ings, as is sometimes assumed, is by no means certain. Other transitions are undoubtedly due to puckering effects of the framework, but too little is yet known to make suggestions about their character. The possible role of the sodium atom in controlling their sequence has yet to be considered. Comparison with effects in $AgNbO_3$ and $AgTaO_3$ (Francombe & Lewis, 1958), which are obviously closely related, may be of considerable interest.

The results of this paper are therefore rather a clearing of the ground for future structural work than an answer to any detailed questions about the actual structures.

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The Crystal Structure of Spermidine Trihydrochloride

By E. Giglio, A.M. Liquori and R. Puliti
Istituto Chimico, Università di Napoli, and Centro Nazionale di Chimica delle Macromolecole (CNR) Sez. III, Napoli, Italy

and A. Ripamonti
Istituto di Chimica, Università di Trieste, Trieste, Italy

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Crystals of spermidine trihydrochloride are monoclinic, space group *Cm*, with $a = 27{\cdot}58 \pm 0{\cdot}02$, $b = 5{\cdot}42 \pm 0{\cdot}01$, $c = 4{\cdot}62 \pm 0{\cdot}01$ Å; $\beta = 90°00' \pm 12'$.

The crystal structure has been solved by analysis of the two-dimensional Patterson functions and then refined by several cycles of three-dimensional Fourier differential synthesis. The carbon and nitrogen atoms of the spermidine molecule lie in the mirror plane at $y = 0$ and the conformation of the chain is extended *trans* planar. Most of the hydrogen atoms have been located by means of a three-dimensional difference synthesis. The molecular packing is mainly determined by the closest contacts between nitrogen and chlorine atoms, which form hydrogen bonds.

Introduction

The aliphatic polyamines such as spermine

$$H_2N–CH_2–CH_2–CH_2–NH–CH_2–CH_2–CH_2–CH_2–NH–CH_2–CH_2–CH_2–NH_2$$

and spermidine

$$H_2N–CH_2–CH_2–CH_2–NH–CH_2–CH_2–CH_2–CH_2–NH_2$$

occur in several biological systems. Many studies have been made on the physiological and pharmacological activities of these polyamines and their strong affinity for the nucleic acids (Razin & Rozansky, 1959; Kaiser, 1963; Mandel, 1962) has been recently stressed on the basis of evidence of various kinds.

In previous papers the molecular conformation of spermine has been established through a detailed investigation of the crystal structure of its hydrochloride (Damiani, Liquori, Puliti & Ripamonti, 1965; Giglio, Liquori, Puliti & Ripamonti, 1966).

The results of this investigation have contributed to the understanding of the molecular mechanism of the interaction between deoxyribonucleic acid (DNA) and spermine (Liquori, to be published) which seems to underlie very important biological and biochemical processes. The crystal structure of spermidine chloride has also been the object of a preliminary investigation and a brief account has been already published (Damiani, Giglio, Puliti & Ripamonti, 1965). In this paper the results of detailed three-dimensional analysis of this structure will be reported.

Experimental

Colourless crystals of spermidine trihydrochloride (L. Light and Co. Ltd, England) were recrystallized from a mixture of ethanol and concentrated hydrochloric acid and sealed in thin-walled glass capillary tubes because of their high hygroscopicity. From precession photographs, taken with Cu *Kα* radiation, the unit-cell parameters were found to be:

$$a=27{\cdot}58\pm0{\cdot}02,\quad b=5{\cdot}42\pm0{\cdot}01,\quad c=4{\cdot}62\pm0{\cdot}01\ \text{Å};$$
$$\beta=90^\circ00'\pm12';\quad U=691\ \text{Å}^3\ .$$

The experimental density, measured by the flotation method, is 1·226 g.cm^{-3} and agrees very well with the value of 1·223 g.cm^{-3}, calculated with two formula units ($2C_7N_3H_{19}\,.\,6HCl$) per unit cell. The systematic absences (*hkl* when $h+k$ is odd) show that there are three possible space groups, *C*2, *C*2/*m* and *Cm*. Since only two spermidine molecules are contained in the unit cell, the space group *Cm* may be chosen; the mirror planes at $y=0$ and $y=\frac{1}{2}$ are entirely compatible with a planar conformation which the molecule may take up.

A single crystal, with approximate cubic shape, was used for the collection of the intensities. The *hk*0, *hk*1, *hk*2, *hk*3, *hk*4, *h*0*l* layers were recorded with Cu *Kα* radiation, using multiple-film equi-inclination Weissenberg photographs. 750 independent reflexions, which represent about 91 %of the total, were visually estimated by means of standard scales and scaled with the aid of the cross-correlation terms. The intensities were corrected for change of spot shape on upper layers (Phillips, 1954) and reduced to structure amplitudes by a data-reduction program written for an IBM 1620 computer (Damiani, De Santis, Giglio & Ripamonti, 1962). No absorption corrections were found necessary and there was no evidence of extinction.

Determination and refinement of the structure

The phases of a large number of the observed *hk*0 and *h*0*l* reflexions were established by the analysis of the respective Patterson functions. These two electron-density projections were refined by structure-factor and Fourier-synthesis calculations until the reliability indices were:

$$R_{hk0}=0{\cdot}15;\quad R_{h0l}=0{\cdot}16\ .$$

An average isotropic temperature factor of 3·5 Å^2 was used for both the projections. At this point, starting with the atomic coordinates derived from the two-dimensional analysis, structure-factor calculations were carried out for all the observed reflexions. The reliability index was found to be 0·21 at this stage.

A refinement of the structure was then carried out by means of differential Fourier syntheses, calculated with a computer program written for the IBM 1620 (Damiani, De Santis, Giglio & Ripamonti, 1963) which uses output data of a fast structure-factor program (Damiani, unpublished) as input data. Scattering factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) were used for C, N and Cl$^-$ and that of McWeeny (1951) for hydrogen atoms. During the first two cycles an overall isotropic temperature constant of 4·5 Å^2 was used and only the positional parameters of the carbon and nitrogen atoms and chloride ions were adjusted.

Table 1. *Final fractional atomic coordinates and their standard deviations* (Å)

	x/*a*	*y*/*b*	*z*/*c*	σ(*x*)	σ(*y*)	σ(*z*)
C(1)	0·0474	0·0000	−0·0270	0·009	—	0·012
C(2)	0·0911	0·0000	0·1645	0·008	—	0·010
C(3)	0·1380	0·0000	−0·0037	0·007	—	0·011
C(4)	0·2262	0·0000	0·0170	0·007	—	0·011
C(5)	0·2712	0·0000	0·2072	0·009	—	0·012
C(6)	0·3177	0·0000	0·0393	0·007	—	0·009
C(7)	0·3600	0·0000	0·2526	0·008	—	0·013
N(1)	0·0021	0·0000	0·1498	0·006	—	0·011
N(2)	0·1809	0·0000	0·1848	0·005	—	0·010
N(3)	0·4066	0·0000	0·0901	0·006	—	0·010
Cl(1)	0·0015	0·5000	0·5051	0·002	—	0·003
Cl(2)	0·1829	0·5000	0·5117	0·002	—	0·003
Cl(3)	0·4088	0·5000	0·7286	0·002	—	0·003

Table 2. *Final temperature factors in the form* $\exp\left[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{13}hl)\right]$

	b_{11}	b_{13}	b_{22}	b_{33}
C(1)	0·0010	−0·0009	0·0360	0·0623
C(2)	0·0009	0·0028	0·0345	0·0358
C(3)	0·0008	−0·0003	0·0230	0·0458
C(4)	0·0008	−0·0007	0·0290	0·0526
C(5)	0·0008	0·0000	0·0525	0·0444
C(6)	0·0007	−0·0020	0·0354	0·0290
C(7)	0·0007	−0·0015	0·0442	0·0568
N(1)	0·0007	−0·0013	0·0275	0·0723
N(2)	0·0006	0·0000	0·0240	0·0551
N(3)	0·0005	0·0001	0·0298	0·0683
Cl(1)	0·0011	−0·0025	0·0285	0·0573
Cl(2)	0·0020	−0·0001	0·0197	0·0573
Cl(3)	0·0011	−0·0030	0·0290	0·0488

Table 3. *Observed and calculated structure factors*

Values are multiplied by 10.

H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL
4	0	0	430	401	-24	0	1	38	47	26	4	1	93	86	-13	2	2	142	144	-22	0	3	64	81	-9	5	3	14	27
6	0	0	495	573	26	0	1	193	161	28	4	1	48	46	20	2	2	88	96	24	0	3	50	41	11	5	3	19	39
8	0	0	471	412	28	0	1	96	80	-28	4	1	60	60	-20	2	2	114	109	-24	0	3	134	110	-11	5	3	19	32
10	0	0	662	581	-28	0	1	105	104	1	5	1	125	119	22	2	2	150	161	26	0	3	65	48	13	5	3	22	33
12	0	0	474	537	30	0	1	18	21	-1	5	1	281	291	-22	2	2	96	91	-26	0	3	71	76	-13	5	3	27	35
14	0	0	245	255	-30	0	1	78	66	3	5	1	84	85	24	2	2	120	98	28	0	3	141	100	15	5	3	57	66
16	0	0	154	140	32	0	1	12	3	-3	5	1	60	66	-24	2	2	79	79	-28	0	3	46	38	-15	5	3	26	32
18	0	0	213	218	-32	0	1	92	83	5	5	1	163	171	26	2	2	68	97	30	0	3	71	74	-17	5	3	33	50
20	0	0	145	139	34	0	1	120	103	-5	5	1	204	209	-26	2	2	41	50	-30	0	3	8	10	0	0	4	314	225
22	0	0	552	553	-34	0	1	61	69	7	5	1	176	173	28	2	2	89	79	1	1	3	264	254	2	0	4	21	25
24	0	0	22	20	1	1	1	425	481	-7	5	1	40	39	-28	2	2	86	88	-1	1	3	104	110	-2	0	4	36	36
26	0	0	53	48	3	1	1	295	285	9	5	1	141	140	30	2	2	10	17	3	1	3	134	124	4	0	4	106	77
28	0	0	97	100	-3	1	1	351	346	-9	5	1	61	65	-30	2	2	17	27	-3	1	3	106	104	-4	0	4	92	97
30	0	0	94	90	5	1	1	547	603	11	5	1	69	73	1	3	2	300	293	5	1	3	183	190	6	0	4	164	142
32	0	0	110	107	-5	1	1	640	665	-11	5	1	79	75	-1	3	2	202	172	-5	1	3	99	102	-6	0	4	68	83
34	0	0	93	98	7	1	1	586	613	13	5	1	62	61	3	3	2	217	180	7	1	3	121	144	8	0	4	83	64
1	1	0	398	360	-7	1	1	79	64	-13	5	1	128	132	-3	3	2	133	122	-7	1	3	218	194	-8	0	4	86	82
3	1	0	137	126	9	1	1	438	481	15	5	1	13	31	5	3	2	159	150	9	1	3	114	130	10	0	4	59	49
5	1	0	566	636	-9	1	1	169	169	-15	5	1	128	130	-5	3	2	159	160	-9	1	3	81	71	-10	0	4	104	85
7	1	0	299	318	11	1	1	174	175	17	5	1	154	144	7	3	2	179	161	11	1	3	39	56	12	0	4	92	58
9	1	0	318	318	-11	1	1	125	134	-17	5	1	86	94	-7	3	2	209	179	-11	1	3	42	45	-12	0	4	50	34
11	1	0	185	171	13	1	1	159	139	19	5	1	62	59	9	3	2	42	35	13	1	3	91	88	14	0	4	70	70
13	1	0	242	222	-13	1	1	394	424	-19	5	1	33	39	-9	3	2	71	72	-13	1	3	109	118	-14	0	4	59	51
15	1	0	201	179	15	1	1	94	77	21	5	1	152	140	11	3	2	417	440	15	1	3	169	152	16	0	4	36	46
17	1	0	270	258	-15	1	1	391	381	-21	5	1	36	35	-11	3	2	384	411	-15	1	3	68	79	-16	0	4	89	78
19	1	0	32	28	17	1	1	391	347	23	5	1	126	68	13	3	2	57	57	17	1	3	65	40	18	0	4	35	62
21	1	0	90	74	-17	1	1	280	245	-23	5	1	121	136	-13	3	2	64	61	-17	1	3	127	117	-18	0	4	50	43
23	1	0	101	99	19	1	1	209	188	0	6	1	49	48	15	3	2	100	109	19	1	3	58	50	20	0	4	24	20
25	1	0	49	47	-19	1	1	84	82	2	6	1	70	68	-15	3	2	91	84	-19	1	3	75	67	22	0	4	68	126
27	1	0	134	129	21	1	1	375	357	-2	6	1	29	31	17	3	2	114	115	21	1	3	70	73	-22	0	4	53	89
29	1	0	73	73	-21	1	1	81	60	4	6	1	117	112	-17	3	2	88	100	-21	1	3	119	95	24	0	4	44	25
31	1	0	44	43	23	1	1	197	165	-4	6	1	41	37	19	3	2	82	84	23	1	3	127	113	-24	0	4	30	36
33	1	0	18	24	-23	1	1	351	346	6	6	1	85	78	-19	3	2	82	83	-23	1	3	30	25	1	1	4	142	141
0	2	0	1192	1344	25	1	1	97	80	-6	6	1	114	119	21	3	2	99	94	25	1	3	73	61	-1	1	4	97	80
2	2	0	122	129	-25	1	1	100	105	8	6	1	56	55	-21	3	2	115	124	-25	1	3	27	28	3	1	4	47	37
4	2	0	345	356	27	1	1	159	150	-8	6	1	29	33	23	3	2	132	140	27	1	3	46	46	-3	1	4	102	89
6	2	0	333	335	-27	1	1	121	129	10	6	1	50	53	-23	3	2	62	59	-27	1	3	19	23	5	1	4	214	184
8	2	0	290	301	29	1	1	131	126	-10	6	1	124	121	25	3	2	74	66	29	1	3	43	41	-5	1	4	183	168
10	2	0	454	460	31	1	1	109	87	12	6	1	128	121	-25	3	2	36	36	-29	1	3	29	45	7	1	4	70	56
12	2	0	427	406	33	1	1	28	28	-12	6	1	64	63	27	3	2	28	22	0	2	3	209	171	-7	1	4	164	116
14	2	0	182	194	0	2	1	126	120	14	6	1	32	36	-27	3	2	21	22	2	2	3	106	100	9	1	4	147	146
16	2	0	133	121	2	2	1	253	294	-14	6	1	37	41	-29	3	2	32	45	-2	2	3	222	223	-9	1	4	97	101
18	2	0	201	194	-2	2	1	74	75	16	6	1	70	80	29	3	2	47	46	4	2	3	64	64	11	1	4	153	171
20	2	0	110	118	4	2	1	393	441	-16	6	1	49	56	0	4	2	235	181	-4	2	3	200	214	-11	1	4	139	133
22	2	0	465	440	-4	2	1	82	112	0	0	2	378	344	2	4	2	173	157	6	2	3	246	242	13	1	4	97	106
26	2	0	37	48	6	2	1	258	299	2	0	2	387	360	-2	4	2	178	147	-6	2	3	221	192	-13	1	4	139	132
28	2	0	85	87	-6	2	1	395	417	-2	0	2	189	270	4	4	2	161	159	8	2	3	99	89	15	1	4	91	115
30	2	0	76	79	8	2	1	137	149	4	0	2	397	386	-4	4	2	86	74	-8	2	3	78	66	-15	1	4	44	40
32	2	0	88	94	-8	2	1	169	169	-4	0	2	149	151	6	4	2	215	193	10	2	3	402	393	17	1	4	89	116
1	3	0	21	13	10	2	1	135	136	6	0	2	452	430	-6	4	2	142	214	-10	2	3	102	90	-17	1	4	107	99
3	3	0	54	48	-10	2	1	425	407	-6	0	2	505	447	8	4	2	71	54	12	2	3	124	110	21	1	4	30	61
5	3	0	342	328	12	2	1	422	404	8	0	2	114	131	10	4	2	88	77	-12	2	3	343	357	-21	1	4	35	55
7	3	0	172	163	-12	2	1	187	193	-8	0	2	50	69	-10	4	2	99	93	14	2	3	70	59	0	2	4	226	201
9	3	0	177	182	14	2	1	166	156	10	0	2	308	277	12	4	2	97	90	-14	2	3	33	35	2	2	4	24	21
11	3	0	107	116	-14	2	1	97	95	-10	0	2	124	162	-12	4	2	73	63	16	2	3	156	169	-2	2	4	53	37
13	3	0	161	150	16	2	1	249	244	12	0	2	74	141	14	4	2	39	41	-16	2	3	138	126	4	2	4	94	67
15	3	0	134	125	-16	2	1	173	173	-12	0	2	239	218	-14	4	2	42	45	18	2	3	149	149	-4	2	4	100	87
17	3	0	193	183	18	2	1	57	43	14	0	2	57	83	16	4	2	165	154	-18	2	3	29	32	6	2	4	139	125
19	3	0	22	24	-18	2	1	160	185	-14	0	2	117	102	-16	4	2	136	136	20	2	3	134	122	-6	2	4	78	72
21	3	0	26	33	20	2	1	30	22	16	0	2	229	277	18	4	2	44	45	-20	2	3	37	32	8	2	4	67	59
23	3	0	37	48	-20	2	1	109	108	-16	0	2	271	263	-18	4	2	89	91	22	2	3	68	64	-8	2	4	88	70
25	3	0	33	34	22	2	1	34	15	18	0	2	82	89	20	4	2	68	63	-22	2	3	61	71	10	2	4	36	42
27	3	0	102	95	-22	2	1	46	61	-18	0	2	217	177	-20	4	2	59	71	24	2	3	40	36	-10	2	4	89	73
29	3	0	49	52	24	2	1	153	140	20	0	2	102	106	22	4	2	107	103	-24	2	3	81	94	12	2	4	70	83
31	3	0	28	32	-24	2	1	30	37	-20	0	2	139	127	-22	4	2	65	61	26	2	3	40	41	-12	2	4	24	29
0	4	0	546	591	26	2	1	152	137	22	0	2	176	178	24	4	2	82	65	-26	2	3	61	65	14	2	4	39	60
2	4	0	53	62	28	2	1	78	70	-22	0	2	88	96	-24	4	2	59	50	28	2	3	83	88	-14	2	4	47	44
4	4	0	190	196	-28	2	1	86	90	24	0	2	128	115	26	4	2	71	64	-28	2	3	33	33	16	2	4	23	39
6	4	0	185	177	30	2	1	14	18	-24	0	2	76	83	-26	4	2	21	31	1	3	3	193	186	-16	2	4	56	68
8	4	0	168	153	-30	2	1	56	55	26	0	2	132	113	1	5	2	146	142	-1	3	3	124	95	18	2	4	21	56
10	4	0	262	249	-32	2	1	76	71	-26	0	2	53	57	-1	5	2	133	117	3	3	3	92	88	-18	2	4	39	37
12	4	0	234	225	1	3	1	222	240	28	0	2	100	92	3	5	2	94	91	-3	3	3	95	83	22	2	4	39	110
14	4	0	113	110	-1	3	1	555	607	-28	0	2	83	102	-3	5	2	76	67	5	3	3	142	143	-22	2	4	50	78
16	4	0	88	80	3	3	1	144	149	-30	0	2	24	32	5	5	2	80	84	-5	3	3	83	78	1	3	4	126	106
18	4	0	126	128	-3	3	1	166	172	32	0	2	100	83	-5	5	2	94	90	7	3	3	126	104	-1	3	4	88	60
20	4	0	56	67	5	3	1	361	342	1	1	2	397	435	7	5	2	102	100	-7	3	3	145	147	3	3	4	24	22
22	4	0	267	273	-5	3	1	361	402	-1	1	2	322	312	-7	5	2	112	104	9	3	3	88	87	-3	3	4	83	66
24	4	0	14	17	7	3	1	322	332	3	1	2	257	269	9	5	2	24	27	-9	3	3	57	50	5	3	4	167	140
26	4	0	34	38	-7	3	1	56	59	-3	1	2	191	169	-9	5	2	24	29	11	3	3	33	46	-5	3	4	142	125
28	4	0	54	59	9	3	1	294	265	5	1	2	243	226	11	5	2	214	236	-11	3	3	33	36	7	3	4	47	37
1	5	0	22	17	-9	3	1	97	115	-5	1	2	225	214	-11	5	2	185	219	13	3	3	61	64	-7	3	4	38	89
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5	5	0	200	181	-11	3	1	145	136	-7	1	2	282	268	-13	5	2	33	40	15	3	3	116	116	-9	3	4	86	77
7	5	0	96	86	13	3	1	107	105	9	1	2	42	18	15	5	2	67	68	-15	3	3	49	58	11	3	4	106	129
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15	5	0	72	69	17	3	1	286	251	13	1	2	102	95	19	5	2	56	47	-19	3	3	49	48	15	3	4	59	87
17	5	0	124	107	-17	3	1	145	169	-13	1	2	102	99	-19	5	2	49	46	21	3	3	65	58	-15	3	4	21	27
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21	5	0	14	14	-19	3	1	53	61	-15	1	2	118	94	-21	5	2	64	69	23	3	3	88	85	-17	3	4	74	77
23	5	0	16	22	21	3	1	250	250	17	1	2	161	151	0	6	2	109	88	-23	3	3	21	23	-21	3	4	24	42
0	6	0	308	272	-21	3	1	46	49	-17	1	2	135	133	2	6	2	83	81	25	3	3	50	45	0	4	4	150	130
2	6	0	26	30	23	3	1	120	116	19	1	2	149	115	-2	6	2	83	75	-25	3	3	18	24	2	4	4	21	9
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10	6	0	131	119	27	3	1	125	114	23	1	2	206	189	-6	6	2	109	111	4	4	3	46	44	6	4	4	130	82
12	6	0	120	108	-27	3	1	107	100	-23	1	2	102	83	8	6	2	30	27	-4	4	3	145	131	-6	4	4	53	50
14	6	0	54	53	29	3	1	96	93	25	1	2	96	90	10	6	2	33	31	6	4	3	172	162	8	4	4	36	34
16	6	0	48	46	31	3	1	72	67	-25	1	2	45	49	-10	6	2	49	52	-6	4	3	137	125	-8	4	4	53	47
0	0	1	284	230	0	4	1	69	67	27	1	2	28	26	12	6	2	47	52	8	4	3	46	45	10	4	4	20	34
2	0	1	329	411	2	4	1	138	150	-27	1	2	32	25	-12	6	2	24	22	-8	4	3	50	49	-10	4	4	56	46
-2	0	1	82	125	-2	4	1	44	48	29	1	2	68	58	0	0	3	190	203	10	4	3	268	242	12	4	4	47	52
4	0	1	607	625	4	4	1	232	231	-29	1	2	49	59	2	0	3	123	122	-10	4	3	79	64	-12	4	4	18	23
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6	0	1	336	381	6	4	1	154	158	-31	1	2	20	50	4	0	3	71	75	-12	4	3	197	220	-14	4	4	24	27
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10	0	1	333	276	10	4	1	81	55	4	2	2	279	272	8	0	3	147	117	18	4	3	109	95	-2	0	5	109	77
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14	0	1	252	211	14	4	1	69	32	8	2	2	106	95	12	0	3	110	117	22	4	3	45	42	-6	0	5	91	77
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16	0	1	313	287	16	4	1	158	155	10	2	2	179	174	14	0	3	54	67	1	5	3	113	108	-8	0	5	59	37
-16	0	1	166	197	-16	4	1	161	169	-10	2	2	126	132	-14	0	3	55	48	-1	5	3	57	59	10	0	5	106	94
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-18	0	1	187	214	-18	4	1	114	118	-12	2	2	152	146	-16	0	3	169	147	-3	5	3	60	54	12	0	5	76	74
20	0	1	28	33	-20	4	1	76	70	14	2	2	70	71	18	0	3	154	176	5	5	3	86	84	-12	0	5	71	67
-20	0	1	138	125	22	4	1	13	6	-14	2	2	80	78	-18	0	3	36	34	-5	5	3	43	48	14	0	5	60	41
22	0	1	49	39	-22	4	1	26	33	16	2	2	225	234	20	0	3	75	145	7	5	3	68	56	16	0	5	56	48
-22	0	1	62	76	24	4	1	97	88	-16	2	2	209	216	-20	0	3	42	37	-7	5	3	83	84	18	0	5	70	48
24	0	1	191	163	-24	4	1	13	21	18	2	2	82	79	22	0	3	58	72	9	5	3	37	36	-18	0	5	39	46

In the following six cycles both the contribution of the hydrogen atoms and anisotropic thermal parameters were introduced in the form:

$$\exp\left[-(b_{11}h^2+b_{12}hk+b_{13}hl+b_{22}k^2+b_{23}kl+b_{33}l^2)\right]$$

neglecting the b_{12} and b_{23} terms. The hydrogen atoms, except those bonded to the terminal nitrogen atoms, were put at expected positions, assuming a C–H bond length of 1·08 Å, with isotropic temperature factors of 5·0 Å^2. The R index for the observed reflexions dropped to 0·098. The refinement was considered complete when the coordinate shifts were generally much less than the corresponding standard deviations. The final atomic parameters with their estimated standard deviations (Cruickshank, 1949) are shown in Table 1. For the numbering of atoms see Fig. 1 where bond lengths and bond angles are also indicated.

The lower accuracy of the z coordinates must be ascribed to the lack of reflexions with $l=5$, which also affects the values of the anisotropic temperature factors, collected in Table 2. Also they must be considered as additional parameters for improving the R index.

The final values of the observed and calculated structure factors are listed in Table 3. The observed and calculated peak electron densities and curvatures are shown in Table 4 and the estimated standard deviations of the electron density and its slopes are:

$$\sigma(\varrho)=0{\cdot}18\ \text{e.Å}^{-3};\ \sigma(A_h)=0{\cdot}53,\ \sigma(A_k)=0.50,\ \sigma(A_l)=0{\cdot}59\ \text{e.Å}^{-4}.$$

The e.s.d.'s for the bond lengths (Ahmed & Cruickshank, 1953) and angles (Darlow, 1960) are reported in Table 5, but their values are possibly too small because series termination errors have not been included. A representation of the final composite projection of the electron density, viewed along the b axis, is shown in Fig. 2. With the purpose of locating the hydrogen atoms a three-dimensional Fourier difference synthesis was calculated, including all the reflexions with $\sin\theta<0{\cdot}6$. The

Table 4. *Peak heights and curvatures*

Values in parentheses are from F_c differential synthesis

	ϱ (e.Å^{-3})	$-A_{hh}$ (e.Å^{-5})	$-A_{kk}$ (e.Å^{-5})	$-A_{ll}$ (e.Å^{-5})	A_{hl} (e.Å^{-5})
C(1)	6·68	61·6	61·5	48·9	−3·6
	(6·71)	(61·5)	(61·8)	(49·5)	(−3·3)
C(2)	7·76	65·2	69·0	60·9	3·2
	(7·86)	(65·1)	(69·1)	(60·1)	(7·3)
C(3)	7·42	72·5	72·6	54·5	−2·4
	(7·35)	(71·3)	(72·3)	(54·2)	(−4·0)
C(4)	7·89	77·3	77·3	55·5	0·0
	(7·82)	(76·2)	(76·6)	(54·8)	(−2·1)
C(5)	6·51	60·3	50·9	49·9	−0·2
	(6·58)	(60·6)	(50·4)	(49·4)	(−1·3)
C(6)	8·79	81·1	78·4	68·2	−3·6
	(8·84)	(80·6)	(77·1)	(67·9)	(−2·4)
C(7)	6·73	70·2	53·5	46·5	−5·0
	(6·65)	(70·5)	(53·7)	(45·4)	(−3·5)
N(1)	9·31	87·4	74·5	52·3	−5·8
	(9·29)	(87·9)	(74·3)	(52·6)	(−5·0)
N(2)	9·62	98·0	88·2	56·8	1·0
	(9·64)	(96·9)	(87·3)	(56·5)	(0·8)
N(3)	9·29	92·2	76·4	57·4	−1·3
	(9·39)	(93·7)	(77·4)	(57·3)	(1·6)
Cl(1)	28·70	284·9	283·2	222·1	−21·6
	(28·61)	(283·4)	(283·0)	(220·5)	(−20·5)
Cl(2)	28·39	226·7	314·6	229·9	0·7
	(28·20)	(225·6)	(309·6)	(226·3)	(0·9)
Cl(3)	29·07	289·9	280·5	220·2	−18·7
	(28·99)	(288·3)	(281·0)	(218·2)	(−17·8)

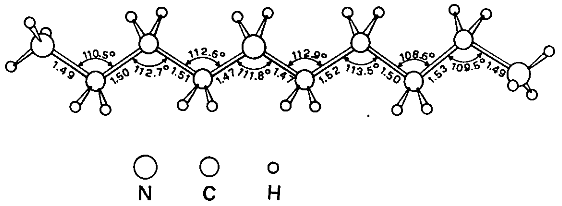

Fig. 1. Atomic numbering within the molecules with bond lengths and bond angles.

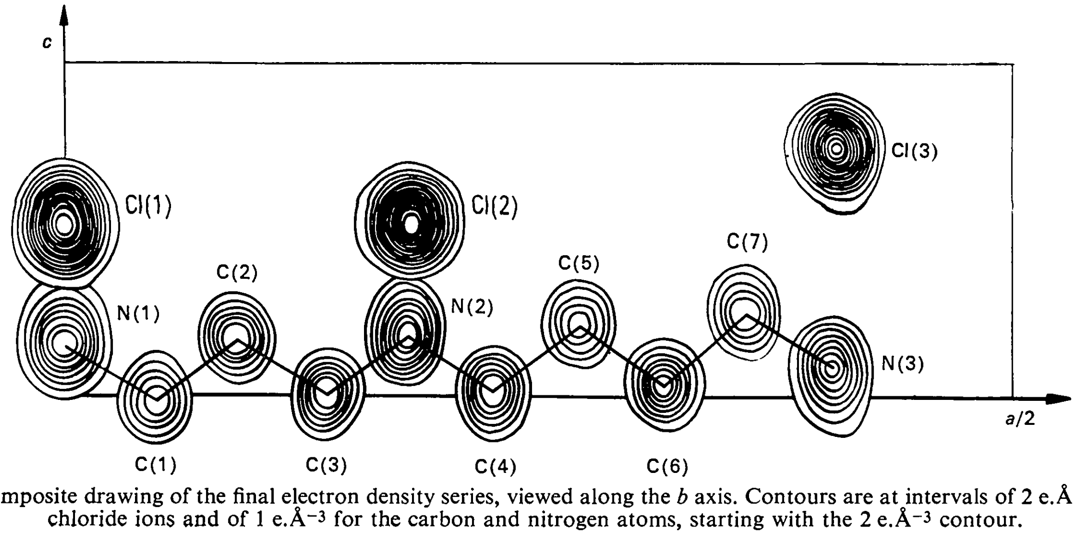

Fig. 2. Composite drawing of the final electron density series, viewed along the b axis. Contours are at intervals of 2 e.Å^{-3} for the chloride ions and of 1 e.Å^{-3} for the carbon and nitrogen atoms, starting with the 2 e.Å^{-3} contour.

hydrogen atoms attached to the carbon atoms were well resolved (Fig. 3) and their bond distances and angles are reasonable. The peak corresponding to the hydrogen atom linked to N(2) gives a reasonable bond angle but the bond length is about 1·4 Å. Some peaks that may be due to the hydrogen atoms of N(1) and N(3) also appear in the difference map, but the values of their electron densities are about 0·2 e.Å^{-3}, too close to the standard deviation of the electron density calculated from the differential Fourier synthesis to be significant.

Table 5. *E.S.D.'s for the bond lengths and angles*

N(1)–C(1)	0·013 Å	N(1)–C(1)–C(2)	56′
C(1)–C(2)	0·013	C(1)–C(2)–C(3)	50′
C(2)–C(3)	0·012	C(2)–C(3)–N(2)	51′
C(3)–N(2)	0·012	C(3)–N(2)–C(4)	52′
N(2)–C(4)	0·011	N(2)–C(4)–C(5)	53′
C(4)–C(5)	0·013	C(4)–C(5)–C(6)	54′
C(5)–C(6)	0·012	C(5)–C(6)–C(7)	48′
C(6)–C(7)	0·013	C(6)–C(7)–N(3)	55′
C(7)–N(3)	0·012		

Discussion

The molecular conformation of spermidine chloride is rigorously planar, at variance with that of spermine chloride, which is twisted (Giglio, Liquori, Puliti & Ripamonti, 1966).

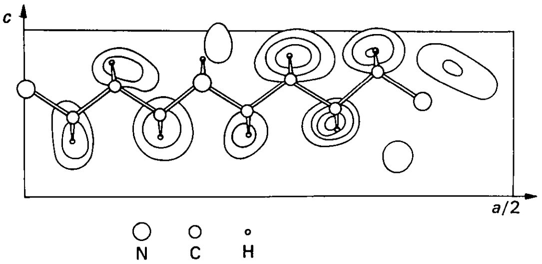

Fig. 3. Section of the Fourier difference synthesis, calculated at $y=-0{\cdot}160$, showing the peaks of the hydrogen atoms and the expected positions, assuming C–H = 1·08 Å. The contours are at intervals of 0·1 e.Å^{-3}, starting from 0·15 e.Å^{-3}.

Bond lengths and angles appear to be normal, with the exception of the small shortening of the C(1)–C(2), C(2)–C(3) and C(5)–C(6) bonds (Fig. 1). However it seems difficult to attach any physical meaning to this difference.

In the spermine and spermidine chlorides the average length of the bonds between carbon and nitrogen atoms is 1·49 Å. This result is in agreement with the value deduced by Hahn (1957) who stated that the bond lengthening of the bonds between carbon and amino nitrogen groups with respect to the N–C$_\alpha$ bonds in peptides was real and could be due to the *sp*^{3} hybridization of the nitrogen atoms.

The difference Fourier synthesis seems to indicate that the secondary amino group in the spermidine molecule is protonated. Unfortunately it is not possible to locate the hydrogen atoms of the $-\overset{+}{\mathrm{N}}\mathrm{H}_3$ groups in the difference map because the peaks around the terminal nitrogen atoms are very low. On the other hand the distances between $-\overset{+}{\mathrm{N}}\mathrm{H}_3$ and Cl$^-$ and the nearly tetrahedral angles between the lines joining chloride ions and nitrogen atoms show the possibility of hydrogen-bond formation.

Table 6. *Intermolecular contacts less than* 4·0 Å

Superscripts refer to the molecules:

I $(\frac{1}{2}+x, \frac{1}{2}+y, z)$; II $(\frac{1}{2}+x, \frac{1}{2}+y, 1+z)$; III $(x-\frac{1}{2}, \frac{1}{2}+y, z)$; IV $(x-\frac{1}{2}, \frac{1}{2}+y, 1+z)$; V $(x, y, 1+z)$; VI $(x, 1+y, z)$.

N(3) ··· N(1)$^{\mathrm{I}}$	3·79 Å	C(7) ··· C(6)$^{\mathrm{V}}$	3·82 Å
Cl(3) ··· N(1)$^{\mathrm{I}}$	3·71	Cl(3) ··· C(6)$^{\mathrm{V}}$	3·96
Cl(3) ··· Cl(1)$^{\mathrm{I}}$	3·87	Cl(3) ··· C(7)$^{\mathrm{V}}$	3·88
Cl(3) ··· C(1)$^{\mathrm{II}}$	3·99	Cl(3) ··· N(3)$^{\mathrm{V}}$	3·18
Cl(3) ··· N(1)$^{\mathrm{II}}$	3·23	Cl(1) ··· C(1)$^{\mathrm{VI}}$	3·87
Cl(1) ··· N(3)$^{\mathrm{III}}$	3·24	Cl(1) ··· C(2)$^{\mathrm{VI}}$	3·99
Cl(1) ··· N(3)$^{\mathrm{IV}}$	3·76	Cl(2) ··· C(3)$^{\mathrm{VI}}$	3·81
C(2) ··· C(1)$^{\mathrm{V}}$	3·92	Cl(2) ··· C(4)$^{\mathrm{VI}}$	3·74
Cl(1) ··· C(1)$^{\mathrm{V}}$	3·69	Cl(2) ··· C(5)$^{\mathrm{VI}}$	3·91
N(2) ··· C(3)$^{\mathrm{V}}$	3·93	Cl(3) ··· C(7)$^{\mathrm{VI}}$	3·74
Cl(2) ··· C(3)$^{\mathrm{V}}$	3·73	Cl(1) ··· N(1)$^{\mathrm{VI}}$	3·17
C(5) ··· C(4)$^{\mathrm{V}}$	3·94	Cl(2) ··· N(2)$^{\mathrm{VI}}$	3·10
Cl(2) ··· C(4)$^{\mathrm{V}}$	3·77		

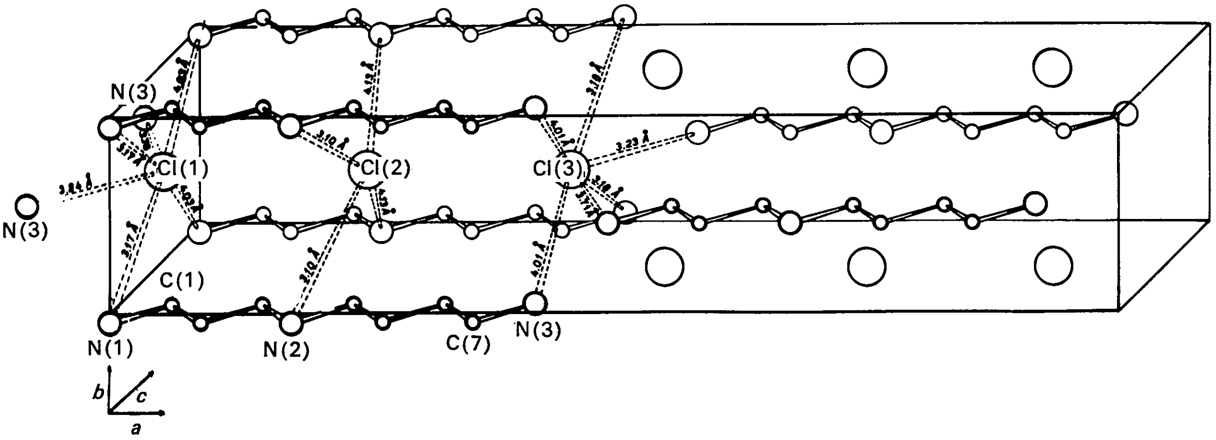

Fig. 4. Clinographic view of the structure showing the closest approaches.

Table 7. *Shortest* $N^+\cdots Cl^-$ *approaches and corresponding angles*

The primed atoms belong to asymmetric units other than that at (x, y, z).

N(1) ··· Cl(1′)	3·17 Å	Cl(1)–N(1)–Cl(1′)	118°
N(1) ··· Cl(1)	3·17	Cl(1)–N(1)–Cl(3′)	108
N(1) ··· Cl(3′)	3·23	Cl(1′)–N(1)–Cl(3′)	108
N(2) ··· Cl(2)	3·10	Cl(2)–N(2)–Cl(2′)	122
N(2) ··· Cl(2′)	3·10		
N(3) ··· Cl(1′)	3·24	Cl(1′)–N(3)–Cl(3′)	107
N(3) ··· Cl(3′)	3·18	Cl(3′)–N(3)–Cl(3′)	117
N(3) ··· Cl(3′)	3·18	Cl(1′)–N(3)–Cl(3′)	107

The situation is summarized in Table 7, where only the shortest $\overset{+}{N}\cdots Cl^-$ approaches are taken into account. Also the C–$\overset{+}{N}H_3\cdots Cl$ angles support this conclusion since their values vary between 106° and 114° with an average value of 108°. These results seem to point to the formation of three hydrogen bonds, at variance with spermine tetrahydrochloride in which the interactions between terminal nitrogen atoms and the four chloride ions surrounding them are equal in pairs and only two chloride ions form angles near to tetrahedral value with nitrogen and carbon atoms. In addition the $-\overset{+}{N}H_3$ and $-\overset{+}{N}H_2^-$ groups in spermidine are surrounded respectively by another three and two chloride ions which are located at distances varying between 3·71 and 4·13 Å. Moreover, it is interesting to note that the arrangement of the chloride ions surrounding each nitrogen atom is very similar to that of the nitrogen atoms surrounding each chloride ion. The crystal packing may be explained on the basis of a layer structure formed by the spermidine molecules being held in sheets by van der Waals forces (Fig. 4). The chloride ions form rows between the sheets and are connected to the protonated amino and imino groups through hydrogen bonds. Such a packing is obviously consistent with the ionic character of the crystal. As to the planar conformation of the molecule, it should be considered that in the case of spermine both a planar and a skewed conformation have been established for different salts. Therefore the possibility cannot be excluded that also protonated spermidine molecules may adopt a skewed conformation characterized by *gauche* state of the bonds connecting the carbon atoms to the amino nitrogens. In view of the probably small energy differences between the two conformations in the case of spermine it may be inferred that under appropriate conditions a skewed conformation of spermidine may also be expected. This might be the case when spermidine interacts with DNA in solution and therefore the same model proposed to explain the mechanism of the interaction between DNA and spermine (Liquori, to be published) may be easily extended to spermidine.

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Sodium Silicate Hydrates. II. The Crystal Structure of $Na_2O.SiO_2.9H_2O$

BY PETER B. JAMIESON AND L. S. DENT GLASSER
Department of Chemistry, University of Aberdeen, Old Aberdeen, Scotland

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The crystal structure of $Na_2O.SiO_2.9H_2O$ has been determined by X-ray structure analysis, using three-dimensional data. The silicon atoms are shown to be surrounded tetrahedrally by four oxygen atoms; the tetrahedra are not linked through a common atom. Each sodium atom is coordinated by six oxygen atoms at the corners of a distorted octahedron; the octahedra share edges to produce helical chains. An attempt to locate hydrogen atoms was unsuccessful, but consideration of bond lengths and angles leads to the conclusion that two hydrogen atoms are probably attached to each silicon–oxygen tetrahedron, and that the constitutional formula is therefore $Na_2(H_2SiO_4).8H_2O$.

Introduction

$Na_2O.SiO_2.9H_2O$ is orthorhombic, *Ibca*, with $a=11{\cdot}74$, $b=17{\cdot}03$, $c=11{\cdot}60$ Å, $Z=8$ (see part I, Jamieson & Dent Glasser, 1966). The uncertainty about the nature of the anion (discussed in part I) made a structure determination seem worth while.