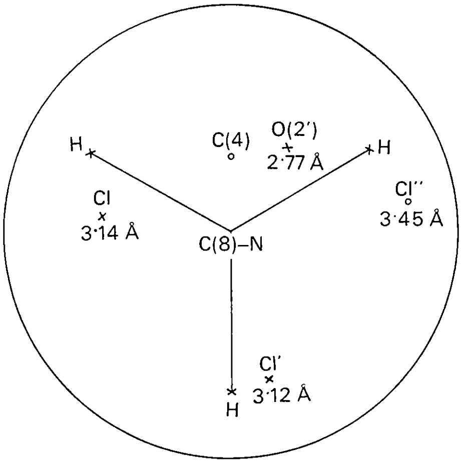

Fig. 12. *cis*-AMCHA . HCl. Stereographic projection showing the distribution of oxygen and chlorine atoms around the amino nitrogen atom. Distances from the nitrogen atom are also given. The direction of the C–N bond is taken as the polar axis. The suggested N–H directions are indicated.

atoms around the nitrogen atom is shown in Fig. 12. It is seen that the three hydrogen bonds (NH · · · Cl, 3·12 Å; NH · · · Cl, 3·14 Å and NH · · · O(2), 2·77 Å) are arranged approximately in tetrahedral directions around the nitrogen atom. In Figs. 10 and 11, the presumed hydrogen bonds are indicated by broken lines. The figures also show the intermolecular short contacts less than 3·7 Å by dotted lines. The molecules are bound to the chain of chlorine atoms through the hydrogen bonds, NH · · · Cl (3·12 Å) and NH · · · Cl (3·14 Å). There is another hydrogen bond (2·98 Å) between the carboxyl oxygen atom O(1) and Cl. This bond and the O(2) · · · HN (2·77 Å) bond hold the carboxyl group firmly within the crystal.

The authors would like to express their sincere thanks to Professor M. Tsuboi for his valuable discussions. They also wish to express their thanks to Dr M. Shimizu, Dr T. Naito and Dr A. Okano of the Central Research Laboratory, Daiichi Seiyaku Co. Ltd for their kindness in supplying the specimens and continued interest throughout the work. Special thanks are also due to the staffs, especially Mr M. Furuhara, Mr G. Ikegami and Miss T. Hiki, of the computation center of the C. Itoh Electronic Computing Service Co. Ltd for their kind cooperation in calculations of full-matrix least-squares on the CDC-G20 computer.

Note added in proof: – The crystal structure of *cis*-AMCHA.HBr has recently been determined independently by Groth & Hassel (1965). The structure is essentially identical with that determined by us (see footnote, this page). We therefore do not contemplate any further work on this substance.

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The Crystal Structure of Barium Diethyl Phosphate

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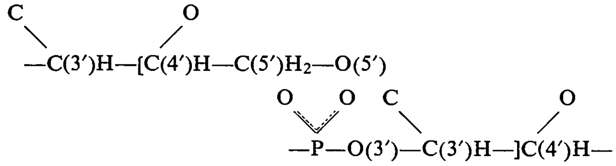
(*Received* 29 *May* 1965 *and in revised form* 31 *July* 1965)

Crystals of barium diethyl phosphate, $Ba[(C_2H_5O)_2PO_2]_2$, are monoclinic, with space group $I2/a$, containing four molecules in a unit cell with lattice constants $a = 14·52$, $b = 18·88$, $c = 6·00$ Å and $\beta = 90·0°$. The structure was refined with anisotropic thermal parameters, using three-dimensional reflexions, by the method of least squares. The final reliability index was 0·09. The diethyl phosphate anion was found to take a configuration with the two C–O bonds in the *gauche* positions to the P–O bonds, in agreement with the conclusion reached from a spectroscopic investigation on an aqueous solution of barium dimethyl phosphate. The angles of internal rotation around the C–O and P–O bonds are compared with those of the proposed models for nucleic acids and synthetic polynucleotides.

Introduction

Natural and synthetic polynucleotides consist of chains of alternating diesterified phosphate and ribose or 2′-deoxyribose groups with a purine or pyrimidine base attached to each sugar residue. The backbone of the chains is formed by such repeating units as shown below, each consisting of six bonds:



$$-\overset{\mathrm{C}}{\mathrm{C(3')H}}-[\overset{\mathrm{O}}{\mathrm{C(4')H}}-\mathrm{C(5')H_2}-\mathrm{O(5')}$$

$$-\overset{\mathrm{O\ \ O}}{\mathrm{P}}-\mathrm{O(3')}-\overset{\mathrm{C}}{\mathrm{C(3')H}}-]\overset{\mathrm{O}}{\mathrm{C(4')H}}-$$

Judging from the studies of the internal rotation on simple compounds it seems that the rotation of each bond is not entirely free but is restricted within a certain range. If the rotation of each bond were specified, the entire polymer conformation could be fixed. Therefore, an accurate knowledge of the conformation of the diester group including four of the six bonds should be especially important for understanding the structure of polynucleotides.

Dunitz & Rollett (1956) determined the structure of dibenzylphosphoric acid, and this structure determination played an important role in the proposition of the structure of nucleic acids. Dibenzylphosphoric acid, however, is not the best model compound for the diester groups in the nucleic acids, since the latter takes the form of a neutral salt in ordinary conditions and the phosphate groups are ionized. For this reason, Shimanouchi, Tsuboi & Kyogoku (1964) have investigated the configuration of the dialkylphosphate anion in aqueous solutions by means of infrared and Raman spectroscopy. They concluded that the anion has a two-fold symmetry axis along the bisecting line of the $\mathrm{P}\Big\langle^{\mathrm{O}}_{\mathrm{O}}$ group, where the two C–O bonds are in the *gauche* positions to the P–O bonds in contrast with the results obtained for dibenzylphosphoric acid that one of the C–O bonds is *gauche* and the other is *trans*. In order to confirm these conclusions and to get further information on the angles of internal rotation about the C–O bond, the crystal structure of barium diethyl phosphate has been investigated. This paper describes the results obtained and gives a comparison of the angles of internal rotation in this anion with those in molecules in other related compounds and in models so far proposed for polynucleotides.

Experimental

Potassium diethylphosphate was obtained by partial hydrolysis of commercial triethyl phosphate in 10% alcoholic potassium hydroxide (Bentley, 1948). After removal of alcohol by distillation, the solution was acidified with hydrochloric acid and then neutralized with barium hydroxide. Barium diethyl phosphate thus obtained was purified by recrystallization from alcohol–water solutions. Slow evaporation of the aqueous solution to dryness at room temperature resulted in large

Table 1. *The final positional parameters and their standard deviations*

	x/a	$\sigma(x)$	y/b	$\sigma(y)$	z/c	$\sigma(z)$
Ba	0·2500	0·0000 Å	0·3272	0·0019 Å	0·5000	0·0000 Å
P	0·1093	0·0058	0·3542	0·0057	0·9754	0·0072
O(1)	−0·0018	0·0145	0·3491	0·0151	0·9577	0·0186
O(2)	0·1353	0·0131	0·4130	0·0113	0·7956	0·0162
O(3)	0·1272	0·0145	0·3813	0·0132	0·2085	0·0192
O(4)	0·1559	0·0131	0·2881	0·0113	0·8873	0·0144
C(1)	0·0412	0·0218	0·6843	0·0302	0·2429	0·0300
C(2)	0·1064	0·0320	0·4844	0·0132	0·8448	0·0384
C(3)	0·1436	0·0232	0·6731	0·0320	0·2188	0·0462
C(4)	0·1267	0·0349	0·5323	0·0283	0·6812	0·0516

Table 2. *The final anisotropic temperature factors and their standard deviations*

The thermal parameters are of the form $T=\exp-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba	0·0043	0·0031	0·0243	0·0000	0·0001	0·0000
$\sigma(\beta)$	(±0·0001)	(±0·0000)	(±0·0015)	(±0·0000)	(±0·0002)	(±0·0000)
P	43	36	287	11	−2	−2
	(2)	(2)	(29)	(2)	(7)	(5)
O(1)	57	59	381	9	−1	8
	(8)	(6)	(73)	(6)	(23)	(18)
O(2)	66	34	300	9	10	20
	(8)	(4)	(60)	(5)	(19)	(13)
O(3)	70	48	419	20	−30	3
	(9)	(6)	(76)	(6)	(23)	(17)
O(4)	61	46	216	23	47	12
	(7)	(4)	(55)	(5)	(18)	(13)
C(1)	58	122	474	−1	−77	−85
	(12)	(15)	(126)	(11)	(34)	(36)
C(2)	164	20	1051	9	146	53
	(26)	(4)	(204)	(8)	(67)	(23)
C(3)	49	120	1189	−5	0	−106
	(12)	(15)	(221)	(12)	(52)	(55)
C(4)	149	83	1262	31	128	213
	(26)	(13)	(319)	(16)	(83)	(56)

needle crystals elongated in the direction of the *c* axis, with well developed {110} planes.

The lattice constants were determined from the (0*kl*) and the (*h*0*l*) precession photographs. The values obtained are

$$a=14{\cdot}52_0\,,\quad b=18{\cdot}87_7\,,\quad c=6{\cdot}00_0\ \text{Å}\,,$$
$$\beta=90{\cdot}0^\circ\,.$$

The density measured by flotation in a mixture of benzene and chloroform is 1·79 g.cm^{-3}. The density calculated on the basis of four chemical units in a cell is 1·710 g.cm^{-3}. A negative piezoelectric test indicated the existence of a centre of symmetry. The intensity of a reflexion of the type *hkl* was not equal to that of the corresponding reflexion of the type $\bar{h}kl$. From these results and the systematic absences observed for *hkl* with $h+k+l\neq 2n$ and *h*0*l* with $h\neq 2n$, the space group was concluded to be *I*2/*a*. The number of barium atoms and of diethyl phosphate anions in a cell were calculated as four and eight, respectively.

The intensity data were collected from equi-inclination Weissenberg photographs of the layers *hk*0 through *hk*4 and 0*kl*, with Cu *Kα* radiation using the multiple film technique. The intensities were estimated visually by comparison with a calibrated intensity strip. The specimen used for the *c*-axis photographs was about 0·07 × 0·07 mm in cross section for which $\mu R=1{\cdot}3$, and no correction was applied for absorption. After correcting for Lorentz and polarization factors, the two sets of data were put on the same scale. During the refinement process at a later stage, the scale factors were further adjusted by a least-squares method. Intensities of 1161 non-zero reflexions were measured in total, of which 50 were obtained both from the *a*- and from the *c*-axis photographs.

Determination and refinement of the structure

From the space group considerations it was at once concluded that the barium atoms must lie on the twofold special positions. Their *y* parameters were easily determined from the *hk*0 and 0*kl* Patterson syntheses. The approximate coordinates of the phosphorus atom were obtained from a two-dimensional Fourier synthesis using the phases calculated on the basis of the barium atom contributions. A three-dimensional difference Fourier synthesis, using the phases determined from the contributions of both the barium and phosphorus atoms, gave the positions for all oxygen and carbon atoms. The second difference Fourier synthesis resulted in only slight shifts in atomic positions. After several cycles of diagonal least-squares refinements, the *R* index dropped to 0·125.

The refinement process was further continued by the least-squares method using the ORFLS program (Busing, Martin & Levy, 1962) on an IBM 7090 computer. Individual anisotropic thermal parameters were taken into account in this process. Three cycles of the refinement reduced the *R* value to 0·09 excluding unobserved reflexions. The final atomic parameters and their standard deviations are given in Tables 1 and 2. In Table 3 are also given the temperature factors and the direction cosines of the principal axes of the vibration ellipsoids. The comparison of the observed and calculated structure factors is given in Table 4. Throughout the work the following atomic scattering factors were used: the Thomas–Fermi–Dirac statistical model for barium (*International Tables for X-ray crystallography*, 1962, p.211), calculation SX-70 for phosphorus, calculation SX-8 for oxygen, calculation SX-6 for carbon (*International Tables*, 1962, p.202).

Table 3. *The temperature factors and the direction cosines of the principal axes of the vibration ellipsoids*

q: the direction cosines of the principal axes relative to the crystallographic axes.

Atom	Axis	*B*(Å^2)	q_a	q_b	q_c
Ba	1	4·36	0·000	1·000	0·000
	2	3·62	0·952	0·000	0·307
	3	3·50	0·307	0·000	−0·952
P	1	5·75	0·489	0·869	−0·071
	2	4·14	0·024	0·067	0·997
	3	2·94	−0·872	0·490	−0·012
O(1)	1	8·60	0·247	0·963	0·109
	2	5·48	−0·154	−0·072	0·986
	3	4·52	0·957	−0·260	0·130
O(2)	1	6·52	0·721	0·593	0·359
	2	4·58	0·659	−0·426	−0·620
	3	3·55	0·215	−0·684	0·698
O(3)	1	8·67	0·650	0·727	−0·222
	2	6·28	−0·146	0·406	0·902
	3	3·74	−0·746	0·555	−0·370
O(4)	1	8·76	0·623	0·741	0·251
	2	3·94	−0·506	0·627	−0·593
	3	2·02	−0·597	0·242	0·765
C(1)	1	18·50	0·057	0·944	−0·325
	2	7·80	−0·654	0·281	0·703
	3	2·60	−0·755	−0·172	−0·633
C(2)	1	19·96	0·642	0·142	0·754
	2	9·44	0·767	−0·115	−0·632
	3	2·37	−0·003	0·983	−0·183
C(3)	1	21·82	0·021	−0·697	0·717
	2	12·25	−0·048	0·715	0·697
	3	4·09	−0·999	−0·049	−0·018
C(4)	1	27·25	0·355	0·546	0·759
	2	10·40	0·935	−0·186	−0·303
	3	4·79	0·024	−0·817	0·577

Discussion of the structure

The crystal structure

Intermolecular interatomic distances less than 3·5 Å are listed in Table 5. In Fig. 1, the two projections of the structure, along the *b* and the *c* axis, are shown. It will be seen that the barium atom is coordinated to eight oxygen atoms from six diethylphosphate anions which are related to each other by a twofold axis and a *b*-glide plane. Each diethylphosphate anion is bound to three barium atoms with its oxygen atoms O(2), O(3) and O(4). As is shown in Fig. 1(*a*), the barium atoms at

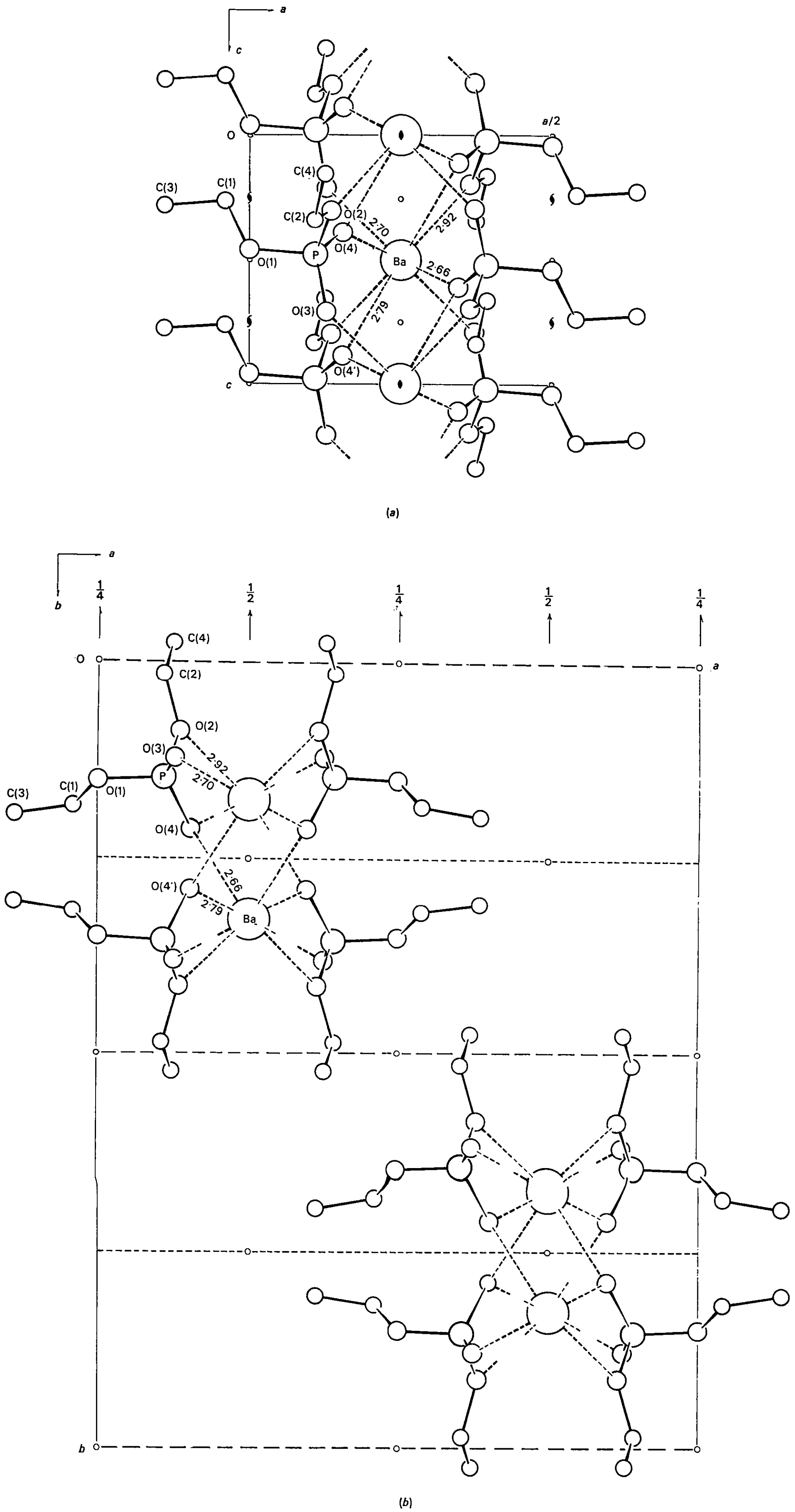


Fig. 1. The crystal structure of barium diethyl phosphate. (*a*) Projection along the *b* axis. (*b*) Projection along the *c* axis.

Table 4. *Observed and calculated structure factors*

H	K	L	|Fobs|	Fcal
2	0	0	116.78	-126.87
4	0	0	68.12	-44.46
6	0	0	88.65	-101.61
8	0	0	230.48	244.43
10	0	0	80.32	-86.39
12	0	0	52.17	52.88
14	0	0	53.08	-61.58
16	0	0	39.72	39.93
18	0	0	16.75	-16.10
3	1	0	93.44	96.03
5	1	0	47.58	-54.18
7	1	0	197.02	190.85
9	1	0	91.35	-99.55
11	1	0	47.77	52.57
13	1	0	57.36	-64.50
15	1	0	44.42	50.60
17	1	0	20.14	-19.71
0	2	0	151.71	-161.33
2	2	0	90.55	96.27
4	2	0	137.11	-133.80
6	2	0	41.19	49.01
8	2	0	61.85	-64.13
10	2	0	55.21	59.33
12	2	0	41.07	-47.38
14	2	0	41.53	33.29
16	2	0	21.22	-15.51
18	2	0	10.32	10.87
1	3	0	40.54	-40.10
3	3	0	104.39	-102.83
5	3	0	41.47	43.96
7	3	0	31.06	31.71
9	3	0	0.00	-8.87
11	3	0	36.89	-36.76
13	3	0	10.65	14.93
15	3	0	0.00	5.57
17	3	0	0.00	1.92
0	4	0	191.46	-205.52
2	4	0	15.72	18.05
4	4	0	12.37	-13.90
6	4	0	49.21	50.20
8	4	0	111.23	-110.58
10	4	0	6.78	-2.00
12	4	0	0.00	-7.69
14	4	0	25.61	29.79
16	4	0	22.61	-21.51
18	4	0	0.00	-0.38
1	5	0	169.09	172.03
3	5	0	64.52	-71.37
5	5	0	103.71	99.76
7	5	0	173.61	-162.14
9	5	0	56.88	55.62
11	5	0	22.92	-17.14
13	5	0	49.17	57.46
15	5	0	53.03	-50.57
0	6	0	270.32	271.43
2	6	0	106.75	-94.42
4	6	0	155.43	147.78
6	6	0	153.79	-143.31
8	6	0	115.07	120.32
10	6	0	41.36	-41.78
12	6	0	64.50	65.70
14	6	0	55.99	-61.89
16	6	0	31.50	29.50
18	6	0	10.45	-12.53
1	7	0	112.48	-98.62
3	7	0	193.72	182.39
5	7	0	170.00	-164.05
7	7	0	103.59	103.75
9	7	0	46.26	-43.51
11	7	0	76.48	70.82
13	7	0	67.22	-67.95
15	7	0	34.56	35.96
17	7	0	18.63	-18.23
0	8	0	60.01	-65.57
2	8	0	131.92	120.20
4	8	0	143.62	-134.91
6	8	0	64.41	55.60
8	8	0	34.35	-31.05
10	8	0	84.50	80.96
12	8	0	46.95	-53.53
14	8	0	24.18	22.52
16	8	0	17.71	-13.78
1	9	0	34.00	33.22
3	9	0	88.09	-89.25
5	9	0	15.50	19.07
7	9	0	15.91	11.89
9	9	0	36.16	35.78
11	9	0	53.47	-52.32
13	9	0	7.25	6.67
15	9	0	0.00	3.45
17	9	0	14.07	14.59
0	10	0	32.08	-33.67
2	10	0	18.46	-17.33
4	10	0	27.16	-23.40
6	10	0	33.55	36.10
8	10	0	33.96	-33.72
10	10	0	31.22	-29.75
12	10	0	0.00	-6.72
14	10	0	20.19	18.71
16	10	0	0.00	-5.00
1	11	0	54.05	51.28
3	11	0	52.18	-54.41
5	11	0	68.19	69.64
7	11	0	64.22	-66.19
9	11	0	24.67	24.45
11	11	0	16.75	-16.82
13	11	0	30.91	30.15
15	11	0	22.67	-21.52
0	12	0	89.96	87.06
2	12	0	77.28	-74.56
4	12	0	92.23	88.03
6	12	0	76.84	-75.86
8	12	0	56.43	58.72
10	12	0	41.90	-41.52
12	12	0	39.29	39.42
14	12	0	24.68	-25.11
16	12	0	14.67	17.21
1	13	0	58.11	-72.42
3	13	0	90.94	93.91
5	13	0	82.32	-85.48
7	13	0	58.35	58.19
9	13	0	44.46	-47.78
11	13	0	46.93	49.97
13	13	0	30.18	-28.32
15	13	0	18.00	18.14
0	14	0	24.96	-27.43
2	14	0	76.65	73.46
4	14	0	83.62	-84.72
6	14	0	48.55	51.33
8	14	0	24.53	-28.33
10	14	0	47.38	50.63
12	14	0	28.85	-28.84
14	14	0	17.64	13.54
1	15	0	0.00	6.35
3	15	0	62.97	-67.08
5	15	0	44.15	47.21
7	15	0	0.00	-8.56
9	15	0	20.60	21.43
11	15	0	29.49	-25.87
13	15	0	14.34	8.67
0	16	0	19.67	-19.10
2	16	0	14.94	-10.50
4	16	0	19.92	16.95
6	16	0	0.00	-3.83
8	16	0	0.00	-4.45
10	16	0	10.21	-8.09
12	16	0	16.76	-1.35
1	17	0	16.85	13.90
3	17	0	27.18	-26.44
5	17	0	21.10	20.33
7	17	0	10.17	-10.02
9	17	0	14.40	10.70
11	17	0	18.92	-15.63
0	18	0	21.20	18.63
2	18	0	35.49	-36.89
4	18	0	48.01	44.18
6	18	0	23.43	-24.09
8	18	0	20.90	16.07
10	18	0	27.67	-26.18
12	18	0	15.42	19.77
1	19	0	28.15	-32.32
3	19	0	44.53	43.21
5	19	0	38.19	-36.01
7	19	0	20.71	21.71
9	19	0	22.89	-25.35
11	19	0	18.67	26.28
0	20	0	23.89	-24.42
2	20	0	32.53	34.21
4	20	0	30.42	-32.70
6	20	0	22.88	23.28
8	20	0	19.97	-19.67
10	20	0	16.26	25.56
1	21	0	19.13	16.84
3	21	0	23.14	-24.62
5	21	0	18.85	16.65
7	21	0	15.67	-12.30
9	21	0	11.58	17.96
0	22	0	0.00	7.37
1	23	0	0.00	-0.69
2	1	1	170.23	-182.72
4	1	1	141.81	136.16
6	1	1	52.75	-43.81
8	1	1	17.57	19.30
10	1	1	71.04	-66.67
12	1	1	34.67	34.61
14	1	1	21.09	-17.07
16	1	1	24.36	14.77
18	1	1	18.90	-19.39
1	2	1	152.77	-135.68
3	2	1	262.92	248.89
5	2	1	187.05	-190.97
7	2	1	24.65	28.78
9	2	1	70.65	-72.94
11	2	1	98.78	102.34
13	2	1	43.26	-42.53
15	2	1	29.39	22.74
17	2	1	32.09	-32.02
0	3	1	40.53	-22.10
2	3	1	132.71	153.44
4	3	1	229.39	-239.95
6	3	1	156.54	165.62
8	3	1	72.59	-72.73
10	3	1	110.14	106.05
12	3	1	73.45	-61.19
14	3	1	46.85	41.81
16	3	1	45.35	-36.11
18	3	1	34.78	36.45
1	4	1	230.28	196.06
3	4	1	194.82	-185.08
5	4	1	176.52	166.75
7	4	1	81.68	-84.17
9	4	1	95.41	88.63
11	4	1	81.56	-83.96
13	4	1	45.57	42.11
15	4	1	40.75	-36.68
17	4	1	34.75	32.99
0	5	1	105.11	101.02
2	5	1	123.15	-123.60
4	5	1	115.37	108.03
6	5	1	90.85	-79.90
8	5	1	99.47	93.51
10	5	1	37.69	-39.89
12	5	1	28.71	27.70
14	5	1	43.12	-36.00
16	5	1	36.94	27.96
1	6	1	89.52	-81.68
3	6	1	33.53	27.33
5	6	1	33.42	-26.06
7	6	1	54.15	52.07
9	6	1	18.14	-9.73
11	6	1	0.00	-2.34
13	6	1	15.67	-15.27
15	6	1	28.85	21.34
17	6	1	0.00	-0.76
0	7	1	33.10	-27.85
2	7	1	51.60	-47.75
4	7	1	25.51	18.07
6	7	1	32.81	-25.06
8	7	1	27.78	5.02
10	7	1	76.83	-60.36
12	7	1	0.00	9.82
14	7	1	0.00	5.73
16	7	1	0.00	6.90
1	8	1	87.32	-74.35
3	8	1	107.20	97.17
5	8	1	79.02	-72.65
7	8	1	39.89	35.77
9	8	1	79.56	-76.55
11	8	1	63.28	60.39
13	8	1	0.00	-18.03
15	8	1	0.00	12.14
17	8	1	23.35	-25.36
0	9	1	108.06	-113.56
2	9	1	127.50	130.90
4	9	1	94.37	-91.89
6	9	1	74.67	75.84
8	9	1	78.30	-79.35
10	9	1	79.20	86.38
12	9	1	40.39	-39.26
14	9	1	31.22	25.72
16	9	1	29.39	-27.28
1	10	1	181.95	160.50
3	10	1	105.76	-102.32
5	10	1	74.78	70.46
7	10	1	72.91	-77.66
9	10	1	83.33	81.90
11	10	1	69.35	-55.87
13	10	1	35.56	34.62
15	10	1	28.64	-29.10
0	11	1	124.30	123.55
2	11	1	89.70	-77.67
4	11	1	63.53	56.79
6	11	1	68.21	-63.29
8	11	1	91.24	82.86
10	11	1	32.27	-31.77
12	11	1	35.35	28.50
14	11	1	35.17	-31.92
16	11	1	20.26	20.21
1	12	1	67.49	-60.05
3	12	1	17.67	9.02
5	12	1	32.30	-26.21
7	12	1	67.20	63.71
9	12	1	24.97	-20.53
11	12	1	14.01	3.00
13	12	1	21.24	-19.39
15	12	1	19.05	19.20
0	13	1	42.33	-36.82
2	13	1	51.10	-40.99
4	13	1	0.00	19.05
6	13	1	19.80	22.23
8	13	1	14.41	-19.71
10	13	1	31.62	-27.41
12	13	1	24.14	3.16
14	13	1	0.00	8.57
1	14	1	53.07	-50.10
3	14	1	54.12	63.75
5	14	1	0.00	-16.79
7	14	1	0.00	4.43
9	14	1	40.14	-35.03
11	14	1	27.31	25.71
13	14	1	13.40	-9.54
15	14	1	9.23	7.55
0	15	1	80.03	-71.02
2	15	1	67.56	58.75
4	15	1	37.73	-33.79
6	15	1	40.78	40.03
8	15	1	47.07	-48.33
10	15	1	34.82	32.06
12	15	1	24.18	-18.78
14	15	1	15.92	19.79
1	16	1	74.60	62.77
3	16	1	28.78	-21.10
5	16	1	47.79	45.94
7	16	1	62.21	-65.57
9	16	1	34.55	35.79
11	16	1	21.42	-16.65
13	16	1	22.33	25.21
0	17	1	75.21	71.54
2	17	1	24.97	-20.84
4	17	1	24.83	26.67
6	17	1	46.35	-53.29
8	17	1	43.37	44.38
10	17	1	17.50	-11.42
12	17	1	17.32	19.44
1	18	1	37.69	-31.77
3	18	1	14.12	16.05
5	18	1	19.36	-21.92
7	18	1	31.44	30.35
9	18	1	13.33	-12.79
11	18	1	0.00	10.98
0	19	1	19.51	-12.55
2	19	1	0.00	8.27
4	19	1	0.00	-6.05
6	19	1	0.00	4.45
8	19	1	0.00	-3.78
10	19	1	0.00	3.67
1	20	1	0.00	-9.71
3	20	1	0.00	4.55
5	20	1	0.00	-7.21
7	20	1	12.39	13.64
9	20	1	14.15	-6.50
0	21	1	25.98	-26.78
2	21	1	0.00	14.88
4	21	1	0.00	-11.35
6	21	1	23.07	22.41
8	21	1	18.28	-18.45
1	22	1	28.92	24.27
3	22	1	15.55	-13.73
5	22	1	23.89	22.31
7	22	1	14.98	-22.87
0	23	1	23.50	23.28
2	23	1	20.05	-17.25
4	23	1	19.18	18.96
-2	1	1	67.42	-71.44
-4	1	1	121.07	124.96
-6	1	1	98.60	-104.10
-8	1	1	21.78	6.09
-10	1	1	61.45	-64.92
-1	2	1	33.89	0.32
-3	2	1	192.01	-233.60
-5	2	1	182.58	167.60
-7	2	1	68.71	-73.35
-9	2	1	74.39	89.10
-11	2	1	105.69	-88.85
-2	3	1	287.96	312.39
-4	3	1	164.73	-186.97
-6	3	1	125.71	138.03
-8	3	1	44.13	-50.63
-10	3	1	123.12	139.13
-12	3	1	79.31	-72.17
-1	4	1	80.42	-88.48
-3	4	1	167.71	171.21
-5	4	1	108.31	-137.60
-7	4	1	129.08	115.23
-9	4	1	102.74	-112.25
-11	4	1	77.04	73.07
-13	4	1	40.75	-39.36
-2	5	1	75.53	-81.52
-4	5	1	73.96	84.39
-6	5	1	109.96	-117.37
-8	5	1	65.18	74.89
-10	5	1	52.54	-54.10
-12	5	1	28.71	32.41
-1	6	1	10.96	11.74
-3	6	1	40.89	31.39
-5	6	1	42.83	42.21
-7	6	1	76.72	-79.05
-9	6	1	25.59	29.33
-11	6	1	28.25	22.00
-13	6	1	21.20	11.98
-2	7	1	133.21	-126.91
-4	7	1	74.78	76.90
-6	7	1	30.94	21.94
-8	7	1	43.05	-40.63
-10	7	1	76.83	-69.87
-12	7	1	35.32	34.08
-1	8	1	87.32	82.35
-3	8	1	182.85	-161.78
-5	8	1	67.34	66.65
-7	8	1	0.00	-5.90
-9	8	1	64.93	60.67
-11	8	1	69.21	-78.23
-13	8	1	0.00	23.67
-2	9	1	154.64	147.59
-4	9	1	84.41	-94.42
-6	9	1	81.52	84.54
-8	9	1	63.75	-61.90
-10	9	1	84.16	81.45
-12	9	1	40.39	-47.82
-14	9	1	34.21	31.52
-1	10	1	116.86	-118.41
-3	10	1	65.57	70.22
-5	10	1	85.24	-87.12
-7	10	1	101.59	108.03
-9	10	1	78.41	-74.32
-11	10	1	40.71	36.55
-13	10	1	39.64	-40.92
-2	11	1	58.03	-63.00
-4	11	1	56.35	55.30
-6	11	1	85.35	-81.65
-8	11	1	77.84	73.99
-10	11	1	20.41	-27.54
-12	11	1	32.59	30.03
-1	12	1	58.35	60.81
-3	12	1	0.00	-16.26
-5	12	1	32.30	28.40
-7	12	1	50.31	-48.04
-9	12	1	28.52	27.75
-11	12	1	0.00	-4.89
-13	12	1	0.00	21.84
-2	13	1	0.00	5.24
-4	13	1	18.93	20.50
-6	13	1	0.00	-8.87
-8	13	1	0.00	-15.39
-10	13	1	0.00	-9.34
-12	13	1	0.00	-0.85
-14	13	1	16.57	2.22
-1	14	1	0.00	7.00
-3	14	1	38.74	-33.42
-5	14	1	44.63	48.17
-7	14	1	35.28	-25.92
-9	14	1	28.39	17.56
-11	14	1	20.16	-15.92
-13	14	1	0.00	12.42
-2	15	1	55.41	53.07
-4	15	1	39.31	-41.95
-6	15	1	45.60	47.68
-8	15	1	40.14	-41.14
-10	15	1	32.23	25.82
-12	15	1	24.18	-20.57
-14	15	1	15.92	24.09
-1	16	1	79.67	-92.30
-3	16	1	47.72	47.98
-5	16	1	37.01	-31.75
-7	16	1	48.91	49.78
-9	16	1	41.68	-39.49
-11	16	1	24.75	21.06
-13	16	1	17.85	-26.14
-2	17	1	56.96	-59.62
-4	17	1	35.10	30.21
-6	17	1	27.96	-30.10
-8	17	1	36.97	39.55
-10	17	1	24.90	-21.25
-12	17	1	24.50	21.68
-1	18	1	34.92	36.75
-3	18	1	24.43	-22.68
-5	18	1	13.69	21.19
-7	18	1	25.65	-22.82
-9	18	1	15.92	15.82
-11	18	1	0.00	-12.14
-2	19	1	19.33	3.19
-4	19	1	0.00	-6.86
-6	19	1	0.00	8.04
-8	19	1	0.00	-4.57
-10	19	1	0.00	0.86
-1	20	1	0.00	10.17
-3	20	1	0.00	-8.36
-5	20	1	0.00	6.41
-7	20	1	0.00	-7.71
-9	20	1	0.00	8.84
-2	21	1	16.49	17.95
-4	21	1	0.00	-11.79
-6	21	1	16.31	17.19
-8	21	1	18.28	-19.53
-1	22	1	26.59	-29.53
-3	22	1	22.42	13.39
-5	22	1	26.01	-15.64
-7	22	1	18.36	25.78
-2	23	1	20.05	-16.36
-4	23	1	17.07	13.51
2	0	2	76.91	-78.14
4	0	2	172.14	171.07
6	0	2	164.91	-159.82
8	0	2	133.18	125.52
10	0	2	28.85	-26.03
12	0	2	77.92	82.35
14	0	2	65.35	-59.40
16	0	2	37.27	30.11
18	0	2	0.00	-11.10
1	1	2	19.57	-119.55
3	1	2	53.75	61.90
5	1	2	145.58	-129.98
7	1	2	135.54	143.96
9	1	2	75.40	-78.04
11	1	2	42.99	49.47
13	1	2	50.54	-53.80
15	1	2	40.57	42.07
17	1	2	19.42	-12.01
0	2	2	173.25	-141.39
2	2	2	70.18	73.79
4	2	2	33.17	-30.09
6	2	2	73.95	77.02
8	2	2	81.77	-87.89
10	2	2	34.39	35.87
12	2	2	39.54	-35.39
14	2	2	20.93	22.53
16	2	2	13.02	-18.35
1	3	2	57.50	45.17
3	3	2	12.23	13.11
5	3	2	15.21	-16.09
7	3	2	0.00	-8.31
9	3	2	42.70	44.93
11	3	2	0.00	-12.11
13	3	2	0.00	-8.77
15	3	2	0.00	1.21
17	3	2	15.07	9.58
0	4	2	90.74	-89.14
2	4	2	35.33	27.37
4	4	2	88.45	-75.68
6	4	2	55.45	58.73
8	4	2	37.34	-38.95
10	4	2	15.74	-13.74
12	4	2	39.75	-34.10
14	4	2	41.22	33.00
16	4	2	0.00	-7.50
1	5	2	155.92	150.52
3	5	2	75.53	-85.30
5	5	2	81.19	73.32
7	5	2	113.32	-105.34
9	5	2	50.32	45.25
11	5	2	39.23	-41.95
13	5	2	49.45	47.57
15	5	2	40.00	-34.20
17	5	2	0.00	6.02
0	6	2	220.35	207.57
2	6	2	155.57	-122.92
4	6	2	102.71	94.25
6	6	2	115.03	-100.55
8	5	2	115.71	111.58
10	5	2	40.79	-46.55
12	5	2	67.53	62.13
14	5	2	45.51	-43.37
16	5	2	32.19	25.53
1	7	2	170.09	-145.73
3	7	2	77.05	72.50
5	7	2	93.93	-87.39
7	7	2	121.13	104.81
9	7	2	52.57	-56.19
11	7	2	55.47	55.54
13	7	2	51.25	-35.05
15	7	2	35.13	32.01
17	7	2	19.07	-19.85
0	8	2	55.57	-59.55
2	8	2	96.09	94.84
4	8	2	65.75	-74.22
6	8	2	69.35	71.93
8	8	2	70.13	-55.91
10	8	2	55.00	53.10
12	8	2	41.58	-38.52
14	8	2	22.52	19.50
16	8	2	22.73	-19.63
1	9	2	0.00	13.97
3	9	2	49.75	-51.37
5	9	2	45.12	47.67
7	9	2	0.00	0.21
9	9	2	37.95	34.94
11	9	2	25.58	-27.33
13	9	2	15.25	5.92
15	9	2	12.01	-3.71
0	10	2	77.38	-77.90
2	10	2	0.00	-2.58
4	10	2	0.00	3.44
6	10	2	12.73	21.37
8	10	2	30.50	-29.73
10	10	2	19.89	-17.53
12	10	2	0.00	-4.32
14	10	2	22.38	15.95
1	11	2	90.58	74.54
3	11	2	37.45	-35.90
5	11	2	44.57	40.84
7	11	2	65.47	-65.52
9	11	2	19.35	18.44
11	11	2	13.53	-16.17
13	11	2	27.12	25.38
15	11	2	19.35	-20.57
0	12	2	58.53	75.91
2	12	2	69.53	-60.54
4	12	2	78.75	79.78
6	12	2	75.75	-74.32
8	12	2	38.71	44.57
10	12	2	26.15	-25.42
12	12	2	40.00	36.03
14	12	2	30.93	-29.52
1	13	2	62.52	-55.74
3	13	2	82.50	92.51
5	13	2	75.27	-84.32
7	13	2	42.12	38.73
9	13	2	30.35	-35.33
11	13	2	41.04	44.55
13	13	2	31.08	-29.57
0	14	2	17.05	-20.53
2	14	2	75.52	89.57
4	14	2	65.55	-80.45
6	14	2	31.44	27.95
8	14	2	21.51	-17.55
10	14	2	44.39	47.12
12	14	2	34.03	-31.69
14	14	2	15.07	12.79
1	15	2	39.25	45.32
3	15	2	51.95	-59.22
5	15	2	19.89	20.21
7	15	2	0.00	3.03
9	15	2	36.26	30.30
11	15	2	29.57	-27.54
13	15	2	0.00	5.76
0	16	2	14.07	-3.83
2	16	2	0.00	-20.38
4	16	2	0.00	6.19
6	16	2	0.00	7.95
8	16	2	0.00	-0.52
10	16	2	0.00	-13.10
12	16	2	0.00	0.75
1	17	2	24.21	21.24
3	17	2	0.00	-17.57
5	17	2	0.00	13.49
7	17	2	0.00	-14.51
9	17	2	11.25	5.39
11	17	2	0.00	-11.50
0	18	2	15.11	24.54
2	18	2	36.73	-35.60
4	18	2	35.35	33.43
6	18	2	20.03	-19.85
8	18	2	14.35	16.15
10	18	2	24.25	-23.53
1	19	2	31.15	-27.43
3	19	2	41.91	44.31
5	19	2	32.01	-31.10
7	19	2	0.00	13.94
9	19	2	25.54	-24.70
0	20	2	0.00	-15.08
2	20	2	34.25	33.53
4	20	2	32.48	-33.33
6	20	2	17.41	16.55
8	20	2	10.14	-16.76
1	21	2	13.53	17.77
3	21	2	17.70	-20.35
5	21	2	15.39	15.34
7	21	2	0.00	-12.54
-1	1	2	204.09	245.99
-3	1	2	107.95	-134.07
-5	1	2	127.28	131.57
-7	1	2	79.54	-85.11
-9	1	2	93.39	78.58
-2	2	2	107.53	111.71
-4	2	2	65.55	-72.50
-6	2	2	59.50	52.57
-8	2	2	52.89	-65.54
-10	2	2	18.38	28.95
-1	3	2	45.33	-44.21
-3	3	2	15.40	21.59
-5	3	2	0.00	-4.50
-7	3	2	0.00	-2.33
-9	3	2	0.00	-10.45
-11	3	2	0.00	20.50
-2	4	2	9.32	4.42
-4	4	2	51.37	-45.98
-6	4	2	68.07	63.23
-8	4	2	65.11	-55.72
-10	4	2	0.00	-3.44
-12	4	2	0.00	-15.51
-1	5	2	145.27	-151.95
-3	5	2	23.09	21.70
-5	5	2	97.05	-93.00
-7	5	2	122.23	119.10
-9	5	2	87.02	-75.89

Table 4 (*cont.*)

-11	5	2	0.00	16.25
-13	5	2	52.49	-41.38
-2	5	2	118.71	-113.91
-4	5	2	77.13	72.75
-6	5	2	106.13	-109.18
-8	5	2	134.73	139.79
-10	5	2	47.09	-42.54
-12	5	2	48.54	41.71
-1	7	2	159.23	190.77
-3	7	2	95.55	-95.40
-5	7	2	81.92	77.45
-7	7	2	92.50	-94.97
-9	7	2	90.54	90.60
-11	7	2	52.52	-50.86
-13	7	2	41.57	40.56
-2	8	2	106.53	105.09
-4	8	2	95.56	-102.10
-6	8	2	50.47	70.55
-8	8	2	35.73	-37.20
-10	8	2	48.24	46.75
-12	8	2	22.34	-45.92
-1	9	2	0.00	1.50
-3	9	2	51.19	54.10
-5	9	2	50.25	-67.97
-7	9	2	0.00	-10.42
-9	9	2	0.00	1.73
-11	9	2	53.21	42.03
-13	9	2	29.42	-17.15
-2	10	2	22.26	-14.96
-4	10	2	34.21	28.35
-6	10	2	25.45	19.00
-8	10	2	51.08	-51.67
-10	10	2	0.00	-5.99
-12	10	2	0.00	5.93
-1	11	2	76.19	-73.36
-3	11	2	17.08	11.50
-5	11	2	38.39	-39.03
-7	11	2	59.36	64.76
-9	11	2	39.75	-40.25
-11	11	2	0.00	13.58
-13	11	2	0.00	-21.20
-2	12	2	73.59	-72.71
-4	12	2	57.45	65.21
-6	12	2	59.93	-60.52
-8	12	2	55.47	57.23
-10	12	2	42.74	-38.52
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9	10	3	57.12	51.06
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-7	9	4	21.58	18.15
-9	9	4	0.00	-1.59
-11	9	4	22.15	18.15
-2	10	4	24.92	20.38
-4	10	4	25.75	15.84
-6	10	4	0.00	-3.23
-8	10	4	30.45	-25.78
-10	10	4	0.00	2.28
-12	10	4	0.00	-0.42
-1	11	4	58.21	-53.53
-3	11	4	22.25	16.43
-5	11	4	28.26	-21.38
-7	11	4	40.41	34.46
-9	11	4	25.57	-28.45
-11	11	4	0.00	11.45
-2	12	4	37.29	-34.64
-4	12	4	42.59	39.51
-6	12	4	51.95	-43.35
-8	12	4	49.50	37.54
-10	12	4	31.53	-26.32
-12	12	4	23.75	25.21
-1	13	4	32.21	35.37
-3	13	4	42.92	-42.55
-5	13	4	51.76	47.57
-7	13	4	40.57	-35.12
-9	13	4	41.55	27.89
-11	13	4	35.45	-33.23
-2	14	4	35.48	37.00
-4	14	4	44.18	-43.33
-6	14	4	25.90	27.19
-8	14	4	15.00	-15.19
-10	14	4	35.52	30.52
-1	15	4	0.00	-14.21
-3	15	4	33.03	32.67
-5	15	4	14.21	-18.24
-7	15	4	0.00	5.85
-9	15	4	0.00	-13.07
-2	16	4	0.00	-6.35
-4	16	4	0.00	6.53
-6	16	4	0.00	3.17
-8	16	4	0.00	-1.94
-1	17	4	9.57	-11.04
-3	17	4	0.00	11.25
-5	17	4	17.23	-14.50
-7	17	4	10.46	9.32
-2	18	4	21.10	-21.12
-4	18	4	27.55	26.75
-6	18	4	15.59	-16.21
-1	19	4	15.78	15.38
-3	19	4	25.55	-29.53
-5	19	4	21.04	25.21
-2	20	4	16.13	16.87
-4	20	4	15.23	-23.64
0	2	0	205.32	-181.33
0	4	0	197.52	-205.52
0	6	0	229.92	271.43
0	8	0	57.32	-65.57
0	10	0	32.75	-33.57
0	12	0	96.42	87.05
0	14	0	31.56	-27.43
0	16	0	20.72	-19.10
0	18	0	20.90	18.63
0	20	0	27.17	-24.42
0	22	0	17.15	7.37
0	24	0	12.53	5.09
0	1	1	49.40	-42.52
0	3	1	25.02	-22.10
0	5	1	85.40	101.02
0	7	1	25.97	-27.85
0	9	1	50.31	-113.56
0	11	1	112.04	123.55
0	13	1	32.42	-36.52
0	15	1	81.78	-71.02
0	17	1	50.36	71.54
0	19	1	23.13	-12.55
0	21	1	32.13	-25.75
0	23	1	28.50	23.28
0	0	2	176.25	152.82
0	2	2	172.20	-141.39
0	4	2	92.03	-89.14
0	6	2	221.93	207.87
0	8	2	49.25	-59.55
0	10	2	65.90	-77.90
0	12	2	52.50	75.91
0	14	2	11.75	-20.53
0	16	2	0.00	-3.53
0	18	2	16.53	24.54
0	20	2	20.52	-15.08
0	22	2	17.34	8.21
0	1	3	65.93	50.45
0	3	3	97.57	-91.29
0	5	3	52.97	75.63
0	7	3	40.43	-40.35
0	9	3	41.54	-47.73
0	11	3	75.99	96.39
0	13	3	15.95	-15.80
0	15	3	45.92	-45.39
0	17	3	47.96	47.89
0	19	3	0.00	-8.32
0	21	3	32.00	-23.28
0	0	4	154.35	145.52
0	2	4	61.45	-56.07
0	4	4	105.45	-94.05
0	6	4	112.51	106.45
0	8	4	41.96	-43.45
0	10	4	42.34	-37.32
0	12	4	40.25	56.35
0	14	4	32.18	-33.64
0	16	4	13.74	-1.34
0	18	4	29.52	14.17
0	20	4	17.54	-13.57
0	1	5	0.00	8.57
0	3	5	52.51	-51.50
0	5	5	67.17	67.96
0	7	5	0.00	-6.13
0	9	5	42.31	-44.05
0	11	5	38.00	38.34
0	13	5	0.00	-8.25
0	15	5	34.97	-26.25
0	17	5	32.25	27.10
0	0	6	36.58	56.91
0	2	6	33.35	-25.25
0	4	6	49.95	-27.08
0	6	6	13.40	47.27
0	8	6	19.32	-22.55
0	10	6	33.32	-14.37
0	12	6	24.53	27.91
0	1	7	19.74	16.58
0	3	7	28.51	-28.91
0	5	7	11.95	15.78

Table 5. *Intermolecular interatomic distances less than* 3.5 Å

Coordination of the barium atom. (Numbers in parentheses indicate the number of vectors of the stated length.)

Ba · · · O(2)	2·92 Å	(2)
Ba · · · O(3)	2·70	(2)
Ba · · · O(4)	2·79	(2)
Ba · · · O(4′)	2·66	(2)

Other shortest interatomic distances

O(3) · · · O(4′)	3·40 Å
O(4) · · · O(4′)	3·33

($\frac{1}{4}$, $\frac{1}{2}-y$, 0), ($\frac{1}{4}$, y, $\frac{1}{2}$), ($\frac{1}{4}$, $\frac{1}{2}-y$, 1), . . . are surrounded by the phosphate anions and bound together through the oxygen atoms. In this way, the barium atoms are piled up in the **c** direction. The same arrangement is also found for the barium atoms at ($\frac{3}{4}$, $\frac{1}{2}+y$, 0), ($\frac{3}{4}$, $\bar{y}$, $\frac{1}{2}$), ($\frac{3}{4}$, $\frac{1}{2}+y$, 1), ... Such piled up groups, with their bulky hydrophobic ethyl groups turned outward, are held together through van der Waals forces between the ethyl groups. This result makes it understandable why the needle crystals are elongated along the *c* axis and easily cleaved on the {110} planes.

The structure of the anion

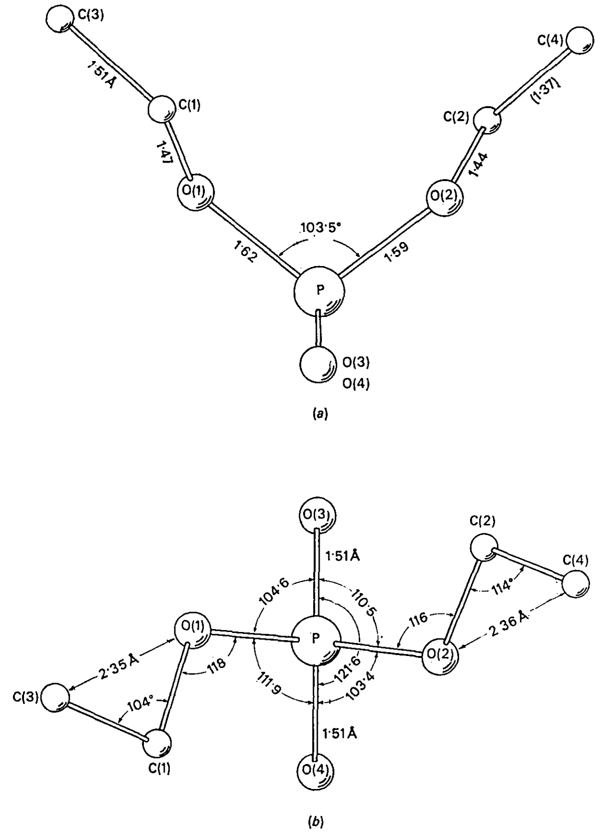


Fig. 2. Diagrammatic representation of the configuration of the diethylphosphate anion, showing bond lengths and angles.

Table 6. *Bond distances and angles found in the diethylphosphate anion*

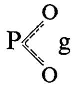
P —O(1)	1·62±0·02 Å
P —O(2)	1·59±0·02
P —O(3)	1·52±0·02
P —O(4)	1·52±0·02
C(1)–O(1)	1·47±0·04
C(2)–O(2)	1·44±0·04
C(1)–C(3)	1·51±0·05
C(2)–C(4)	1·37±0·06
O(1)–P —O(2)	103·5±0·8°
O(1)–P —O(3)	104·6±0·8
O(1)–P —O(4)	111·9±0·8
O(2)–P —O(3)	110·5±0·8
O(2)–P —O(4)	103·4±0·8
O(3)–P —O(4)	121·6±0·8
C(1)–O(1)–P	118·0±2·0
C(2)–O(2)–P	116·0±2·0
C(3)–C(1)–O(1)	104·0±3·0
C(4)–C(2)–O(2)	114·0±3·0

Some shortest interatomic distances within the anion

P —C(1)	2·65±0·04 Å
P —C(2)	2·58±0·04
O(1)–O(2)	2·52±0·03
O(1)–O(3)	2·48±0·03
O(1)–O(4)	2·60±0·03
O(2)–O(3)	2·55±0·03
O(2)–O(4)	2·44±0·03
O(3)–O(4)	2·64±0·03
O(1)–C(2)	3·08±0·04
O(1)–C(3)	2·35±0·05
O(2)–C(1)	3·16±0·04
O(2)–C(4)	2·36±0·05
O(3)–C(2)	2·94±0·04
O(4)–C(1)	3·01±0·04

All the bond distances and bond angles found in the diethyl phosphate anion are given in Table 6 together with their standard deviations. The geometry of the anion is also shown in Fig. 2. Except for the C–C distance of the ethyl group, C(2)–C(4), there are neither abnormal distances nor angles compared with those found in structures so far determined. It is to be noted that all the bond distances found in the ethyl ester group, P–O(2)–C(2)–C(4), are more or less shorter than the corresponding bond distances found in the P–O(1)–C(1)–C(3) group, suggesting a certain kind of interaction to exist between the ester group and the barium atoms lying at short distances from O(2). As to the C(2)–C(4) bond, the bond length of 1·37 Å for it seems to be too short compared with the usual C–C bond distances for alkyl compounds. The shortening can be only partly accounted for by large angular oscillations of C(4) around the C(2) atom, since the estimated shortening according to Cruickshank's formula (Cruickshank, 1956) does not exceed 0·05 Å. Except for this discrepancy, which is to be clarified in future, the structure obtained in the present study is a reasonable one and is enough for the following discussion.

Angles of internal rotation around C–O *and* P–O *bonds*

Although all the atoms in the diethylphosphate anion are located at the general positions, their configuration is almost equivalent to that with a twofold axis bisecting the  $\mathrm{P}\genfrac{}{}{0pt}{}{\diagup \mathrm{O}}{\diagdown \mathrm{O}}$ group. It is also found that each of the C–O bonds is in the *gauche* position to its second next P=O bond and each of the P=O bonds is in the *trans* position to the C–C bond, in agreement with the conclusion obtained from the spectroscopic investigation on the dialkylphosphate anions in aqueous solution (Shimanouchi, Tsuboi & Kyogoku, 1964). The angles of internal rotation, τ, around the C–O and P–O bonds are listed in Table 7 together with those calculated from the reported atomic coordinates of dibenzyl phosphate (Dunitz & Rollett, 1956) and di-*p*-chlorophenyl hydrogen phosphate (Calleri & Speakman, 1964). Here, the angle τ is defined as the angle formed by the projection of the upper bond with that of the lower one when the projection is taken along the bond which has been presumed to be the rotation axis (Tsuboi, 1963). Positive angles are taken as measured anti-clockwise from the lower bond when viewed from the upper bond (Fig. 3). It is the same sense as that of the turning direction of the right handed screw which advances in a positive direction along the chain. In the case of diethyl phosphate, dibenzylphosphoric acid and di-*p*-chlorophenyl hydrogen phosphate, the positive directions are taken as (O → P → O → C →), while in polynucleotides they are taken as (→ O(5′) → P → O(3′) →] along the chain.

The angles of internal rotation obtained for such simple compounds as the above ought not strictly be to compared with those of the polynucleotide chains especially for the P–O(3′) and O(3′)–C(3′) bonds, since the awkward sugar residues are attached through the O(3′)–C(3′) bonds. It is better to compare the values obtained with those of the C(5′)–O(5′) and O(5′)–P bonds of the chains (τ_2 and τ_3). These angles are, therefore, calculated for some of the proposed models of polynucleotide chains from the given atomic coordinates and are listed in Table 7. The angles found in ribonucleic acid (Fuller, 1961) and deoxyribonucleic acid (DNA) C-form (Marvin, Spencer, Wilkins & Hamilton, 1961) deviate considerably from the values obtained in the present determination, while in DNA A-form (Langridge, Seeds, Wilson, Hooper, Wilkins & Hamilton, 1957), DNA B-form (Langridge, Marvin, Seeds, Wilson, Hooper, Wilkins & Hamilton, 1960) and polyadenylic acid (Rich, Davies, Crick & Watson, 1961), the angles do not differ appreciably from those found in the diethylphosphate anion.

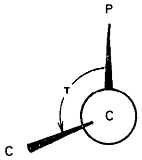


Fig. 3. Definition of the angles of internal rotation

Polynucleotide chains will take a configuration minimizing the energy. This condition, however, will not be fulfilled by staggered conformations alone. As Morgan (1958) has pointed out, it may be related to many factors such as hydrogen bonding, van der Waals forces and electrostatic attractions. Besides these, various effects of solvents, such as hydrations to the phosphate groups and hydrophobic bonds between the base residues, will also be important. In the present case, however, it is plausible that a similar conformation to that found in the solid state is also found in aqueous solutions, since no great difference has been observed in the infrared spectra between barium diethyl phosphate in aqueous solution and in the solid state (Kyogoku, Tsuboi & Shimanouchi, 1965). This implies that such a staggered conformation as has been found in the present study, which has a larger dipole moment than other possible staggered conformations, should be a most stable form in a polar solvent such as water.

The authors wish to express their thanks to Professor M. Tsuboi for his valuable discussions. This work is partly supported by a grant from the United States Public Health Service No. 10024-01.

Table 7. *Angles of internal rotation around* C–O *and* P–O *bonds found in some model compounds and polynucleotides*

Double signs indicate that two kinds of mutually enantiomorphous molecules exist in the crystal

	Barium diethyl phosphate(1)	Dibenzyl phosphoric acid(2)	di-*p*-chlorophenyl hydrogen phosphate(3)
τ_1	∓173·8° [P–O(1)–C(1)–C(3)]	±175·5 [P–O(3)–C(1)–C(2)]	±81·6 [O(1′)–P–O(1)–C(4)]
τ_2	±71·6 [O(2)–P–O(1)–C(1)]	±66·6 [O(4)–P–O(3)–C(1)]	
τ_3	±68·2 [O(1)–P–O(2)–C(2)]	±172·0 [O(3)–P–O(4)–C(8)]	
τ_4	∓177·3 [P–O(2)–C(2)–C(4)]	±175·9 [P–O(4)–C(8)–C(9)]	
τ_2'	±172·6 [O(3)–P–O(1)–C(1)]	∓173·2 [O(1)–P–O(3)–C(1)]	∓160·7 [O(2′)–P–O(1)–C(4)]
τ_3'	±175·0 [O(4)–P–O(2)–C(2)]	∓73·2 [O(2)–P–O(4)–C(8)]	

	DNA–B(4)	DNA–B(5)	DNA–A(5)	DNA–C(6)	RNA(7)	poly A(8)
τ_2 [C(4′)–C(5′)–O(5′)–P]	−147·6°	−148·4	−173·4	143·4	−173·4	168·3
τ_3 [C(5′)–O(5′)–P–O(3′)]	−79·7	−169·5	−59·5	−45·4	−33·2	−74·6
τ_4 [O(5′)–P–O(3′)–C(3′)]	−78·0	39·1	−69·4	−148·1	−102·1	−77·9

(1) Present study.
(2) Dunitz & Rollett (1956).
(3) Calleri & Speakman (1964).
(4) Langridge *et al.* (1960).
(5) Langridge *et al.* (1957).
(6) Marvin *et al.* (1961).
(7) Fuller (1961).
(8) Rich *et al.* (1961).

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The Crystal Structure of Lucidusculine Hydriodide

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(*Received* 2 *October* 1965)

Crystals of lucidusculine hydriodide ($C_{24}H_{35}O_4N\,.\,HI$) are orthorhombic, with space group $P2_12_12_1$ and lattice parameters $a=15{\cdot}94$, $b=14{\cdot}29$, $c=10{\cdot}20$ Å, containing four molecules in the unit cell. The structure was solved by the heavy atom method using three-dimensional Fourier and difference Fourier syntheses. The refinement was carried out by full-matrix least-squares calculations including isotropic temperature factors. The final R index for 1092 nonzero reflexions was 0·133. The absolute configuration was established by the anomalous dispersion method.

The molecule is composed of four six-membered rings, three of which have the boat configuration and one the chair configuration. The iodine atom lies between the two alcoholic hydroxyl groups of the same molecule, and a hydrogen-bonded chelate structure is suggested. Within the crystal, the molecules are linked together by hydrogen bonds in the **a** direction, forming a chain which is packed sideways by van der Waals forces.

Introduction

The diterpene alkaloid lucidusculine was extracted from *Aconitum lucidusculum* by Majima & Morio (1931, 1932). Later, the chemical structure of this compound was studied by Suginome, Amiya & Shima (1959) who suggested the presence of an allyl acetate group, a secondary hydroxyl group and an *N*-ethyl group. Amiya (1960, 1961) obtained a phenanthrene derivative by selenium oxide reduction and proposed a partial structure. Further study by chemical methods was suspended owing to difficulties in getting enough of the sample. The present X-ray study is therefore undertaken in order to determine the molecular structure of lucidusculine.

Experimental

We isolated lucidusculine from *Aconitum yoesoensis* Nakai and purified it in the form of the quaternary ammonium perchlorate. In order to determine the molecular structure, a heavy atom salt, the hydriodide, was prepared by exchanging the anion ClO_4^- with the I^- anion over the ion exchange resin Amberlite IRA-410. The crystals of lucidusculine hydriodide were recrystallized from aqueous methanol. They are colorless prisms with well developed {110} planes and elongated along the c axis. The density was measured by the flotation method with a mixture of benzene and carbon tetrachloride. The cell dimensions and space group were determined from rotation and Weissenberg photographs taken with Cu $K\alpha$ radiation.

Crystal data

Lucidusculine hydriodide $C_{24}H_{35}O_4N\,.\,HI$.

Mol.wt. 529·0

m.p. 249–250°C

Orthorhombic

$a=15{\cdot}94\pm0{\cdot}02,\quad b=14{\cdot}29\pm0{\cdot}02,\quad c=10{\cdot}20\pm0{\cdot}015$ Å

$U=2349{\cdot}8$ Å^3