangement along the chain. In Fig. 6 these two cases are distinguished by subscripts 1 and 2. As in the case of ice, it may be not necessary to assume that the O–H bonds are permanently oriented towards the same neighbours. Movements of the hydrogen atoms from positions about 1 Å from the one oxygen

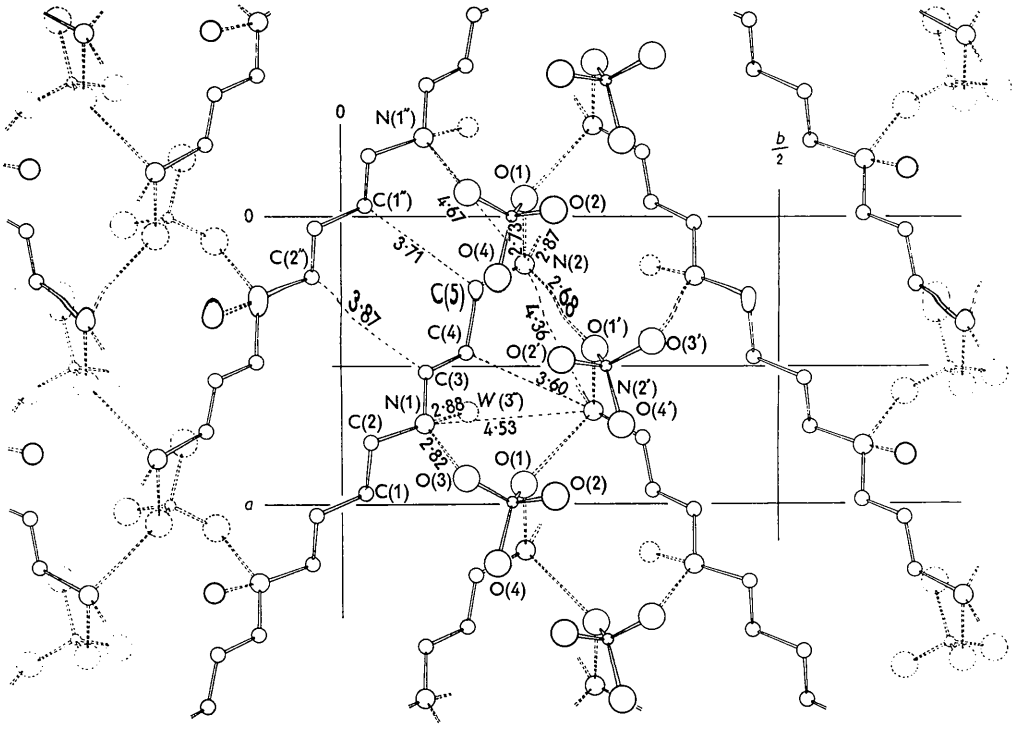

Fig. 7. Partial projection of the structure along the *c* axis showing the molecular sheet of spermine. Some of the phosphate ions and water oxygen atoms of the adjoining upper sheet and lower sheet are also shown by solid circles and broken circles respectively. Hydrogen bonds between the sheets are indicated by double broken lines. Some shortest intermolecular contacts are also indicated.

atom to a similar position near the other oxygen atom of the bonds cause the molecules to change their orientation. We might expect a disordered arrangement of hydrogen atoms between pairs of possible positions as in the case of ice. In the present investigation, however, it was not attempted to locate hydrogen atoms experimentally.

The molecular sheets of spermine: Fig. 7 is a partial projection of the structure along the *c* axis showing the molecular arrangement of spermine. The figure also shows the phosphate ions and some of the water molecules. As seen in the figure, the spermine molecules are tilted at about 57° from the *b* axis and arranged in parallel, keeping a distance of about 4 Å (van der Waals contacts) from adjacent molecules in the *a* direction.

The closest approach of methylene–methylene groups is $3{\cdot}71_0$ Å from C(5) to C(1'') and of methylene–nitrogen is $3{\cdot}59_6$ Å from N(2') to C(4). Some of the shorter intermolecular contacts are shown in Fig. 5 and Fig. 7. None of the van der Waals distances are unusually small. Adjacent molecules in the **b** direction (related by a glide operation to each other) are oppositely inclined and form a planar herring-bone arrangement of the molecules as seen in Fig. 7.

The hydrogen bonds from the amino and imino nitrogen to the phosphate and water oxygen atoms of the adjoining sheets are arranged tetrahedrally around the nitrogen atoms (Table 11) and hold the molecules to form a molecular sheet. It will be noted that of the ten such N–H · · · O hydrogen bonds which bind a molecule of spermine to the phosphate–water sheets, only two are those to the water molecules. All of the rest link the molecule strongly to the phosphate ions. The hydrogen bond distance $2{\cdot}68_2$ Å from N(2) to O(1) is rather short as compared with the usual value and may be compared with the

Table 11. *Arrangement of hydrogen bonds around the amino and imino nitrogen atoms of the spermine molecule*

C(5)–N(2) · · · O(1′)	106·9 ± 0·4°
C(5)–N(2) · · · O(2′′)	116·2
C(5)–N(2) · · · O(1)	107·2
O(1) · · · N(2) · · · O(2′′)	110·1 ± 0·3
O(1) · · · N(2) · · · O(1′)	107·9
O(2′′) · · · N(2) · · · O(1′)	108·3
C(3)–N(1) · · · *W*(3′′)	104·3 ± 0·4
C(2)–N(1) · · · *W*(3′′)	110·1
C(3)–N(1) · · · O(3)	98·9
C(2)–N(1) · · · O(3)	106·6
W(3′′) · · · N(1) · · · O(3)	125·4 ± 0·3

N(21)–O(2″) bond (2·619 Å) found in adenosine-5′-phosphate (Kraut & Jensen, 1963).

To conclude the discussion, it may be of interest to consider the framework features as a whole comparing with the structure of nucleic acids. As already described, the chains of phosphate groups in the phosphate–water sheets are running along the *a* axis with a separation of 11·6 Å in the **b** direction. Within the sheet, the chains are bound together by the hexagonal planar network of hydrogen bonds formed by the water molecules which fill up the spaces between the chains. The sheets are not completely flat. The oxygen atoms O(1) of the phosphate groups protrude about 1·5 Å from the sheets and form strong hydrogen bonds to the spermine molecules. The networks are wrinkled and the spermine molecules lie along the shallow grooves on the network as seen in Fig. 5. The molecules are arranged obliquely to the phosphate chain making an angle of about 33°, so that strong hydrogen bonds are formed from N(1) and N(2) to the oxygen atoms of a chain. In this way, the phosphate chains of the same sheet as well as of the adjoining sheets are bound together strongly by the spermine molecules.

As for the arrangement of phosphate groups, we noticed a certain similarity between that found in crystalline deoxyribonucleic acid (DNA) and in spermine phosphate. Langridge, Marvin, Seeds, Wilson, Hooper, Wilkins & Hamilton (1960) have shown the arrangement of phosphate groups along the polynucleotide helices in the *B* form of LiDNA (Fig. 13 and Fig. 14 in their paper). In this structure, two oxygen atoms O(2) and O(3) of the phosphate group, which share one negative formal charge, are turned outwards and are readily available for interaction with proteins, water, *etc.* The distance between successive phosphate groups along the helix is about 7·3 Å, which may be compared to the *a*-translation period of 7·96 Å along the phosphate chains in spermine phosphate. The perpendicular distance between two nucleotide chains (chain *A* and *B* of the same molecule, measured across the shallow) in LiDNA is about 13 Å, while in the latter structure, the separation of the phosphate chains within the same sheet is found to be about 11·6 Å = $b/2$.

The present study of the crystal structure of spermine phosphate hexahydrate has demonstrated how the phosphate ions interact with the molecules of spermine and water within the crystals. Further discussions on the biochemical function of spermine from the structural point of view will be published elsewhere.

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