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The Crystal Structure of Spermine Tetrahydrochloride

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Crystals of spermine tetrahydrochloride, $\overset{+}{N}H_3[CH_2]_3\overset{+}{N}H_2[CH_2]_4\overset{+}{N}H_2[CH_2]_3\overset{+}{N}H_3 . 4Cl^-$, are monoclinic, space group $P2_1/c$, with 2 formula units in a cell with dimensions: $a=8{\cdot}60$, $b=7{\cdot}88$, $c=15{\cdot}26$ Å, $\beta=121°\,30'$. The structure has been determined by the interpretation of Patterson projections and application of Harker–Kasper inequalities and then refined by three-dimensional differential syntheses.

The charged molecule of spermine is not zigzag planar, two of the four bonds between carbon atoms and imino nitrogen atoms being in *gauche* conformations. The average value of the C–C single bonds is $1{\cdot}52_2 \pm 0{\cdot}009$ Å. The C–N bonds are equal within experimental error with an average value of $1{\cdot}49_6 \pm 0{\cdot}009$ Å. The two bond angles within the chain adjacent to the bonds in *gauche* conformation appear significantly larger than the tetrahedral values.

The strongest interactions in the crystals occur between the $\overset{+}{N}H_2$ and $\overset{+}{N}H_3$ groups and the chloride ions. The distances N · · · Cl as well as their directions indicate the formation of N–H · · · Cl hydrogen bonds.

The structure determination of spermine tetrahydrochloride, $\overset{+}{N}H_3[CH_2]_3\overset{+}{N}H_2[CH_2]_4\overset{+}{N}H_2[CH_2]_3\overset{+}{N}H_3 . 4Cl^-$, has been carried out as part of a program of crystallographic studies of biologically important aliphatic polyamines. The salts of these compounds are being studied in an effort to gain a detailed understanding of the chain conformation of the protonated molecules. A preliminary report of this structure has been published (Damiani, Liquori, Puliti & Ripamonti, 1965). When the three-dimensional refinement had been completed and the crystal structure of spermine phosphate hexahydrate was in progress, the structure analysis of the latter compound was reported by Iitaka & Huse (1965). They found that the protonated spermine molecule has a fully extended conformation and that the $\overset{+}{N}H_2$ and $\overset{+}{N}H_3$ groups form N–H · · · O hydrogen bonds which hold together sheets of spermine molecules and parallel sheets of monohydrogen phosphate ions and water molecules. At variance with results obtained for spermine phosphate the charged molecular chains do not assume a zigzag planar conformation in the crystals of spermine tetrahydrochloride. In view of this unexpected result, a comparison of the crystal structures of the two different salts of spermine appears of particular interest.

Experimental

Crystals of spermine tetrahydrochloride suitable for X-ray examination were grown by cooling a warm solution of the free base in a 4:1 mixture of ethanol and concentrated hydrochloric acid. They are monoclinic prismatic elongated along **b**.

The unit-cell dimensions, determined from precession photographs taken with Cu $K\alpha$ radiation, are

$$a=8{\cdot}60 \pm 0{\cdot}01\,, \quad b=7{\cdot}88 \pm 0{\cdot}01\,, \quad c=15{\cdot}26 \pm 0{\cdot}02 \text{ Å}$$
$$\beta=121°\,30' \pm 12'\,.$$

The observed density of the crystals, measured by flotation, is 1·321 g.cm^{-3}. The density calculated on the basis of two formula units ($C_{10}N_4H_{30}Cl_4$) per unit cell is 1·318 g.cm^{-3}.

The space group is determined uniquely as $P2_1/c$ (C^5_{2h}) by the systematic absences of X-ray reflexions. Intensities of $h0l$, $h1l$ and hkl with h from 0 to 7 reflexions were collected on multiple-film equi-inclination Weissenberg photographs taken about the b and a axes respectively. Crystals cut down to form nearly cubic specimens about 0·2 mm on an edge were used. A total of 1500 reflexions were estimated visually and corrected for Lorentz and polarization factors. The data were then correlated and placed upon a common scale. Absorption corrections were not made.

Determination and refinement of the structure

The space group requires that the molecular chains be located at centres of symmetry and that two chlorine atoms be contained in the asymmetric unit. These requirements suggested that the structure could be solved by means of a direct analysis of the sharpened Patterson projections. However, the Patterson projections on (100) and (010) could not be readily interpreted on the assumption that the molecular chains have a fully extended conformation. Furthermore the Cl–Cl vectors were not easily recognizable. Therefore the application of Harker–Kasper inequalities was attempted. The signs of 42% and 22% respectively of the $h0l$ and $0kl$ reflexions were derived in this way, allowing the cal-

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Table 1. *Final atomic coordinates and their standard deviations*

	x/a	y/b	z/c	σ_x	σ_y	σ_z
C(1)	−0·0464	0·0661	0·0155	0·0068 Å	0·0061 Å	0·0054 Å
C(2)	−0·0055	0·0312	0·1240	0·0117	0·0065	0·0069
C(3)	−0·2915	0·1598	0·1029	0·0071	0·0060	0·0055
C(4)	−0·3632	0·2889	0·1477	0·0069	0·0061	0·0053
C(5)	−0·5680	0·2973	0·0808	0·0076	0·0074	0·0064
N(1)	−0·0876	0·1597	0·1607	0·0058	0·0049	0·0046
N(2)	−0·6445	0·4250	0·1207	0·0055	0·0056	0·0050
Cl(1)	0·0160	0·0384	0·3812	0·0016	0·0013	0·0012
Cl(2)	0·4134	0·2583	0·3231	0·0023	0·0017	0·0015

culation of reasonable electron density projections. All atoms could be identified and their coordinates were adjusted to give the best agreement with the Patterson projections by considering a plausible model for the molecular chains.

A preliminary refinement of the structure was then carried out through cycles of calculations of structure factors and Fourier syntheses. After three cycles of calculations for the (010) and two cycles for the (100) projections structure factors for all observed reflexions were calculated. The R index was 0·19, using an average isotropic temperature factor of 2·9 Å^2.

The structure now essentially determined, was refined by means of several three-dimensional differential syntheses.

Atomic scattering factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for C, N and Cl$^-$ and the McWeeny (1951) atomic scattering factor for hydrogen were used. The refinement was started isotropically. When convergence was reached, the contribution of the hydrogen atoms was included, and the heavy atoms were treated anisotropically while the hydrogen parameters were held constant. The coordinates of the hydrogen atoms were calculated by assuming tetrahedral configurations for the carbon and nitrogen atoms with C–H and N–H bond lengths of 1·08 Å. The orientation of the NH_3 group with respect to the adjacent CH_2 group was assumed to be such that the hydrogen atoms were staggered, looking along the C–N bond.

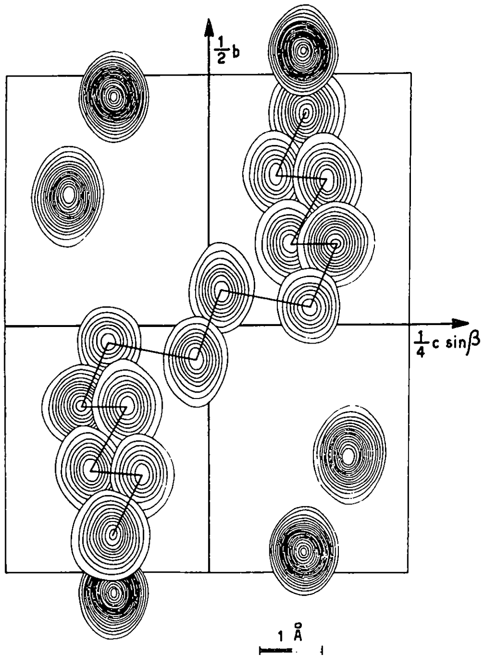

Fig. 1. Composite drawing of the final three-dimensional Fourier synthesis of electron density viewed along **a**. Contours are at intervals of 1 e.Å^{-3} around the carbon and nitrogen atoms and at intervals of 2 e.Å^{-3} around the chloride ions, beginning with 1 e.Å^{-3} contour.

An average isotropic B value of 4·0 Å^2 was assigned to the hydrogen atoms. Anisotropic thermal parameters for the heavier atoms were adjusted by comparison of the observed and calculated electron density curvatures. The final R value was 0·105, including only the observed reflexions. The coordinates and the temperature parameters of the heavier atoms, used in the last structure factor calculation, are given in Tables 1 and 2 respectively. The structure factors calculated from these values, together with the observed structure factors, are listed in Table 3. The electron densities and their curvatures at the atomic positions are given in Table 4. The significant differences of the electron density values for atoms of the same species may be ascribed either to finite summation effects or to the anisotropy of the thermal motion. The interference of these two effects does not allow, of course, any physical meaning to be attached to the anisotropic thermal parameters. The standard deviations of coordinates, estimated according to Cruickshank (1949), are given in Table 1 together with the positional parameters. The standard deviations of electron density and its first derivatives are: $\sigma(\varrho)=0·17$ e.Å^{-3}, $\sigma(A_h)=0·51$ e.Å^{-4}, $\sigma(A_k)=0·50$ e.Å^{-4}, $\sigma(A_l)=0·47$ e.Å^{-4}.

Table 2. *Final anisotropic thermal parameters*

The temperature factor is of the form
$\exp\,[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{13}hl)]$

	b_{11}	b_{22}	b_{33}	b_{13}
C(1)	0·0122	0·0121	0·0032	0·0074
C(2)	0·0185	0·0097	0·0030	0·0065
C(3)	0·0133	0·0117	0·0031	0·0056
C(4)	0·0123	0·0124	0·0036	0·0073
C(5)	0·0121	0·0159	0·0041	0·0057
N(1)	0·0107	0·0109	0·0026	0·0056
N(2)	0·0129	0·0124	0·0041	0·0070
Cl(1)	0·0125	0·0107	0·0027	0·0058
Cl(2)	0·0207	0·0141	0·0039	0·0086

Finally two three-dimensional Fourier syntheses were calculated together with a synthesis of electron density, shown in Fig. 1, and a difference synthesis, which confirmed the hydrogen positions, shown in Fig. 2.

The amplitudes ($F_o - F_c$) of the reflexions out to $\sin\theta = 0{\cdot}6$, taken as differences between the observed structure factors and those calculated from the heavier atoms alone, were included in the difference Fourier summation. As can be seen in Fig. 2, every hydrogen atom, located at assumed positions, falls very near or on peaks greater than 0·3 e.Å^{-3}. No other positive region in the difference map exceeds 0·2 e.Å^{-3} with the exception of two peaks about 0·5 e.Å^{-3} associated with the chloride ions.

Table 3. *Measured and calculated structure factors multiplied by* 10

H	K	L	FOBS	FCAL
0	0	2	70	-70
0	0	4	1445	-1335
0	0	6	429	396
0	0	8	323	298
0	0	10	137	137
0	0	12	36	-29
0	0	14	189	-206
0	0	16	128	134
0	1	1	144	-150
0	1	2	293	-326
0	1	3	325	381
0	1	4	390	-463
0	1	5	463	488
0	1	6	219	220
0	1	7	56	-56
0	1	8	72	70
0	1	9	237	-222
0	1	10	160	-154
0	1	11	117	120
0	1	12	146	147
0	1	13	164	171
0	1	14	79	-91
0	1	15	65	-56
0	1	16	103	-112
0	2	0	92	-99
0	2	1	167	-197
0	2	2	384	442
0	2	3	144	-166
0	2	4	221	-251
0	2	5	73	87
0	2	6	305	-363
0	2	7	79	88
0	2	8	560	621
0	2	9	85	-93
0	2	10	122	118
0	2	11	126	-115
0	2	12	375	-382
0	2	13	33	-50
0	2	15	33	35
0	2	16	124	119
0	3	1	223	-235
0	3	2	155	-169
0	3	3	296	317
0	3	4	316	354
0	3	5	153	166
0	3	6	210	-236
0	3	7	99	-106
0	3	8	155	-179
0	3	9	94	-106
0	3	10	176	195
0	3	12	122	-129
0	3	13	108	127
0	3	14	61	-69
0	3	15	83	64
0	4	0	436	493
0	4	1	187	-204
0	4	2	155	-166
0	4	3	192	-196
0	4	4	216	-253
0	4	5	83	98
0	4	6	133	168
0	4	7	74	86
0	4	8	27	-32
0	4	9	79	-82
0	4	10	42	39
0	4	11	90	-124
0	4	14	113	-99
0	4	15	49	54
0	5	1	42	-51
0	5	2	406	429
0	5	3	70	-71
0	5	4	201	-220
0	5	5	56	66
0	5	6	90	-105
0	5	8	13	14
0	5	9	54	-43
0	5	10	72	-87
0	5	11	22	28
0	5	12	117	125
0	5	13	9	-32
0	5	14	47	-33
0	6	0	131	-127
0	6	1	45	-45
0	6	2	79	73
0	6	3	122	-143
0	6	4	45	-50
0	6	5	36	53
0	6	6	146	-160
0	6	7	153	199
0	6	8	88	96
0	6	9	101	-117
0	6	10	20	-18
0	6	11	196	-201
0	6	12	33	-37
0	6	13	67	56
0	7	1	70	85
0	7	2	49	-49
0	7	3	106	-116
0	7	4	133	-145
0	7	5	140	-159
0	7	6	131	-145
0	7	8	79	-98
0	7	9	38	32
0	7	10	185	184
0	7	11	49	-45
0	8	0	36	-48
0	8	1	246	-262
0	8	2	113	-111
0	8	3	174	-193
0	8	4	27	45
0	8	5	176	184
0	8	6	74	78
0	8	7	97	103
0	8	8	126	-136
0	8	9	61	-50
0	9	2	144	157
0	9	3	36	-46
0	9	4	31	-38
0	9	5	24	-23
0	9	6	33	-41
0	0	0	135	-144
0	0	1	22	-11
1	0	0	171	194
1	0	2	786	773
-1	0	2	142	-164

H	K	L	FOBS	FCAL
1	0	4	535	-524
-1	0	4	230	234
1	0	6	110	-104
-1	0	6	81	-68
1	0	8	655	645
-1	0	8	499	468
-1	0	10	155	151
1	0	12	192	-186
-1	0	12	395	-393
1	0	14	49	59
-1	0	14	45	-65
-1	0	16	146	149
1	1	0	29	-24
1	1	1	311	317
-1	1	1	103	-92
1	1	2	20	6
-1	1	2	185	-180
1	1	3	339	316
-1	1	3	67	-71
1	1	4	510	474
-1	1	4	682	714
1	1	5	248	236
-1	1	5	402	400
1	1	6	289	-279
-1	1	6	253	-240
1	1	7	31	-24
-1	1	7	155	147
1	1	8	108	-93
-1	1	8	488	-496
1	1	9	149	-147
-1	1	9	176	-169
1	1	10	153	152
-1	1	10	332	315
1	1	11	67	65
1	1	12	101	-107
-1	1	12	58	-77
1	1	13	164	178
-1	1	13	146	145
1	1	14	13	-7
-1	1	14	160	-143
-1	1	15	15	-3
-1	1	16	160	165
-1	1	17	85	-94
1	2	1	185	-181
-1	2	1	752	-888
1	2	2	404	-420
-1	2	2	357	394
1	2	3	404	-342
-1	2	3	253	-252
1	2	4	174	-183
-1	2	4	820	-887
1	2	5	110	86
-1	2	5	422	434
1	2	6	162	150
-1	2	6	162	159
1	2	7	74	74
-1	2	8	216	249
-1	2	9	235	-242
1	2	10	223	192
-1	2	10	33	41
-1	2	11	99	-112
1	2	12	81	-84
1	2	13	31	-32
1	2	14	162	-136
-1	2	14	144	-138
-1	2	15	49	70
-1	2	16	103	100
1	3	0	72	71
1	3	1	336	-379
-1	3	1	113	-95
1	3	2	341	369
-1	3	2	463	503
1	3	3	101	114
-1	3	3	302	341
1	3	4	167	-168
-1	3	4	415	-427
1	3	5	178	193
-1	3	5	158	165
1	3	6	31	-21
-1	3	6	262	-293
1	3	7	47	-54
-1	3	7	68	-120
1	3	8	153	-159
-1	3	8	160	189
-1	3	9	117	-122
-1	3	10	70	-76
-1	3	11	45	61
1	3	12	239	211
-1	3	12	36	39
-1	3	13	88	87
1	3	14	169	-146
-1	3	14	61	-62
-1	3	16	183	-171
1	4	0	115	-108
1	4	1	42	-51
-1	4	1	160	-169
1	4	2	316	306
-1	4	2	99	93
1	4	3	287	-286
-1	4	3	205	-201
1	4	4	262	-272
-1	4	4	27	26
1	4	5	49	82
-1	4	5	58	71
1	4	6	205	-216
-1	4	6	307	-324
1	4	7	309	322
-1	4	7	189	238
1	4	8	363	354
-1	4	8	248	275
1	4	9	103	-122
-1	4	9	155	-189
-1	4	10	119	127
1	4	11	359	-294
-1	4	11	250	-258
1	4	12	174	-175
-1	4	12	262	-274
-1	4	13	81	88
-1	4	14	47	50
-1	4	15	110	98
1	5	0	275	-257
1	5	1	76	-64
-1	5	1	36	-31
1	5	2	205	192
-1	5	2	36	32

H	K	L	FOBS	FCAL
-1	5	3	54	59
1	5	4	282	285
-1	5	4	38	-32
-1	5	5	45	-60
1	5	6	305	-308
-1	5	6	219	-238
-1	5	7	94	-80
1	5	8	45	-57
-1	5	8	126	-142
1	5	9	108	-123
1	5	10	144	139
-1	5	10	248	254
1	5	11	42	-29
1	5	12	65	-70
1	5	13	99	106
-1	5	14	183	-182
1	6	0	257	240
1	6	1	255	-259
-1	6	1	291	-278
1	6	2	124	-126
-1	6	2	196	-211
1	6	3	189	-183
-1	6	3	341	-338
1	6	4	56	-70
-1	6	4	253	-267
1	6	5	131	108
-1	6	5	219	214
-1	6	6	248	257
1	6	7	101	119
-1	6	7	174	186
1	6	8	106	-110
1	6	9	31	-25
-1	6	9	124	-138
1	6	10	56	37
-1	6	10	85	-103
1	6	11	103	-131
-1	6	11	133	-143
-1	6	12	40	42
-1	6	13	29	40
-1	6	14	74	-68
1	7	0	113	106
-1	7	1	47	-47
1	7	2	174	166
-1	7	2	268	263
1	7	3	90	-78
-1	7	3	90	-90
1	7	4	72	-81
-1	7	5	54	61
-1	7	6	142	-147
1	7	8	76	-67
1	7	9	47	-34
-1	7	9	76	-73
-1	7	12	49	53
1	8	0	137	-132
-1	8	1	122	-123
1	8	2	72	77
1	8	3	144	-164
1	8	4	31	-20
-1	8	4	54	57
1	8	5	54	72
-1	8	5	72	85
1	8	6	92	-81
-1	8	6	110	-112
1	8	7	151	135
-1	8	7	74	93
-1	8	9	42	-67
1	8	10	79	-51
-1	9	2	45	-51
1	9	4	61	64
-1	9	4	88	84
1	9	5	81	-74
-1	9	5	110	-114
1	9	6	70	-95
1	9	7	63	14
2	0	0	1091	1082
-2	0	2	22	-11
2	0	4	33	-36
-2	0	4	980	-1044
-2	0	6	546	550
2	0	8	76	77
-2	0	8	427	432
2	0	10	212	230
-2	0	10	196	-192
2	0	12	126	-120
-2	0	12	70	-32
2	0	14	90	-84
-2	0	14	83	-89
-2	0	16	74	104
-2	0	18	79	85
2	1	0	510	602
2	1	1	248	-280
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2	1	3	13	18
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-2	1	7	210	-222
2	1	8	221	-214
-2	1	8	302	291
2	1	9	124	-134
-2	1	9	257	-254
2	1	10	15	21
-2	1	10	65	-56
2	1	11	38	-45
-2	1	11	176	171
2	1	12	187	189
-2	1	12	85	-76
2	1	13	135	139
-2	1	13	155	147
2	1	14	110	-111
-2	1	14	79	76
-2	1	15	94	-59
-2	1	16	149	-159
-2	1	17	81	-94
2	2	0	284	252
2	2	1	160	-166
-2	2	1	167	-207
2	2	2	524	573

H	K	L	FOBS	FCAL
-2	2	2	287	-311
2	2	3	153	-172
-2	2	3	11	-4
2	2	4	551	-544
-2	2	4	42	34
2	2	5	246	261
-2	2	5	72	-64
2	2	6	174	-171
-2	2	6	110	-113
2	2	7	131	126
-2	2	7	97	-107
2	2	8	411	459
-2	2	8	325	373
2	2	9	216	-213
-2	2	9	38	-41
2	2	10	63	61
-2	2	10	124	140
2	2	11	92	-78
-2	2	11	92	-98
2	2	12	110	-103
-2	2	12	454	-449
2	2	13	88	68
-2	2	13	29	-25
2	2	14	56	-49
-2	2	15	67	78
-2	2	16	167	159
2	3	0	131	-148
2	3	1	169	-168
-2	3	1	85	82
2	3	2	262	285
-2	3	2	40	-42
2	3	3	178	161
-2	3	3	216	215
2	3	4	171	201
-2	3	4	131	162
2	3	5	149	174
-2	3	5	221	-206
2	3	6	280	-295
-2	3	6	171	-186
2	3	7	117	-113
-2	3	7	131	-120
2	3	8	51	60
-2	3	8	438	-499
2	3	9	103	-119
-2	3	9	88	101
2	3	10	70	77
-2	3	10	201	229
2	3	11	65	76
-2	3	11	27	21
2	3	12	81	-82
-2	3	12	106	108
2	3	13	88	85
-2	3	13	29	40
-2	3	14	253	-252
-2	3	17	76	-111
2	4	0	329	384
2	4	1	257	-271
-2	4	1	257	-288
2	4	2	235	-254
-2	4	2	203	250
2	4	3	97	-98
-2	4	3	574	-664
2	4	4	20	27
-2	4	4	565	-669
2	4	5	61	46
-2	4	5	133	155
2	4	6	67	-64
-2	4	6	94	83
2	4	7	81	109
-2	4	7	314	362
2	4	8	51	-60
-2	4	8	253	297
2	4	9	20	24
-2	4	9	174	-202
2	4	10	207	187
-2	4	10	65	-74
2	4	11	140	-136
-2	4	11	250	-279
2	4	12	90	-80
-2	4	12	31	-34
-2	4	14	72	-70
-2	4	15	74	59
-2	4	16	31	38
2	5	0	151	151
2	5	1	72	-91
-2	5	1	117	-118
2	5	2	192	202
-2	5	2	273	302
2	5	3	20	-12
-2	5	3	15	-11
2	5	4	85	-104
-2	5	4	149	-149
2	5	5	29	19
-2	5	5	187	193
2	5	6	31	-40
-2	5	6	219	-241
-2	5	7	47	33
2	5	8	61	-64
-2	5	8	106	126
2	5	9	20	-5
-2	5	9	169	-184
2	5	10	106	80
-2	5	10	63	-69
2	5	12	58	60
-2	5	13	99	86
-2	5	15	22	-23
2	6	0	47	-52
2	6	1	63	-88
-2	6	1	174	-204
2	6	2	103	99
-2	6	2	119	-108
2	6	3	226	-251
-2	6	3	131	-118
2	6	4	196	-209
-2	6	4	162	160
2	6	5	103	135
-2	6	5	76	96
2	6	6	18	23
-2	6	6	133	-142
2	6	7	232	220
-2	6	7	110	127
2	6	8	124	127
-2	6	8	49	-52
2	6	9	108	-98
-2	6	9	110	-141

H	K	L	FOBS	FCAL
2	6	10	169	-153
-2	6	10	101	125
2	6	11	167	-146
-2	6	11	178	-154
-2	6	12	70	-70
-2	6	13	81	81
2	7	0	117	-128
2	7	1	22	27
-2	7	1	94	-97
2	7	2	117	134
-2	7	2	11	7
-2	7	3	29	-37
2	7	4	113	135
-2	7	4	18	27
2	7	5	74	-67
2	7	6	169	-176
-2	7	6	76	-82
2	7	7	22	-3
-2	7	7	31	-32
2	7	8	47	-45
-2	7	8	124	-136
2	7	9	27	-41
-2	7	9	22	22
-2	7	10	171	183
-2	7	12	33	42
-2	7	13	18	-9
2	8	0	29	-26
2	8	1	97	-108
-2	8	1	142	-139
2	8	2	146	-156
-2	8	2	45	51
2	8	3	90	-88
-2	8	3	90	-105
2	8	4	61	59
-2	8	4	56	-56
2	8	5	61	46
-2	8	5	162	157
-2	8	6	40	47
2	8	7	58	67
-2	8	7	63	65
-2	8	8	33	-46
-2	8	9	79	-84
-2	8	10	58	-60
-2	8	11	38	-42
2	9	0	31	24
2	9	1	22	19
-2	9	1	45	52
2	9	2	18	30
-2	9	2	169	156
2	9	3	42	-29
-2	9	3	92	-90
-2	9	5	63	-64
-2	9	6	108	-122
-2	9	7	67	78
-2	9	8	51	55
3	0	0	1080	1026
3	0	2	467	413
-3	0	2	377	-374
3	0	4	849	-884
-3	0	4	128	-107
3	0	6	20	34
-3	0	6	97	-83
3	0	8	517	563
-3	0	8	203	171
3	0	10	22	17
-3	0	10	336	320
3	0	12	108	-100
-3	0	12	445	-418
-3	0	14	176	-171
-3	0	16	316	288
-3	0	18	18	-16
3	1	0	404	-358
3	1	1	135	-113
-3	1	1	259	-258
3	1	2	65	-20
-3	1	2	277	-270
3	1	3	241	226
-3	1	3	400	408
3	1	4	117	112
-3	1	4	164	-156
3	1	5	228	208
-3	1	5	327	322
3	1	6	24	16
-3	1	6	33	50
-3	1	7	339	-343
3	1	8	97	109
-3	1	8	339	-331
3	1	9	90	-103
-3	1	9	232	-233
3	1	10	113	-116
-3	1	10	146	136
-3	1	11	192	184
3	1	12	29	-37
-3	1	12	124	121
3	1	13	108	123
-3	1	13	144	134
-3	1	14	257	-238
-3	1	15	113	-110
-3	1	16	65	70
-3	1	17	164	-148
-3	1	18	58	60
3	2	0	343	371
3	2	1	51	65
-3	2	1	239	-236
3	2	2	79	-75
-3	2	2	284	325
3	2	3	167	-162
-3	2	3	160	-151
3	2	4	99	98
-3	2	4	786	-1027
-3	2	5	144	-138
3	2	6	180	-162
-3	2	6	20	-18
3	2	7	133	145
3	2	8	61	60
-3	2	8	646	685
3	2	10	207	227
-3	2	10	146	-144
3	2	11	90	-87
-3	2	11	128	-127
3	2	12	137	-139
-3	2	12	219	-205
-3	2	13	81	-78
-3	2	14	47	-48
-3	2	15	45	51

H	K	L	FOBS	FCAL
-3	2	16	67	58
-3	2	17	24	-22
3	3	0	237	261
3	3	1	253	-284
-3	3	2	137	158
3	3	3	24	46
-3	3	3	70	97
3	3	4	49	45
-3	3	4	160	-143
3	3	5	228	226
-3	3	5	126	129
3	3	6	70	73
-3	3	6	343	-382
3	3	7	36	-39
-3	3	7	115	97
3	3	8	169	-181
-3	3	8	275	280
3	3	9	108	-101
-3	3	9	214	-217
3	3	10	67	59
3	3	11	51	33
-3	3	11	106	-96
3	3	12	83	97
-3	3	12	235	-248
-3	3	13	160	170
-3	3	14	47	44
-3	3	16	67	-66
-3	3	17	113	-99
3	4	0	176	176
3	4	1	15	-39
-3	4	1	216	-248
3	4	2	185	184
-3	4	2	257	-264
3	4	3	149	-150
-3	4	3	106	-82
3	4	4	266	-289
-3	4	4	18	14
3	4	5	74	94
-3	4	5	158	169
-3	4	6	18	21
3	4	7	149	129
-3	4	7	22	-30
3	4	8	94	117
-3	4	8	72	94
3	4	9	24	-15
-3	4	9	268	-293
3	4	10	33	-43
-3	4	10	94	92
3	4	11	94	-79
-3	4	11	128	-120
-3	4	12	226	-251
-3	4	13	164	154
-3	4	14	22	14
-3	4	15	70	60
-3	4	16	183	174
-3	4	17	103	-94
3	5	0	241	-249
-3	5	1	36	-33
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-3	5	6	72	72
-3	5	7	128	-130
-3	5	8	235	-247
3	5	9	45	-59
-3	5	9	85	98
3	5	10	67	67
-3	5	10	45	28
-3	5	11	97	101
-3	5	12	131	148
-3	5	13	45	-46
-3	5	14	219	-197
-3	5	16	38	-33
3	6	0	31	-14
3	6	1	76	-51
-3	6	1	198	-177
3	6	2	70	-78
-3	6	2	108	97
3	6	3	85	-90
-3	6	3	230	-237
3	6	4	38	31
-3	6	4	97	-101
-3	6	5	196	182
3	6	6	103	-97
-3	6	6	38	35
3	6	7	83	105
-3	6	7	176	182
-3	6	8	33	23
3	6	9	49	28
-3	6	9	187	-191
-3	6	10	76	-81
-3	6	11	151	-161
-3	6	12	97	101
-3	6	13	58	65
-3	6	15	79	89
3	7	0	83	83
3	7	1	15	13
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-3	7	2	192	197
3	7	3	122	-109
-3	7	3	61	-53
3	7	4	27	28
3	7	5	74	-91
-3	7	5	36	-49
3	7	6	49	43
-3	7	6	275	-283
3	7	7	36	30
-3	7	7	40	42
3	7	8	72	-104
-3	7	8	85	87
-3	7	10	110	121
-3	7	12	81	-63
-3	7	13	18	17
3	8	0	81	-81
3	8	1	85	-98
-3	8	1	169	-172
3	8	2	38	39
-3	8	2	101	-93
3	8	3	226	-211

Table 3 (*cont.*)

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
-3	8	3	45	-46	-4	4	7	164	156	-5	1	10	198	-192	-5	7	10	153	158	-6	5	5	94	-77	-7	3	17	49	-41
-3	8	4	131	129	4	4	8	99	67	-5	1	11	174	158	-5	7	11	76	-76	-6	5	6	126	-132	-7	3	18	83	86
3	8	5	124	122	-4	4	8	395	356	-5	1	12	235	229	-5	7	12	74	-64	-6	5	7	81	-90	7	4	0	122	141
-3	8	5	67	80	-4	4	9	305	-283	-5	1	13	42	27	-5	7	13	42	23	-6	5	8	85	-84	7	4	1	36	-20
-3	8	6	27	-32	4	4	10	112	96	-5	1	14	20	21	5	8	0	24	14	-6	5	9	72	74	-7	4	1	164	-182
-3	8	7	81	78	-4	4	10	164	-164	-5	1	15	153	-141	-5	8	1	115	-107	-6	5	10	183	203	-7	4	2	65	-56
-3	8	8	90	-86	-4	4	11	164	-167	-5	1	16	183	-162	5	8	2	47	-42	-6	5	12	97	-91	7	4	3	103	-92
-3	8	10	74	73	-4	4	12	99	-90	-5	1	17	119	-108	-5	8	2	51	-39	-6	5	13	31	16	-7	4	3	72	-85
-3	8	11	103	-108	-4	4	13	103	87	-5	1	18	51	44	-5	8	4	45	49	-6	5	14	128	-135	7	4	4	40	-34
3	9	0	74	-73	-4	4	14	90	88	-5	1	19	9	12	-5	8	5	97	103	-6	5	15	58	38	-7	4	4	133	-152
3	9	1	22	34	-4	4	15	76	60	5	2	0	88	76	-5	8	6	59	36	-6	5	16	133	112	-7	4	5	103	119
3	9	2	124	101	-4	4	17	65	-52	5	2	1	115	132	-5	8	7	49	38	6	6	0	47	43	-7	4	6	133	157
-3	9	2	54	49	4	5	1	135	-112	-5	2	1	54	-54	-5	8	8	92	-88	6	6	1	54	-46	-7	4	8	45	29
-3	9	3	38	-46	-4	5	1	65	28	5	2	2	221	230	-5	8	9	85	-85	-6	6	1	180	-166	-7	4	9	90	-108
-3	9	4	24	-21	4	5	2	67	56	-5	2	2	72	-55	-5	8	10	67	73	6	6	2	42	-33	-7	4	10	72	-80
-3	9	5	56	-43	-4	5	2	167	149	-5	2	3	31	-11	-5	8	11	79	-77	-6	6	2	31	-22	-7	4	11	58	-44
-3	9	7	38	30	4	5	3	56	-24	5	2	4	85	-59	6	0	0	36	12	6	6	3	119	-93	-7	4	13	76	87
4	0	2	343	366	-4	5	3	122	111	-5	2	4	305	-378	6	0	2	196	184	-6	6	3	99	-96	-7	4	14	47	-49
-4	0	2	56	-39	4	5	4	219	212	-5	2	5	15	-29	6	0	4	155	-131	-6	6	5	133	135	-7	4	15	115	109
4	0	4	99	102	4	5	5	54	23	5	2	6	216	-211	-6	0	4	196	-181	-6	6	6	106	84	-7	4	16	88	87
-4	0	4	483	-483	4	5	6	81	-52	-5	2	6	27	-37	6	0	6	126	-141	-6	6	7	54	41	-7	4	17	81	-77
4	0	6	296	-310	-4	5	6	420	-404	5	2	7	88	79	-6	0	6	194	-200	-6	6	8	45	-46	7	5	1	38	-43
-4	0	6	174	-150	4	5	8	230	-173	-5	2	7	92	80	6	0	8	235	217	-6	6	9	133	-126	7	5	2	90	98
4	0	6	189	169	-4	5	8	33	24	-5	2	8	375	483	-6	0	8	372	405	-6	6	11	85	-75	-7	5	2	149	174
-4	0	8	553	548	4	5	9	42	-23	-5	2	9	90	-84	-6	0	10	29	-21	-6	6	12	72	57	7	5	3	27	-12
4	0	10	230	196	-4	5	9	81	-61	-5	2	10	183	-174	-6	0	12	442	-439	-6	6	13	115	95	-7	5	4	85	-92
-4	0	10	90	-54	-4	5	10	221	230	-5	2	11	153	-167	-6	0	14	61	50	-6	6	15	101	96	-7	5	5	61	47
-4	0	12	302	-278	-4	5	12	106	-90	-5	2	12	271	-299	-6	0	16	106	86	6	7	0	54	-46	-7	5	6	151	-205
-4	0	14	122	-113	-4	5	13	110	95	-5	2	13	47	44	-6	0	18	74	-67	6	7	1	36	12	-7	5	8	90	84
-4	0	16	36	42	-4	5	14	117	-105	-5	2	14	85	67	6	1	0	38	-27	6	7	2	117	111	-7	5	9	31	-31
-4	0	18	106	107	-4	5	16	65	-53	-5	2	15	101	97	6	1	1	198	-183	-6	7	2	155	150	-7	5	10	88	93
4	1	0	576	493	4	6	0	146	119	-5	2	17	70	-54	-6	1	1	79	-73	-6	7	4	142	-130	-7	5	11	49	33
4	1	1	61	-53	4	6	1	122	-133	-5	2	18	36	28	6	1	2	31	-21	-6	7	6	92	-82	-7	5	13	45	50
-4	1	1	76	-63	-4	6	1	255	-238	5	3	0	167	186	-6	1	2	79	-76	-6	7	8	106	86	-7	5	14	58	-63
4	1	2	38	-21	4	6	2	135	116	5	3	1	137	-117	6	1	3	58	42	-6	7	9	49	29	-7	5	15	36	-37
-4	1	2	248	211	-4	6	2	266	-223	-5	3	1	153	154	-6	1	3	271	245	-6	7	11	56	46	-7	5	16	45	-38
4	1	3	88	84	4	6	3	174	-176	5	3	2	22	17	6	1	4	158	151	-6	7	12	24	19	-7	6	1	113	-143
-4	1	3	115	149	-4	6	3	153	-133	-5	3	2	31	8	-6	1	4	119	116	-6	8	1	49	-51	-7	6	3	33	-11
4	1	4	40	-33	4	6	4	171	-161	5	3	3	101	-92	6	1	5	144	116	-6	8	2	36	44	-7	6	5	128	144
-4	1	4	237	223	4	6	5	164	127	-5	3	3	115	130	-6	1	5	49	46	-6	8	3	47	-31	-7	6	6	79	-87
4	1	5	113	107	-4	6	5	165	167	5	3	4	126	124	-6	1	6	135	-131	-6	8	4	76	64	-7	6	7	58	34
-4	1	5	79	88	4	6	6	33	-19	-5	3	4	196	209	-6	1	7	259	-277	-6	8	5	70	57	-7	6	8	117	132
-4	1	6	481	-475	-4	6	6	67	44	5	3	5	110	90	6	1	8	47	-47	-6	8	6	47	-45	-7	6	9	135	-165
4	1	7	20	26	4	6	7	178	127	-5	3	5	79	-69	-6	1	8	67	-72	-6	8	7	92	85	-7	6	10	70	82
-4	1	7	110	-126	-4	6	7	83	55	5	3	6	63	-39	-6	1	9	146	-146	-6	8	9	85	-78	-7	6	11	65	-70
4	1	8	110	-100	-4	6	8	27	-16	-5	3	6	289	-340	-6	1	10	192	192	7	0	0	194	173	-7	6	12	99	-113
-4	1	8	284	264	-4	6	9	180	-182	-5	3	7	113	-110	-6	1	11	76	79	7	0	2	61	26	-7	6	13	103	125
4	1	9	29	-34	-4	6	10	176	160	-5	3	8	90	-79	-6	1	12	151	-149	-7	0	2	74	-47	-7	6	14	65	57
-4	1	9	113	-102	-4	6	11	158	-119	-5	3	9	108	-100	-6	1	13	59	85	7	0	4	29	-21	-7	7	3	61	63
4	1	10	90	79	-4	6	12	99	-88	-5	3	10	198	225	-6	1	14	85	-81	-7	0	4	343	-313	-7	7	4	49	-47
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-4	1	12	436	-402	-4	6	14	161	-82	-5	3	12	151	-164	-6	1	16	135	113	-7	0	6	47	38	-7	7	6	24	-37
-4	1	13	45	26	-4	6	15	106	92	-5	3	13	128	133	-6	1	17	180	-159	-7	0	8	103	113	-7	7	7	18	-28
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-4	1	15	70	-67	4	7	1	42	39	-5	3	15	92	-87	-6	1	19	15	-7	-7	0	12	113	-121	-7	7	10	85	99
-4	1	16	90	86	-4	7	1	119	-99	-5	3	16	61	51	6	2	0	325	365	-7	0	14	85	-87	-7	7	11	18	20
-4	1	17	85	-89	4	7	2	203	181	-5	3	17	126	-118	6	2	1	29	23	-7	0	16	128	123	-7	7	12	24	-33
-4	1	18	74	-81	-4	7	2	113	95	-5	3	18	38	-22	-6	2	1	65	-51	7	1	0	45	31	8	0	0	56	47
4	2	0	490	508	4	7	3	65	32	5	4	0	275	334	-6	2	2	117	-118	7	1	1	108	-118	8	0	2	94	112
-4	2	1	363	-360	-4	7	4	128	-99	5	4	1	167	-190	6	2	3	61	-28	-7	1	1	24	15	-8	0	2	216	-189
4	2	2	83	64	4	7	5	90	-35	-5	4	1	198	-229	-6	2	3	76	-84	7	1	2	90	81	8	0	4	83	-83
-4	2	2	250	-238	-4	7	5	56	53	5	4	2	40	-37	6	2	4	164	-150	-7	1	2	119	150	-8	0	4	160	-147
4	2	3	298	-249	4	7	6	103	-88	-5	4	2	137	-119	-6	2	4	258	-367	7	1	3	47	-30	-8	0	6	88	73
-4	2	3	101	-91	-4	7	7	88	-63	5	4	3	128	-99	-6	2	5	79	-65	-7	1	3	51	80	-8	0	8	325	255
4	2	4	438	-387	-4	7	9	88	59	-5	4	3	235	-277	-6	2	6	131	159	7	1	4	90	-81	-8	0	10	131	-123
-4	2	4	176	-150	-4	7	10	47	31	5	4	4	192	-199	6	2	7	97	85	-7	1	4	341	-255	-8	0	12	429	-426
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4	2	10	38	18	-4	8	3	67	-49	-5	4	12	51	-54	-6	2	15	47	31	-7	1	12	38	-40	-8	1	3	160	131
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-4	2	11	244	-237	-4	8	5	133	101	-5	4	15	94	87	-6	2	18	54	43	-7	1	15	103	-112	-8	1	6	153	135
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-4	2	14	56	-54	-4	8	9	161	-76	5	5	0	106	-101	6	3	2	142	145	-7	1	18	74	59	-8	1	9	65	-62
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-4	3	2	124	119	-4	9	7	88	75	-5	5	8	24	-26	-6	3	8	192	200	-7	2	4	63	-61	-8	1	18	29	33
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4	3	6	164	-123	5	0	6	36	-30	-5	6	1	174	-170	-6	3	15	153	-144	-7	2	10	85	-50	-9	0	14	74	64
-4	3	6	76	-58	-5	0	6	219	249	5	6	2	42	20	-6	3	16	99	-82	-7	2	11	119	-149	9	1	0	22	25
4	3	7	54	28	5	0	8	81	78	-5	6	2	108	112	-6	3	17	49	-34	-7	2	12	194	-252	9	1	1	113	-110
-4	3	7	144	-141	-5	0	8	76	60	5	6	3	117	-120	-6	3	18	115	111	-7	2	13	108	131	-9	1	3	88	73
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-4	3	8	167	-154	-5	0	10	72	-51	5	6	4	54	45	-6	4	1	237	-267	-7	2	15	90	86	-9	1	7	101	-98
4	3	9	151	-119	-5	0	12	386	-372	-5	6	4	49	38	6	4	2	178	156	-7	2	16	108	99	-9	1	8	99	85
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-4	3	13	124	110	5	1	1	257	-233	-5	6	9	151	-160	-6	4	6	29	14	-7	3	1	18	-27	-9	1	13	65	53
-4	3	14	264	-243	-5	1	1	164	-125	-5	6	11	135	-127	-6	4	8	214	236	7	3	2	85	80	-9	1	14	13	-7
-4	3	15	101	-74	5	1	2	255	246	-5	6	12	74	-50	-6	4	9	230	-237	-7	3	2	29	-32	-9	1	15	72	-68
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-4	4	1	291	-261	5	1	5	210	198	5	7	2	31	27	-6	4	15	79	62	-7	3	6	79	-92	-10	0	12	153	-113
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-4	4	3	284	-257	-5	1	6	38	36	-5	7	3	18	29	6	5	1	54	-68	-7	3	9	94	-103	-10	1	5	81	-64
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4	4	5	38	23	5	1	8	76	82	-5	7	5	33	-24	6	5	3	24	-14	-7	3	13	63	62	-10	1	11	88	75
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4	4	6	174	-132	-5	1	9	131	-136	-5	7	7	74	53	6	5	4	201	158	-7	3	15	70	-66	-10	1	14	56	-40
4	4	7	158	140	5	1	10	24	-37	-5	7	9	42	40	-6	5	4	85	75	-7	3	16	99	91	-10	1	15	110	-103

Discussion of the structure

The most interesting result of this investigation is the molecular conformation found for spermine, which in the crystal structure of the hydrochloride is not zigzag planar, in contrast with that found by Iitaka & Huse (1965) in the crystals of spermine phosphate hexahydrate. In fact, the bonds C(2)–N(1) and C(2′)–N(1′) are in *gauche* conformation and the centrosymmetric molecule is characterized by three approximately planar groupings of atoms. The grouping C(2)N(1)C(3) C(4)C(5)N(2) and that related by the centre of symmetry C(2′)N(1′)C(3′)C(4′)C(5′)N(2′), as well as the grouping N(1)C(2)C(1)C(1′)C(2′)N(1′) form zigzag planar chains.

The equation of the least-squares plane through atoms N(1)C(2)C(1)C(1′)C(2′)N(1′) calculated according to Schomaker, Waser, Marsh & Bergman (1959) with unit weight for all atoms is

$$6{\cdot}3164x+4{\cdot}4195y-0{\cdot}8993z=0$$

where x, y and z are crystallographic coordinates, expressed as fractions of unit-cell edges. The deviations in Å of the individual atoms from the plane are

N(1)	−0·008,	C(2)	0·008,	C(1)	0·015 Å
N(1′)	0·008,	C(2′)	−0·008,	C(1′)	−0·015 Å

Table 4. *Final electron densities* (e.Å^{-3}) *and curvatures* (e.Å^{-5}) *at the atomic positions*

Values in parentheses are from F_c differential synthesis

	ϱ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{hk}	A_{hl}	A_{kl}
C(1)	9·06	76·0	80·9	87·1	1·3	39·1	−0·6
	(9·15)	(76·4)	(80·3)	(86·5)	(−1·5)	(39·4)	(−0·5)
C(2)	7·58	44·0	76·6	68·5	0·0	23·6	−0·5
	(7·89)	(43·9)	(77·2)	(68·2)	(−3·7)	(23·8)	(1·2)
C(3)	9·18	72·9	82·5	85·7	0·0	37·3	−2·7
	(9·29)	(70·7)	(83·6)	(84·5)	(−1·1)	(37·7)	(0·8)
C(4)	9·13	74·3	81·4	88·9	−2·9	40·5	−2·5
	(9·07)	(73·1)	(81·2)	(88·3)	(−3·6)	(40·7)	(0·5)
C(5)	7·99	67·7	67·1	74·1	1·9	28·0	−3·3
	(8·21)	(66·0)	(68·5)	(73·7)	(−0·2)	(28·3)	(1·5)
N(1)	11·77	89·3	101·1	103·6	0·5	44·4	−3·6
	(11·97)	(87·9)	(102·0)	(103·1)	(1·1)	(44·7)	(−4·1)
N(2)	11·20	92·8	88·2	95·1	5·5	45·6	−4·3
	(11·15)	(90·2)	(89·5)	(93·8)	(2·7)	(45·9)	(−2·7)
Cl(1)	37·22	314·2	374·7	398·1	−3·6	163·8	0·3
	(37·56)	(309·6)	(377·7)	(396·0)	(−0·3)	(165·6)	(0·5)
Cl(2)	29·93	219·9	292·7	305·2	17·6	124·2	0·6
	(30·50)	(221·7)	(293·2)	(304·5)	(5·1)	(124·1)	(−2·9)

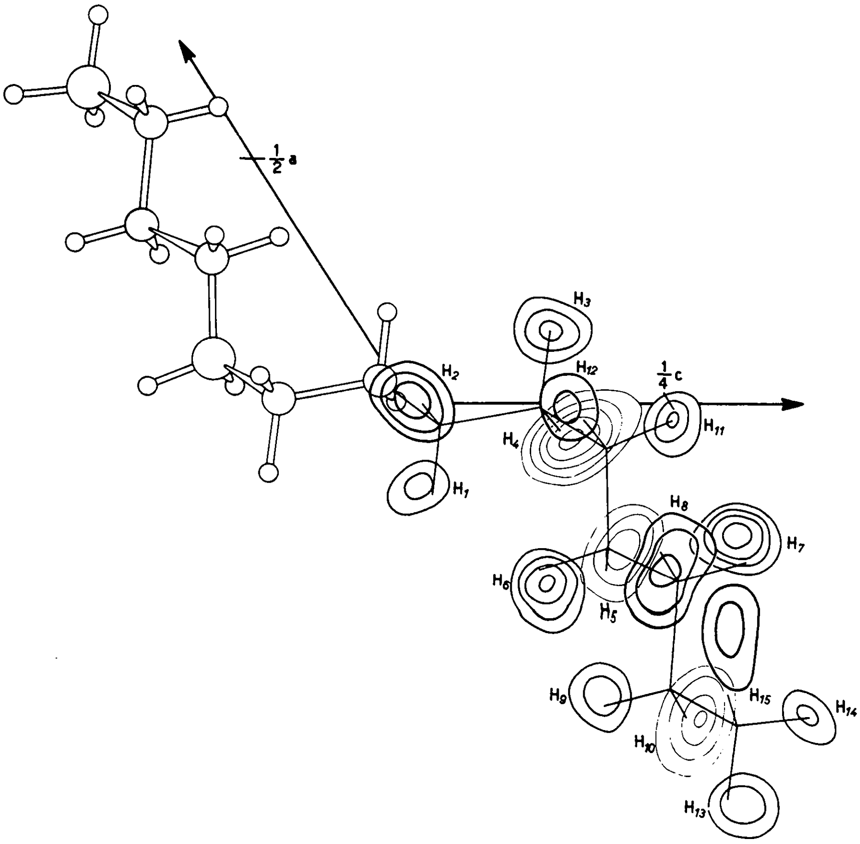

Fig. 2. Composite drawing of the final three-dimensional difference map viewed along **b**. The amplitudes (F_o-F_c) of the reflexions out to $\sin\theta=0{\cdot}6$ were included and taken as the difference between observed structure factors and those calculated from the heavier atoms alone. The hydrogen atoms are located at assumed positions. Contours are at intervals of 0·1 e.Å^{-3}, beginning with the 0·2 e.Å^{-3}.

The least-squares plane of the atoms C(2)N(1)C(3) C(4)C(5)N(2) is

$$3\cdot4226x + 5\cdot4992y - 10\cdot913z = -1\cdot2102$$

and the deviations from it are:

C(2)	0·010,	N(1)	0·035,	C(3)	−0·032 Å
C(4)	−0·056,	C(5)	0·019,	N(2)	0·024 Å

The dihedral angle between these two planes is 62·8°. This value is close to the value of 66·0° of the angle between the planes of the atoms C(1)C(2)N(1) and C(2)N(1)C(3′), which corresponds to the angle of rotation around the bond C(2)–N(1). The angle of rotation about the C(2′)–N(1′) is −66·0°, owing to the operation of the centre of symmetry.

The bond lengths and angles are shown in Fig. 3 and given in Table 5 together with their standard deviations. The C(4)–C(5) bond length is significantly shorter than the other crystallographically distinct C–C single bonds, but it seems difficult to attach any physical meaning to this difference. On the other hand the average value of the C–C bond lengths of $1\cdot52_2$ Å is close to the value of 1·533 Å proposed by Bartell (1959) for normal hydrocarbons and agrees well with the accurate average value of 1·524 Å of the C–C single bonds, found by Wright & Marsh (1962) in the aliphatic carbon chain of lysine. The three C–N bond lengths are equal within experimental error. The average value of $1\cdot49_6$ Å is longer than the normal C–N single bond length and agrees well with the value deduced by Hahn (1957) for the $\mathrm{C{-}\overset{+}{N}H_3}$ single bond from a review of the data reported in α-amino-acids, peptides and salts of aliphatic amines. This result suggests that there is no significant difference in the bond lengths between carbon and tetrahedral nitrogen atoms of either protonated amino or imino groups.

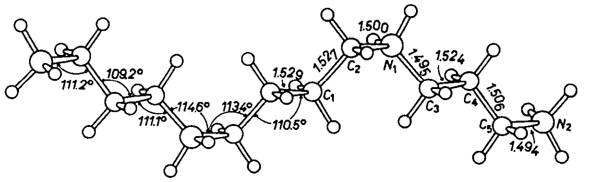

Fig. 3. Bond lengths and angles in a protonated spermine molecule.

The bond angles at C(1), C(4) and C(5) with an average value of 110·3° are close to the tetrahedral value, while the C(1)–C(2)–N(1) and C(2)–N(1)–C(3) bond angles, equal to 113·4° and 114·6° respectively, are appreciably larger. The widening of these angles is not surprising in view of the steric effect due to the *gauche* conformation of the C(2)–N(1) bond.

A drawing of the structure viewed along (010) is shown in Fig. 4. The short approaches, found between the charged quaternary nitrogen atoms and the chloride ions, indicate that the crystal packing is dominated by hydrogen bonds formed between nitrogen as donor and chlorine as acceptor atoms. The shortest N ··· Cl distances are listed in Table 6 together with the C–N ··· Cl angles. All the other distances between non-bonded atoms are greater than the normal van der Waals values.

N(1) has two short intermolecular distances, one to Cl(1) of $3\cdot14_5$ Å and the other one to $\mathrm{Cl_I}(1)$ of $3\cdot17_8$ Å. The angles between the C(2)–N(1) and N(1)–C(3) bonds and the N(1) ··· Cl(1) and N(1) ··· $\mathrm{Cl_I}(1)$ lines are close to the tetrahedral angle. This situation indicates hydrogen bond formation between the charged imino group and two chloride ions.

N(2) has four $\mathrm{Cl^-}$ neighbors, namely Cl(2) at $3\cdot14_6$ Å, $\mathrm{Cl_I}(2)$ at $3\cdot13_0$ Å, $\mathrm{Cl_I}(1)$ at $3\cdot30_2$ Å and $\mathrm{Cl_{II}}(1)$ at $3\cdot28_7$ Å.

Donohue (1952) pointed out that an arrangement of four chloride ions at short distances from an $\mathrm{\overset{+}{N}H_3}$ is rather common in chloride salts of organic bases. From a review of the structures reported up to that time, he

Table 5. *Bond lengths and angles and their standard deviations*

Bond	l	σ_l	Angle	α	σ_α
C(1′)–C(1)	$1\cdot52_9$ Å	0·012 Å	C(1′)–C(1)–C(2)	110·5°	0·5°
C(1) –C(2)	$1\cdot52_7$	0·010	C(1) –C(2)–N(1)	113·4	0·6
C(2) –N(1)	$1\cdot50_0$	0·010	C(2) –N(1)–C(3)	114·6	0·5
N(1)–C(3)	$1\cdot49_5$	0·008	N(1)–C(3)–C(4)	111·1	0·5
C(3) –C(4)	$1\cdot52_4$	0·009	C(3) –C(4)–C(5)	109·2	0·5
C(4) –C(5)	$1\cdot50_6$	0·009	C(4) –C(5)–N(2)	111·2	0·5
C(5) –N(2)	$1\cdot49_4$	0·009			

Table 6. N ··· Cl *distances and* C–N ··· Cl *angles*

The atomic coordinates are derived from the values of Table 1 by the given relations

Distance	d	Angle	θ
N(1)(x, y, z) ····· Cl(1)(x, y, z)	$3\cdot14_5$ Å	C(2) –N(1) ···· Cl(1)	105·6°
N(1) ··········· $\mathrm{Cl_I}(1)(\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z)$	$3\cdot17_8$	C(3) –N(1) ··· Cl(1)	102·7
N(2′)($1+x, y, z$) ·· Cl(2)(x, y, z)	$3\cdot14_6$	C(2) –N(1) ··· $\mathrm{Cl_I}(1)$	112·3
N(2′) ·········· $\mathrm{Cl_I}(2)(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$	$3\cdot13_0$	C(3) –N(1) ··· $\mathrm{Cl_I}(1)$	99·9
N(2′) ·········· $\mathrm{Cl_I}(1)$	$3\cdot30_2$	C(5′)–N(2′) ··· Cl(2)	104·0
N(2′) ·········· $\mathrm{Cl_{II}}(1)(x, \frac{1}{2}-y, -\frac{1}{2}+z)$	$3\cdot28_7$	C(5′)–N(2′) ··· $\mathrm{Cl_I}(2)$	109·0
		C(5′)–N(2′) ··· $\mathrm{Cl_I}(1)$	143·9
		C(5′)–N(2′) ··· $\mathrm{Cl_{II}}(1)$	86·0

argued that three N · · · Cl distances may be considered hydrogen bonds and that the fourth N · · · Cl contact, found approximately directed along the C–N bond, may be due to packing requirements. However, in spermine tetrahydrochloride the $\overset{+}{N}H_3 \cdots Cl^-$ interactions can be considered equal in pairs. The N(2′) · · · Cl(2) and N(2′) · · · $Cl_I(2)$ lengths are appreciably shorter than the N(2′) · · · $Cl_I(1)$ and N(2′) · · · $Cl_{II}(1)$ lengths. The C(5′)–N(2′) · · · Cl(2) and C(5′)–N(2′) · · · $Cl_I(2)$ angles are 104·0° and 109·0° respectively while the C(5′)–N(2′) · · · $Cl_I(1)$ and C(5′)–N(2′) · · · $Cl_{II}(1)$, equal to 143·9° and 86·0° respectively, are significantly different from the tetrahedral value. This arrangement of the Cl^- ions around the protonated amino group in addition to the positions of the peaks due to the hydrogen atoms in the Fourier difference map indicates the formation of only two normal hydrogen bonds. The other two weaker $\overset{+}{N}H_3 \cdots Cl^-$ interactions are likely to be due to bifurcated hydrogen bond formation (Fuller, 1959). A similar situation was found in L-lysine monohydrochloride dihydrate (Wright & Marsh, 1962) and in diglycine hydrochloride (Hahn & Buerger, 1957), with the exception that the four acceptor atoms around the $\overset{+}{N}H_3$ group are in these cases oxygen and chlorine atoms.

The large size of the chloride ions may be an important factor, which contributes to the formation of this arrangement. In this connection it is interesting to note that the two chloride ions, which have the shortest Cl · · · Cl distances in spermine tetrahydrochloride and in diglycine hydrochloride, equal to $3{\cdot}82_4$ Å and to 4·09 Å respectively, are those involved in the bifurcated hydrogen bonds.

In view of the different conformation of the charged molecular chains in spermine tetrahydrochloride and in spermine phosphate hexahydrate (Iitaka & Huse, 1965) it appears particularly interesting to compare the crystal structures of the two salts. In spermine phosphate hexahydrate O · · · O hydrogen bonds hold together water molecules and monohydrogen phosphate ions in parallel sheets alternate with sheets of charged spermine molecules, which assume a zigzag planar conformation. All ten protons of the nitrogen atoms participate in a network of N–H · · · O hydrogen bonds formed between the two kinds of sheets. From these structural features it appears that the strongest O · · · O hydrogen bonds are probably dominant in determining the crystal packing.

Consequently, the charged molecular chains are arranged to satisfy the most favorable conditions for N–H · · · O hydrogen bond formation.

In spermine tetrahydrochloride the strongest interactions occur between charged imino and amino groups and chloride ions. Therefore it seems likely that these interactions, together with the large size of the chloride ions, determine the crystal packing. In any case it may be inferred that at variance with the C–C bonds of linear paraffins the *gauche* states of C–N bonds are energetically much closer to the *trans* states, thus allowing the spermine molecule to take up either a *trans* planar (Iitaka & Huse, 1965) or a skewed conformation according to the crystal forces. A similar conclusion may be drawn for spermidine although only the crystal structure of the hydrochloride has been investigated

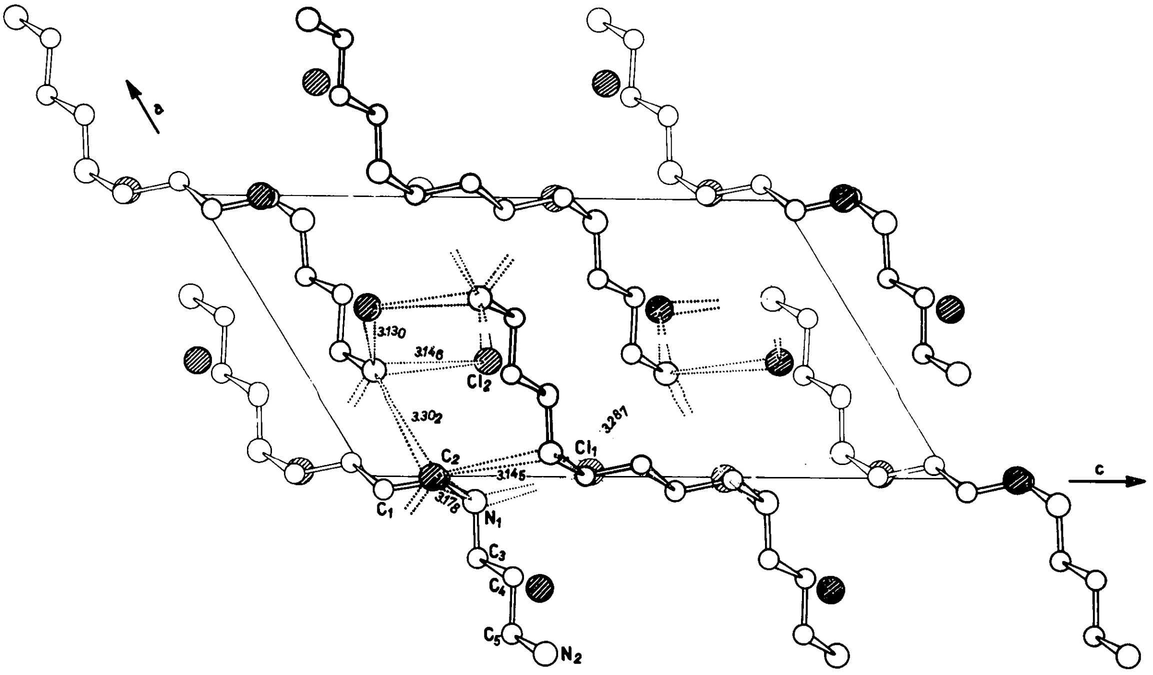

Fig. 4. Projection of the structure on the (010) plane. The shortest contacts between nitrogen and chlorine atoms are shown.

and its molecular conformation is transplanar (Damiani, Giglio, Puliti & Ripamonti, 1965). Both spermine and spermidine interact with deoxyribonucleic acid (DNA) in solution, as inferred by the increased helix coil transition temperature of the macromolecule and by the electrochemical behaviour (Liquori and coworkers, to be published).

Such a strong affinity may be readily explained if a skewed conformation is assumed which allows a stereospecific interaction leading to a cross linking of the DNA strands in the narrow groove of the double helix.

Model studies indicate that a conversion from the *B* structure to the *A* structure is likely to be thus induced. These considerations which will be developed in more detail elsewhere appear to support a stereochemical model for the ribonucleic acid synthesis on a DNA template, proposed by one of us (Liquori, to be published), which appears to be accelerated in the presence of spermine and spermidine (Weiss & Fox, 1964).

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The Crystal Structure of Tutton's Salts. III. Copper Ammonium Sulfate Hexahydrate

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The crystal structure of copper ammonium sulfate hexahydrate, $Cu(NH_4)_2(SO_4)_2 . 6H_2O$, has been determined by a three-dimensional X-ray analysis, using Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). The crystals are monoclinic, space group $P2_1/a$, 2 molecules per cell. The cell dimensions are:

$$a = 9{\cdot}27, \quad b = 12{\cdot}44, \quad c = 6{\cdot}30 \text{ Å}, \quad \beta = 106{\cdot}1°.$$

The water molecules are arranged about the copper ion in an octahedron which shows orthorhombic distortion, the three metal–oxygen bond distances being 2·22, 2·10, and 1·96 Å.

Introduction

In a continuing study (Montgomery & Lingafelter, 1964*b*) of the structures of an isomorphous series of hydrated double sulfates (Tutton's salts), one of the primary points of interest was the behavior of the copper(II) ion. In general, this ion exhibits a 4+2 arrangement of ligands when there are six present, and it was expected that the copper salt would show a coordination configuration of the water molecules about the central ion which would differ from the general pattern of the rest of the series. In support of this expectation, it was noted that the angle β for the copper salt is about one degree less than the average for the series. This salt was, therefore, one of the first to be examined when the general structure of the Tutton's salts had been established.

Experimental

The procedure followed was essentially that for the isomorphous zinc salt (Montgomery & Lingafelter, 1964*a*) except that the crystal needle was ground to approximate a cylinder (along **c**) ($\mu = 59{\cdot}16$ cm^{-1}, $\mu R = 0{\cdot}31$). The cell dimensions (calibrated with $a_0 = 5{\cdot}6387$ Å for NaCl) were found to be: $a = 9{\cdot}267 \pm 0{\cdot}02$, $b = 12{\cdot}445 \pm 0{\cdot}015$, $c = 6{\cdot}298 \pm 0{\cdot}005$ Å, $\beta = 106°9' \pm 6'$. Systematic absences, $h0l$ when h is odd, $0k0$ when k is odd – space group $P2_1/a$, $Z = 2$.