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The Structure of Dodecahydro-1,4,7,9b-Tetraazaphenalene Trihydrochloride Hemihydrate, $C_9H_{18}N_4 . 3HCl . \frac{1}{2}H_2O$

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The molecular structure of an organic compound of composition $C_9H_{18}N_4$ was established by a crystal structure determination of an orthorhombic HCl derivative, $C_9H_{18}N_4 . 3HCl . \frac{1}{2}H_2O$. The space group is $Pna2_1$ with $a = 19{\cdot}2_1$, $b = 11{\cdot}2_0$, $c = 6{\cdot}91_7$ Å (Cu $K\alpha$ $\lambda = 1{\cdot}5418$ Å). There are four molecules per unit cell. Determination of the unit cells and space groups of the $C_9H_{18}N_4$ compound and of a hexagonal HCl derivative eliminated most of the structures initially proposed.

The approximate structure of the orthorhombic HCl derivative was obtained by analysis of a three-dimensional sharpened Patterson function. Refinement of the positional parameters of the 17 heavier atoms was carried out by the method of least squares with individual isotropic temperature factors. The final R index for the 1144 observed reflections of non-zero weight is 0·093, and the estimated limits of error are 0·014–0·019 Å in bond distances involving C, N, and Cl, and 0·9–1·1° in bond angles.

The $C_9H_{18}N_4$ molecule can be described as a symmetrical puckered ring structure consisting of three fused piperimidine rings with one of the N atoms in the central pyramidal position. The molecule possesses non-crystallographic threefold symmetry.

Introduction

During an investigation of the reaction of acrolein with ammonia, a white crystalline solid of unknown structure and of composition $C_9H_{18}N_4$ was prepared in these laboratories (Van Winkle, McClure & Williams, 1964), and a number of possible structures for the ammonia–acrolein reaction product were proposed. Attempts to establish the structure of this material by infrared and nuclear magnetic resonance studies had been unsuccessful. An X-ray investigation of the structure of this material was therefore undertaken.

Preliminary results

When the X-ray work was first initiated very little was known about the chemistry of the $C_9H_{18}N_4$ compound and no derivatives containing heavy atoms were available. Single crystals of $C_9H_{18}N_4$ were therefore grown and X-ray precession patterns taken. Because of their hygroscopic nature, it was necessary to grow the single crystals in thin walled glass capillaries by sublimation under high vacuum. Most of these crystals were trigonal plates.

The precession data showed that the $C_9H_{18}N_4$ compound is cubic with $a_0 = 10{\cdot}1_6$ Å (Cu $K\alpha$ $\lambda = 1{\cdot}5418$ Å). Since the crystals were very hygroscopic, accurate density measurements were difficult; approximate measurements showed that the density was between 1·1 and 1·3 g.cm^{-3}. Measurements of the liquid (Van Winkle, McClure & Williams) gave $d = 1{\cdot}05$ g.cm^{-3} at ~ 120 °C. The X-ray data gave $d = 0{\cdot}288(n)$ where n is the number of molecules per unit cell. The only value of n that will give a density in the observed range is 4. There were no systematic extinctions; the unit cell is therefore primitive and the probable space group $P23$ (T^1) or $P\bar{4}3m$ (T_d^1). In either space group, the molecules must lie along the threefold axis, limiting the proposed structures to the cage structure [Fig. 1(*a*)] and the puckered arrangements [Fig. 1(*b*) & (*c*)]. The latter were subsequently proposed by organic chemists to meet the requirements of a threefold axis.

The marked decline in intensity with scattering angle indicated that the molecules in the crystal possessed large temperature factors or that disorder was present. The ease of sublimation of the crystal also suggested large thermal motion. Because of the absence of heavy atoms, the uncertainty of the configuration, and the large thermal motion or disorder, no further work was carried out on this material.

Hydrogen chloride was found to form a crystalline derivative with $C_9H_{18}N_4$. Crystals were grown slowly from a solution of $C_9H_{18}N_4$ and dilute aqueous hydrochloric acid in methyl alcohol. The initial crystalline modification obtained was a disordered hexagonal form. Although the unit cell can be described in terms of a pseudo-cell with $a = 11{\cdot}2_3$, $c = 6{\cdot}97_6$ Å (Cu $K\alpha$ $\lambda = 1{\cdot}5418$ Å) with two molecules of $C_9H_{18}N_4 . 3HCl$ plus an unknown number of H_2O molecules per unit cell, faint reflections indicate that the true unit cell is quadrupled with $a = 22{\cdot}4_5$, $c = 6{\cdot}97_6$ Å. Approximate density measurements showed the density to be between 1·2 and 1·4 g.cm^{-3} in agreement with that calculated for two molecules per pseudo-unit cell ($1{\cdot}29_9$ g.cm^{-3}). This material was not suitable for complete structure determination because of the disorder; however, packing considerations, based on the shortness of the c axis and the systematic absence of reflections of the type $hh\bar{2h}l$ with $l = 2n+1$, enabled the cage form to be eliminated as a possible configuration.

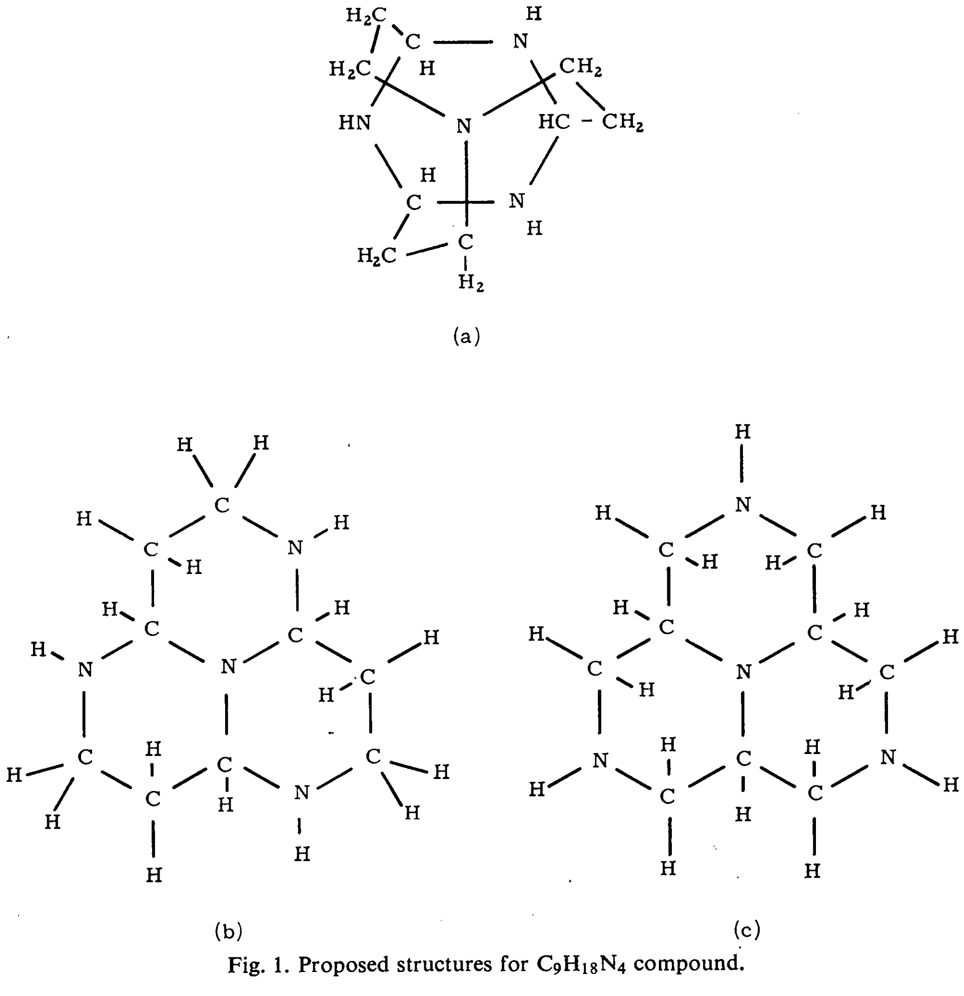
It is unlikely that the disordered hexagonal form resulted from twinning of the orthorhombic form which was subsequently prepared and used for the structure determination, since the $a_{\text{orth}}/b_{\text{orth}}$ ratio differed from the value $\sqrt{3}$ by ~ 1%. In addition the hexagonal form was far more hygroscopic than the orthorhombic form.

The elimination of the cage structure made it possible to proceed with chemical methods for the establishment of the structure (Van Winkle, McClure & Williams). The puckered ring configuration [Fig. 1(*b*)] was confirmed by J. D. McClure and J. L. Van Winkle during the period when the more detailed structure determination was being carried out.

It was called to the author's attention by the referee that the work of Delépine (1943) on the reaction product of crotonaldehyde and ammonia ($C_{12}H_{24}N_4$) would also indicate that the puckered configuration of Fig. 1(*b*) was the most probable structure for $C_9H_{18}N_4$.

Experimental

An orthorhombic modification of $C_9H_{18}N_4 . 3HCl$ which was free of disorder was prepared. The crystals were grown slowly from a solution of $C_9H_{18}N_4$ and concentrated hydrochloric acid in methyl alcohol. Three-dimensional intensity data for Cu *Kα* and Mo *Kα* radiation were collected using the multiple-film equiinclination Weissenberg technique. The crystals were sealed in thin-walled glass capillaries. Ni filtered copper *Kα* radiation was used for layers 0 to 5 about the *c* axis and zirconium-filtered Mo *Kα* for the layers 6 to 9. Precession data for the [*hk*0], [*h*0*l*], and [0*kl*] zones were also taken with Mo *Kα* radiation; they were used to place all the reflections on a single scale. The intensities were estimated visually with calibrated intensity strips taken with the same crystals. The crystals used in this work were rectangular needles elongated along the *c* axis and 0·27 and 0·31 mm in cross-section. Since the linear absorption coefficient for copper radiation for this salt is ~ 53 cm^{-1}, approximate absorption corrections were applied to the data taken with copper radiation. The absorption corrections were calculated on the assumption that the crystal was a cylindrical rod. The absorption factor as a function of sinθ was represented by an empirical equation involving two empirical constants which were evaluated for each zone. The absorption corrections were computed


(a)

(b) (c)

Fig. 1. Proposed structures for $C_9H_{18}N_4$ compound.

and at the same time the Lorentz and polarization corrections were applied with a Bendix G 15 computer.

The unit-cell dimensions for the orthorhombic modification of $C_9H_{18}N_4 . 3HCl$ were $a=19{\cdot}2_1$, $b=11{\cdot}2_0$, $c=6{\cdot}91_7$ Å (Cu $K\alpha$ $\lambda=1{\cdot}5418$ Å). The systematic absence of reflections $0kl$ with $k+l=2n+1$ and $h0l$ with $h=2n+1$ establishes the space group as $Pna2_1$ or $Pnam$. Comparison of the calculated density $0{\cdot}325(n)$ g.cm^{-3} with rough density measurements ($\varrho_M=1{\cdot}2$–$1{\cdot}4$ g.cm^{-3}) show there are four molecules per unit cell, requiring them to be in special positions $4(c)$, and hence planar, in space group $Pnam$. This seemed very unlikely and the space group was therefore assumed to be $Pna2_1$.

Determination of the structure

The observed intensities were placed on an approximate absolute scale by Wilson's (1942) method and a three-dimensional sharpened Patterson map was computed from the entire data (1226 terms). A sharpening function of the type

$$M(s)=\frac{(Zi)^2}{f_i^2}\exp\left\{-\left[\frac{\pi^2}{p}\left(\frac{2\sin\theta}{\lambda}\right)^2\right]\right\}$$

(Lipson & Cochran, 1953), with $p\simeq7{\cdot}25$, was used. The arrangement of the chlorine atoms in the unit cell was determined from the interpretation of the Patterson sections $P(uv0)$ and $P(uv\frac{1}{2})$. The symmetrical array of peaks near the origin of $P(uv0)$ (Fig. 2) were interpreted as C–N intramolecular vector interactions (Beevers & Ehrlich, 1959) and led to two possible orientations of the $C_9H_{18}N_4$ molecule which, in conjunction with the arrangement of Cl^- ions determined from the Patterson map, resulted in two trial structures. Structure factors and $(hk0)$ electron-density projections for both trial structures were computed. Although there was considerable overlap in the projection, the main features of the $C_9H_{18}N_4$ molecule were apparent for one of the trial structures. A second two-dimensional $(hk0)$ electron-density projection was computed with adjusted parameters for the C, N, and Cl atoms. The R index for the subsequent structure factors dropped from 0·45 to 0·30 where $R=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$. Structure factors, and a three dimensional Fourier synthesis were then calculated with the x and y parameters from the $(hk0)$ electron-density projection and estimated z parameters calculated from one of several possible puckered configurations. The R index for the complete data dropped from 0·28 to 0·22.

The refinement

Since the structure was now essentially determined, refinement was carried out by a series of least-squares calculations on an IBM 7090 computer using the Busing–Levy (1959*a*) program with a compatibility package. Atomic form factors of McWeeny (1951) for C, N, O, and H, and Dawson's (1960) values for Cl^- were used. In the initial least-squares computations, neither the oxygen, the presence of which was unsuspected, nor the hydrogen atoms were included. Individual isotropic temperature factors, which were adjusted during the least-squares refinement, were used. The scale factors for the various n-level data were also adjusted during the least-squares refinement. The function $\Sigma w(|F_o|-S|F_c|)^2$ was minimized, where S is a scale factor. A weighting scheme similar to that suggested by Hughes (1941) was used. The higher levels were given lower weights since these data were believed to be somewhat less accurate.

After seven cycles of least squares the R index dropped to 0·135 but was not appreciably reduced upon the addition of hydrogen atoms or upon further cycles. An $(hk0)$ electron-density projection was therefore computed to see if any additional atoms were present in the crystals. The projection clearly showed the presence of an atom at $x=0{\cdot}52$, $y=0{\cdot}29$ and equivalent positions, which was assumed to be the oxygen of a water molecule. A three-dimensional Fourier synthesis was then calculated to get the z parameter of the oxygen; it indicated that the oxygen positions were not always occupied. Structure factor calculations also suggested that the H_2O molecule was only present in approximately one half of the positions. Additional evidence that the H_2O positions were only statistically occupied approximately one half of the time followed from least-squares calculations. The temperature factor for the oxygen atom increased from an assumed value of $B=4{\cdot}0$ to $B\simeq15{\cdot}0$ Å^2 if one H_2O molecule were present, while B only increased to the more reasonable value of 5·8 Å^2 for $\frac{1}{2}H_2O$. One half of an oxygen atom was therefore added in all subsequent calculations. The oxygen positional parameters and isotropic temperature factors were adjusted during the least-squares calculations but no further attempt was made to adjust the fractional weight of the oxygen atom. Other similar hydrate structures containing fractional or variable water content have been reported (Hughes & Yakel, 1961; Gerdil & Marsh, 1960; Marsh & Glusker, 1961; Gerdil, 1961).

Definite maxima at, or close to, the positions assumed for 18 of the hydrogen atoms appeared in the

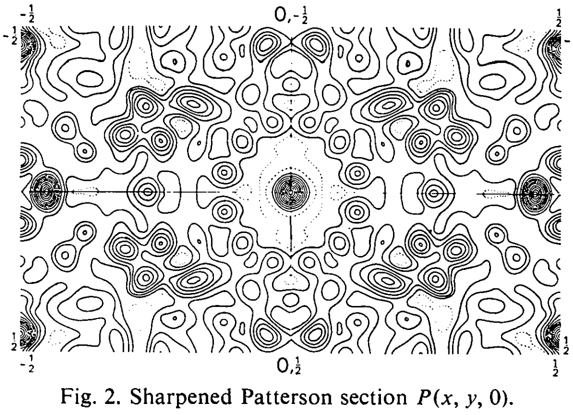


Fig. 2. Sharpened Patterson section $P(x, y, 0)$.

Table 1. *Observed and calculated structure factors*

The six columns within each group contain the values of h, k, 10 F_o, 10$|F_c|$, 10 A_c and 10 B_c. Unobserved structure factors are listed as 10 F_o=0 and have threshold values of 10 F_o ranging from ~30–45 for $hk0-hk2$ and from ~35–50 for $hk3-hk9$. Reflections marked with a prime (′) were given zero weight in the least-squares calculations.

HK0

		6320	6320	6320
2	0	519	560	-560
4	0	547	556	-556
6	0	304	252	-252
8	0	612	606	-606
10	0	229	274	274
12	0	321	312	-312
14	0	76	53	53
16	0	435	477	477
18	0	105	132	-132
20	0	189	168	-168
22	0	158	145	-145
24	0	50	33	33
26	0	65′	90	90
0	2	393	452	452
0	4	868	929	929
0	6	344	347	347
0	8	292	246	-246
0	10	186′	129	129
0	12	202	208	-208
0	14	53	44	-44
1	1	83′	69	-69
1	2	229	186	-186
1	3	336	329	-329
1	4	723	701	701
1	5	203	173	173
1	6	357	325	-325
1	7	45	56	-56
1	8	143	129	129
1	9	0	7	7
1	10	67	70	70
1	11	44′	62	62
1	12	0	7	-7
1	13	0	10	10
1	14	0	24	24
1	15	61	65	65
2	1	547	546	546
2	2	742	779	779
2	3	1014	992	992
2	4	349	299	299
2	5	767	778	778
2	6	375	342	-342
2	7	216	225	225
2	8	0	43	-43
2	9	435	447	447
2	10	92	83	-83
2	11	0	25	25
2	12	0	2	2
3	1	414	422	-422
3	2	51	36	36
3	3	57	62	-62
3	4	265	276	-276
3	5	101′	64	-64
3	6	190	153	153
3	7	0	11	-11
3	8	154	146	146
3	9	147	115	115
3	10	53	68	-68
3	11	0	6	6
3	12	0	44	44
3	13	119	117	117
4	1	969	1017	1017
4	2	1066	1038	1038
4	3	91	103	103
4	4	730	701	-701
4	5	392	437	437
4	6	86	76	-76
4	7	450	432	432
4	8	137	140	-140
4	9	423	389	-389
4	10	139	125	125
4	11	234	235	235
4	12	0	9	9
4	13	54	37	-37
5	1	93	84	84
5	2	391	337	-337
5	3	708	745	-745
5	4	400	381	-381
5	5	328	292	292
5	6	295	312	-312
5	7	299	320	-320
5	8	381	396	-396
5	9	115	64	64
5	10	74	105	-105
5	11	77	55	55
5	12	0	54	-54
5	13	81	77	-77
6	1	391	417	-417
6	2	851	855	-855
6	3	514	518	518
6	4	144	122	122
6	5	188	177	-177
6	6	81	96	96
6	7	301	263	-263
6	8	0	63	63
6	9	101	103	103
6	10	0	4	4
6	11	167	155	-155
6	12	54	37	37
7	1	887	957	957
7	2	274	268	-268
7	3	586	583	583
7	4	347	282	-282
7	5	41	72	72
7	6	318	316	-316
7	7	61	80	80
7	8	99	117	-117
7	9	109	82	-82
7	10	155	186	-186
7	11	156	164	-164
7	12	127	128	-128
7	13	68	71	-71
8	1	257	273	273
8	2	504	495	495
8	3	254	263	-263
8	4	172	156	156
8	5	0	44	-44
8	6	56	52	52
8	7	0	51	-51
8	8	297	269	269
8	9	107	119	-119
8	10	0	29	-29
8	11	62	35	-35
8	12	99	86	86
9	1	410	371	371
9	2	676	685	685
9	3	395	398	398
9	4	209	198	198
9	5	164	183	183
9	6	508	489	489
9	7	80	64	-64
9	8	122	121	121
9	9	66	42	-42
9	10	133	145	145
9	11	44	45	-45
9	12	125	142	142
10	1	190	178	-178
10	2	211	222	-222
10	3	109	100	-100
10	4	159	157	157
10	5	43	40	-40
10	6	367	358	358
10	7	65	58	58
10	8	99	104	-104
10	9	0	32	-32
10	10	139	118	118
10	11	75	51	51
10	12	68	74	-74
11	1	379	343	-343
11	2	73	46	46
11	3	266	286	-286
11	4	425	447	447
11	5	136	108	-108
11	6	370	373	373
11	7	73	78	78
11	8	159	177	177
11	9	41	39	39
11	10	133	148	148
12	1	304	307	-307
12	2	181	187	-187
12	3	61	18	-18
12	4	160	185	-185
12	5	282	241	-241
12	6	235	244	-244
12	7	0	22	-22
12	8	103	87	87
12	9	113	130	130
12	10	46	63	-63
13	1	423	439	-439
13	2	140	129	129
13	3	59	50	-50
13	4	64	45	-45
13	5	219	206	-206
13	6	227	217	-217
13	7	158	205	205
13	8	46	60	60
13	9	0	9	-9
14	1	142	171	171
14	2	136	141	141
14	3	418	417	-417
14	4	0	22	22
14	5	129	127	-127
14	6	65	72	-72
14	7	133	120	-120
14	8	76	84	-84
14	9	132	158	-158
14	10	130	114	-114
15	1	148	138	-138
15	2	277	283	-283
15	3	45	25	25
15	4	125	160	-160
15	5	46	36	36
15	6	110	98	-98
15	7	0	55	-55
15	8	104	109	-109
15	9	45	49	49
15	10	85	93	-93
16	1	52	54	-54
16	2	430	432	432
16	3	125	124	124
16	4	114	111	111
16	5	79	70	70
16	6	0	78	78
16	7	77	56	56
16	8	0	29	-29
16	9	80	70	70
16	10	0	34	34
17	1	139	158	158
17	2	42	76	-76
17	3	0	42	-42
17	4	0	35	-35
17	5	66	53	53
17	6	123	148	-148
17	7	46	36	36
18	1	0	34	-34
18	2	124	144	144
18	3	286	292	292
18	4	0	28	-28
18	5	167	174	174
18	6	0	17	-17
18	7	160	149	149
18	8	73	76	76
18	9	106	113	113
19	1	0	24	-24
19	2	0	10	-10
19	3	113	130	130
19	4	46	33	-33
19	5	65	87	-87
20	1	82	99	99
20	2	220	228	-228
20	3	0	28	28
20	4	93	97	-97
20	5	56	47	47
20	6	92	83	-83
21	4	62′	30	-30
21	5	72	27	-27
22	1	114	129	-129
22	2	120	109	-109
22	3	0	3	3
22	4	51	60	-60
22	5	0	38	-38
23	1	128	131	131

HK1

2	0	712	828	-228	-796
4	0	568	713	-24	713
6	0	548	681	-20	-680
8	0	429	478	-172	-446
10	0	261	251	-36	249
12	0	398	448	-64	-443
14	0	81	61	44	43
16	0	67	40	-36	18
18	0	220	173	-18	172
20	0	154	143	2	143
22	0	113	127	-5	-127
24	0	81	49	37	-32
0	1	863	979	187	961
0	3	180	123	122	16
0	5	457	515	97	-506
0	7	501	557	10	-557
0	9	176	225	-9	-225
0	11	258	260	18	-259
1	1	168′	93	56	75
1	2	85	70	-47	52
1	3	578	614	-1	614
1	4	469	499	-64	495
1	5	136	125	102	73
1	6	87	59	59	
1	7	370	353	15	353
1	8	210	187	39	183
1	9	0	62	-	62
1	10	73	71	-1	-71
1	11	0	48	21	44
1	12	83	87	1	-87
1	13	148	117	14	117
1	14	51	71	-26	-66
2	1	281	212	-119	-175
2	2	756	940	-91	936
2	3	312	331	-14	-330
2	4	277	290	-111	268
2	5	93	64	-53	35
2	6	289	272	72	262
2	7	125	134	-24	-132
2	8	115	53	-11	52
2	9	367	351	-15	-351
2	10	146	111	1	-111
2	11	0	23	-19	13
2	12	47′	69	-8	-69
2	13	67	48	-15	-45
2	14	118	131	7	-131
3	1	0	22	-11	-19
3	2	426	450	-34	449
3	3	204	177	7	-177
3	4	307	297	-25	-296
3	5	309	283	-246	139
3	6	582	586	-7	586
3	7	58	55	27	48
3	8	0	27	27	1
3	9	348	355	46	352
3	10	151	154	41	148
3	11	142	146	22	144
3	12	118	123		123
3	13	0	25	18	16
4	1	159	151	46	144
4	2	317	281	133	248
4	3	419	447	16	446
4	4	357	369	159	133
4	5	166	124	-118	38
4	6	312	278	-9	278
4	7	287	293	2	293
4	8	82	67	30	60
4	9	184	162	-27	160
4	10	161	223	-33	-221
4	11	176	191	35	187
4	12	139	137	-6	-137
4	13	108	117	10	117
5	1	580	670	7	-670
5	2	269	302	-3	-302
5	3	617	704	80	-699
5	4	172	137	-76	114
5	5	206	216	-72	-204
5	6	358	342	-55	-338
5	7	49	50	-22	-45
5	8	53	37	-39	3
5	9	117	104	-60	-84
5	10	40	46	-45	5
5	11	99	90	30	85
5	12	0	24	13	20
6	1	199	203	-53	-195
6	2	[illegible]	58	47	35
6	3	205	216	-108	187
6	4	93	51	-51	5
6	5	323	327	[illegible]	[illegible]
6	6	169	153	-6	-153
6	7	187	182	40	177
6	8	44	40	-20	-35
6	9	394	408	41	406
6	10	144	130	-42	-123
6	11	62	55	-8	-55
6	12	0	16	8	14
7	1	503	554	162	-529
7	2	97	92	9	92
7	3	293	258	71	248
7	4	459	485	180	-450
7	5	538	655	-73	-651
7	6	211	219	-31	-217
7	7	138	105	26	101
7	8	261	272	1	-272
7	9	104	76	6	-76
7	10	127	119	-9	-118
7	11	86	69	-19	-66
8	1	63	89	59	67
8	2	202	180	175	42
8	3	192	182	54	-174
8	4	276	231	-87	-216
8	5	73	61	-17	59
8	6	0	35	-9	34
8	7	116	97	10	97
8	8	0	57	26	51
8	9	187	150	5	-150
8	10	0	60	-8	59
8	11	0	12	-11	4
8	12	0	17	8	15
8	13	86	106	-23	-103
9	1	292	269	-170	209
9	2	249	218	135	-171
9	3	173	139	15	139
9	4	266	235	17	-234
9	5	404	415	-1	415
9	6	116	113	15	-112
9	7	0	27	20	-19
9	8	249	250	-8	-250
9	9	0	42	-18	-38
9	10	116	139	-12	-137
9	11	0	32	-6	-32
9	12	0	4	1	-4
9	13	83	78	13	-77
10	1	259	286	-114	-262
10	2	280	256	3	-256
10	3	71	57	30	48
10	4	66	39	-32	-21
10	5	111	107	9	-107
10	6	83	96	-2	96
10	7	137	117	54	104
10	8	0	63	14	62
10	9	132	126	13	125
10	10	119	154	19	152
10	11	0	30	-2	-30
11	1	529	542	-16	541
11	2	247	217	-65	-207
11	3	519	563	34	562
11	4	278	282	11	282
11	5	0	3	3	
11	6	267	269	-36	-267
11	7	338	363	55	358
11	8	231	216	-32	214
11	9	84	83	-	-83
11	10	109	103	-3	103
11	11	67	81	7	-81
12	1	81	73	-5	73
12	2	42′	71	-	71
12	3	78	93	9	-92
12	4	160	173	-48	-166
12	5	76	26	-13	22
12	6	264	267	-57	-261
12	7	127	122	-74	-97
12	8	167	135	27	132
12	9	44′	72	1	72
12	10	0	36	-14	-33
12	11	102	109	-4	108
12	12	132	122	12	121
13	1	78	72	-23	-68
13	2	192	197	-7	197
13	3	185	168	53	160
13	4	0	24	-10	-22
13	5	0	5	1	4
13	6	334	354	7	354
13	7	178	188	27	-186
13	8	204	217	38	213
13	9	70	73	-29	-64
13	10	101	94	4	94
13	11	0	44	-27	-34
13	12	122	139	16	138
14	1	90	78	33	71
14	2	83	62	47	-25
14	3	185	152	-1	-152
14	4	188	167	2	-167
14	5	111	115	-18	-98
14	6	0	35	34	7
14	7	55	48	-8	-47
14	8	110	147	-24	-145
14	9	127	120	-13	-120
15	1	120	76	-	-76
15	2	152	158	-24	-156
15	3	465	490	-23	-489
15	4	263	276	11	276
15	5	135	72	-21	-69
15	6	0	15	1	15
15	7	214	176	-13	-175
15	8	69	63	18	61
16	1	240	237	-33	-236
16	2	123	126	-3	126
16	3	192	200	72	187
16	4	0	24	11	21
16	5	142	130	18	-129
16	6	0	29	3	-29
16	7	216	231	-7	-231
16	8		11	7	9
17	1	159	135	-13	-134
17	2	154	133	-17	132
17	3	123	154	25	152
17	4	67	88	9	-88
17	5	171	153	-6	-153
18	1	56	91	10	91
18	2	137	126	-40	120
18	3	76	72	-39	-60
18	4	181	170	10	170
18	5	0	24	-5	-24
18	6	67	54	9	54
19	1	91	73	13	72
19	2	0	17	-5	-17
19	3	102	89	-47	-75
19	4	0	37	-5	-36
19	5	117	113	-12	112
19	6	53	47	-16	44
19	7	0	26	-7	-25
19	8	78	67	9	-67
20	1	0	6	-3	5
20	2	0	17	17	1
20	3	101	92	-9	92
20	4	105	92	4	92
20	5	157	148	-3	148
20	6	94	76	19	74
20	7	85	56	-18	53
20	8	70	80	[illegible]	-79
21	1	0	21	5	-20
21	2	0	52	-1	-52
21	3	0	17	15	-6
21	4	58	67	-9	67
21	5	0	45	7	-44
21	6	138	133	-17	-132

HK2

0	0	2575′	3721	3609	-909
2	0	317	320	-316	44
4	0	515	569	-552	-139
6	0	197	188	-183	45
8	0	416	461	-448	-109
10	0	280	282	247	134
12	0	233	251	-251	17
14	0	95	71	65	-30
16	0	368	410	409	-28
18	0	90	103	-97	33
20	0	160	144	-139	39
22	0	148	130	-119	52
0	2	343	366	365	-21
0	4	612	714	696	-160
0	6	147	123	111	80
0	8	247	198	-194	38
0	10	131	94	82	-46
0	12	180	182	-180	4
1	1	134	128	-38	122
1	2	212	220	-215	50
1	3	265	219	-164	145
1	4	482	528	515	-116
1	5	247	217	89	-198
1	6	249	238	-217	98
1	7	80	70	-6	70
1	8	159	134	130	35
1	9	0	28	20	19
1	10	57	65	65	3
1	11	48	74	70	25
1	12	0	22	8	20
2	1	314	278	262	-91
2	2	622	694	688	92
2	3	633	691	682	-111
2	4	205	182	182	1
2	5	567	616	570	-234
2	6	240	231	-228	34
2	7	185	205	204	13
2	8	0	22	-3	22
2	9	372	392	391	-32
2	10	100	87	-87	-2
2	11	0	27	25	9
2	12	0	13	2	13
3	1	400	444	-442	-37
3	2	113	100	58	81
3	3	83	72	-61	37
3	4	289	307	-222	212
3	5	267	247	-186	-163
3	6	194	172	55	-163
3	7	51	35	17	-30
3	8	129	103	68	-78
3	9	136	107	61	-88
3	10	45	53	-49	21
4	1	583	691	689	-56
4	2	617	720	-696	187
4	3	178	166	86	-143
4	4	497	524	-520	70
4	5	382	407	382	141
4	6	162	130	-89	-95
4	7	370	390	389	-13
4	8	131	121	-120	12
4	9	300	287	-279	67
4	10	128	115	72	-90
4	11	201	216	216	2
4	12	0	31	17	26
4	13	88	33	-33	5
5	1	88	83	83	3
5	2	257	273	-263	74
5	3	457	485	-448	186
5	4	348	353	-332	121
5	5	262	229	227	-30
5	6	238	260	-250	70
5	7	230	251	-246	51
5	8	314	343	-343	13
5	9	48	46	42	-19
5	10	130	147	-121	-83
5	11	82	65	32	-56
5	12	0	52	-52	5
5	13	85	70	-70	8
6	1	287	344	-331	91
6	2	568	654	-639	140
6	3	313	327	327	-15
6	4	288	267	-17	-267
6	5	144	150	-150	6
6	6	0	46	44	1
6	7	235	224	-223	18
6	8	0	46	45	-9
6	9	115	81	81	-11
6	10	41	45	30	34
6	11	149	170	-158	-62
6	12	0	39	39	1
7	1	577	696	669	-193
7	2	265	257	-182	181
7	3	460	493	458	-182
7	4	227	181	-114	121
7	5	180	146	70	126
7	6	289	271	-270	8
7	7	110	100	91	42
7	8	81	101	-101	-7
7	9	100	87	-86	13
7	10	130	150	-140	53
7	11	129	145	-144	7
7	12	122	112	-111	-11
8	1	269	231	169	-157
8	2	408	440	433	79
8	3	218	242	-199	139
8	4	177	161	144	72
8	5	0	40	-39	-8
8	6	46	55	54	10
8	7	92	67	-62	-25
8	8	253	251	250	21
8	9	125	103	-101	19
8	10	0	26	-16	20
8	11	0	27	-27	1
8	12	101	92	90	20
9	1	349	357	298	-197
9	2	462	508	478	-172
9	3	364	357	346	86
9	4	192	173	102	-139
9	5	150	150	150	-3
9	6	401	424	423	-14
9	7	90	72	-33	65
9	8	108	108	105	-27
9	9	0	41	-35	21
9	10	119	124	123	-15
9	11	0	48	-48	1
9	12	121	116	110	-35
10	1	138	113	-68	90
10	2	232	248	-216	-122
10	3	124	93	-92	-17
10	4	129	94	87	-36
10	5	0	38	-35	16
10	6	283	275	265	-72
10	7	41	50	50	-4
10	8	81	91	-88	24
10	9	0	36	-35	-8
10	10	136	112	111	8
11	1	283	253	-225	116
11	2	96	79	51	-49
11	3	249	248	-246	-27
11	4	410	385	379	-70
11	5	92	77	-52	56
11	6	293	321	320	-27
11	7	0	48	48	6
11	8	152	176	175	23
11	9	0	43	27	-33
11	10	129	149	148	20
12	1	246	256	-253	32
12	2	166	167	-167	
12	3	0	19	-8	17
12	4	120	137	-130	42
12	5	217	198	-194	36
12	6	186	208	-194	74
12	7	136	111	-67	-88
12	8	126	82	44	-69
12	9	105	80	79	13
13	1	373	393	-393	6
13	2	132	103	84	-59
13	3	136	79	-77	-19
13	4	0	39	-39	-4
13	5	235	216	-211	-47
13	6	153	156	-154	24
13	7	134	167	150	-73
13	8	95	78	62	47
14	1	160	174	169	44
14	2	137	129	128	10
14	3	342	339	-336	46
14	4	0	33	27	19
14	5	132	99	-98	11
14	6	57	56	-54	14
14	7	111	110	-80	75
14	8	73	68	-63	24
14	9	124	150	-148	-21
14	10	122	103	-100	24
15	1	139	112	94	60
15	2	222	211	-205	49
15	3	0	22	-1	-22
15	4	148	161	-160	-18
15	5	0	56	49	28
15	6	89	86	-85	12

Table 1 (*cont.*)

Table 2. *Atom parameters*

Atom	x	$\sigma(x)$ $\times 10^4$	y	$\sigma(y)$ $\times 10^4$	z	$\sigma(z)$ $\times 10^4$	(Å^2)	$\sigma(B)$
C(1)	0·4461	(6)	0·4229	(10)	0·0202	(28)	3·28	0·23
C(1′)	0·3828	(6)	−0·0087	(10)	−0·0177	(34)	3·49	0·24
C(1″)	0·1980	(6)	0·3012	(10)	0·0042	(34)	3·35	0·21
C(2)	0·4660	(6)	0·2979	(11)	−0·0568	(29)	3·60	0·25
C(2″)	0·3089	(6)	0·0233	(11)	−0·0749	(25)	3·11	0·23
C(2″)	0·2507	(6)	0·3890	(11)	−0·0638	(24)	3·02	0·21
C(3)	0·4124	(5)	0·2081	(10)	0·0195	(24)	2·80	0·21
C(3′)	0·2920	(5)	0·1488	(9)	0·0024	(33)	2·70	0·18
C(3″)	0·3231	(5)	0·3578	(10)	0·0250	(26)	2·51	0·22
N(1)	0·3731	(5)	0·4460	(9)	−0·0605	(21)	2·80	0·19
N(1′)	0·4317	(5)	0·0918	(10)	−0·0685	(23)	2·98	0·20
N(1″)	0·2233	(5)	0·1837	(8)	−0·0631	(20)	2·73	0·18
N(2)	0·3426	(4)	0·2387	(7)	−0·0519	(18)	2·32	0·15
Cl(1)	0·1220	(2)	−0·0239	(3)	0·0024	(13)	3·69	0·07
Cl(2)	0·5710	(1)	−0·0386	(3)	−0·0071	(13)	3·66	0·07
Cl(3)	0·3084	(2)	0·6991	(3)	0·0000	0	4·01	0·07
O(1)	0·4783	(12)	0·7124	(24)	−0·0870	(56)	5·81	0·61

three-dimensional electron-density map; they were used to modify the positional parameters previously calculated on the assumption of tetrahedral bonds and C–H and N–H bond distances of 1·10 and 1·05 Å respectively. The positional parameters for these 18 hydrogen atoms are listed in Table 4. They were included in the structure factor calculations with an isotropic temperature factor $B=4{\cdot}0$ Å^2, but were not varied in the least-squares calculations. The positional parameters of the remaining three protons, which occupy the polar positions about the N atoms, were calculated on the assumption of tetrahedral bonds and an N–H distance of 1·05 Å; they are also listed in Table 4 but were not included in the structure factor calculations. Approximate N–H $\cdots$ Cl bond angles calculated from the positional parameters assumed for the hydrogen atoms are given in Table 5.

Three more cycles of least-squares calculations were carried out. At this point the corrections in the parameters were all less than their standard deviations.

Table 3. *Bond distances and angles*

Bond	Bond distance	σ
C(1)–C(2)	1·547 Å	0·019 Å
C(1′)–C(2′)	1·518	0·018
C(1″)–C(2″)	1·491	0·018
C(2)–C(3)	1·529	0·017
C(2′)–C(3)′	1·541	0·018
C(2″)–C(3″)	1·555	0·017
C(1)–N(1)	1·531	0·016
C(1′)–N(1)′	1·509	0·016
C(1″)–N(1″)	1·477	0·016
C(3″)–N(1)	1·500	0·016
C(3)–N(1′)	1·485	0·016
C(3′)–N(1″)	1·454	0·016
C(3)–N(2)	1·469	0·014
C(3′)–N(2)	1·452	0·014
C(3″)–N(2)	1·484	0·014
N(1) · · · Cl(3)	3·122	0·014
N(1′) · · · Cl(2)	3·077	0·014
N(1″) · · · Cl(1)	3·089	0·014
N(1) · · · Cl(1′)	3·045	0·014
N(1′) · · · Cl(2′)	3·092	0·014
N(1″) · · · Cl(3′)	3·081	0·014
Cl(1) · · · O	3·547	0·025
Cl(2) · · · O	3·361	0·025
Cl(3) · · · O	3·315	0·025

Angle		σ
C(1)–C(2)–C(3)	108·2°	1·1°
C(1′)–C(2′)–C(3′)	108·6	1·1
C(1″)–C(2″)–C(3″)	109·7	1·1
C(2)–C(3)–N(2)	110·4	1·0
C(2′)–C(3′)–N(2)	113·4	1·1
C(2″)–C(3″)–N(2)	106·7	0·9
C(2)–C(3)–N(1′)	105·6	1·0
C(2′)–C(3′)–N(1″)	108·9	1·1
C(2″)–C(3″)–N(1)	105·7	1·0
N(1)–C(1)–C(2)	104·9	1·1
N(1′)–C(1′)–C(2′)	110·2	1·1
N(1″)–C(1″)–C(2″)	105·0	1·1
C(3)–N(2)–C(3″)	108·8	0·9
C(3′)–N(2)–C(3)	111·1	0·9
C(3″)–N(2)–C(3′)	111·0	0·9
C(3″)–N(1)–C(1)	109·4	1·0
C(3′)–N(1″)–C(1″)	116·0	1·1
C(3)–N(1′)–C(1′)	113·7	1·0
N(2)–C(3″)–N(1)	106·8	0·9
N(2)–C(3)–N(1′)	107·2	0·9
N(2)–C(3′)–N(1″)	109·6	1·1
Cl(3) · · · O · · · Cl(2)	122·5	1·5

Table 4. *Hydrogen positional parameters*

Atom	Bonded to	*x*	*y*	*z*
H(1)	C(1)	0·446	0·423	0·181
H(2)	C(1)	0·485	0·488	−0·050
H(3)	C(1′)	0·385	−0·025	0·139
H(4)	C(1′)	0·395	−0·095	−0·070
H(5)	C(1″)	0·201	0·296	0·159
H(6)	C(1″)	0·150	0·376	−0·072
H(7)	C(3)	0·412	0·208	0·180
H(8)	C(3′)	0·282	0·111	0·154
H(9)	C(3″)	0·323	0·357	0·180
H(10)	C(2)	0·466	0·297	−0·217
H(11)	C(2)	0·516	0·281	0·000
H(12)	C(2′)	0·312	0·045	−0·240
H(13)	C(2′)	0·274	−0·045	−0·030
H(14)	C(2″)	0·250	0·390	−0·220
H(15)	C(2″)	0·224	0·473	−0·003
H(16)	N(1)	0·357	0·536	0·000
H(17)	N(1′)	0·471	0·029	0·007
H(18)	N(1″)	0·188	0·116	0·022
H(19)	N(1)	0·372	0·444	−0·211
H(20)	N(1′)	0·435	0·101	−0·220
H(21)	N(1″)	0·220	0·182	−0·217

Table 5. *Hydrogen-bond angles*

N(1)–H(16) · · · Cl(3)	157°
N(1′)–H(17) · · · Cl(2)	146
N(1″)–H(18) · · · Cl(1)	145
N(1)–H(19) · · · Cl(1′)	164
N(1′)–H(20) · · · Cl′(2)	155
N(1″)–H(21) · · · Cl(3′)	169

The final positional and temperature-factor parameters for the seventeen heavy atoms, together with their standard deviations, are given in Table 2. The calculated and observed structure factors are listed in Table 1. The weights were reduced in the least-squares calculations for several intense low-angle reflections whose observed *F*'s were appreciably smaller, presumably because of extinction, than their calculated *F*'s; a few additional reflections which were difficult to measure because of spot shape or background overlap were given zero weight.

A three-dimensional Fourier synthesis was computed from the complete data with signs and phases calculated from the final parameters. A composite drawing of this map is shown in Fig. 3.

Accuracy of the results

Although the refinement could have been carried further by the use of anisotropic temperature factors and by the adjustment of the hydrogen parameters by least-squares, it was stopped at this point because of the uncertainty of the exact water content and the large number of parameters involved. In addition, the primary object of this work was to establish the molecular configuration of the $C_9H_{18}N_4$ molecule. The *R* index including only those reflections of non-zero weight (1144) terms is 0·096. Of the 1530 reflections 304 were unobserved, 68 of these had *F*(cal.) values greater than the minimum threshold value. If these are included with *F*(obs.) taken equal to the threshold value, the *R* index is 0·110 (1212 terms).

The standard deviations in the positional parameters calculated by the Busing–Levy (1959*a*) least-squares program are listed in Table 2. With the exception of the oxygen atom whose standard deviations are slightly larger, they range from 0·0029 to 0·0123 Å for $\sigma(x)$, from 0·0030 to 0·0123 Å for $\sigma(y)$ and from 0·0083 Å to 0·0223 Å for $\sigma(z)$. The corresponding standard deviations in the parameters of the oxygen atom are 0·022 Å, 0·025 Å, and 0·034 Å respectively. The standard deviations of the principal bond distances and angles calculated with the Busing–Levy (1959*b*) crystallographic function and error program are listed in

Table 3; they range from 0·0165 to 0·018$_6$ Å for the C–C bonds, from 0·013$_8$ to 0·014$_2$ Å for the central pyramidal bonds and from 0·015$_3$ to 0·016$_3$ Å for the other C–N bonds.

The calculated standard deviations in the temperature factors (Table 2) range from 0·18 to 0·25 Å^2 for the carbon atoms, from 0·16 to 0·19 Å^2 for the N atoms, and from 0·065 to 0·19 Å^2 for the N atoms, and from 0·065 to 0·07$_2$ Å^2 for the Cl^- ions. The standard deviations of the temperature factor for the oxygen atom of the H_2O molecule is somewhat higher (0·54 Å^2).

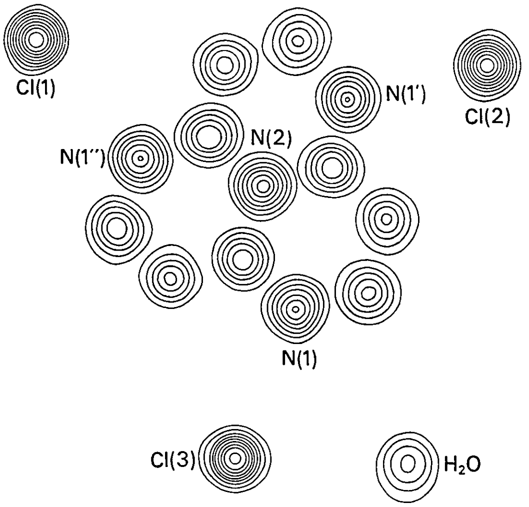


Fig. 3. Composite drawing of electron density map, viewed along the *c* axis.

Discussion of the structure

The principal bond distances and angles and their standard deviations are given in Table 3; the distances and angles are also shown in Fig. 4.

Since the refinement did not include anisotropic temperature factors, it is probably not worthwhile to discuss the individual bond distances and angles in detail. With the exception of one short C–C bond (1·49$_2$ Å) and one long C–N bond (1·53$_1$ Å), the C–C and C–N distances are all normal. The other five C–C bonds

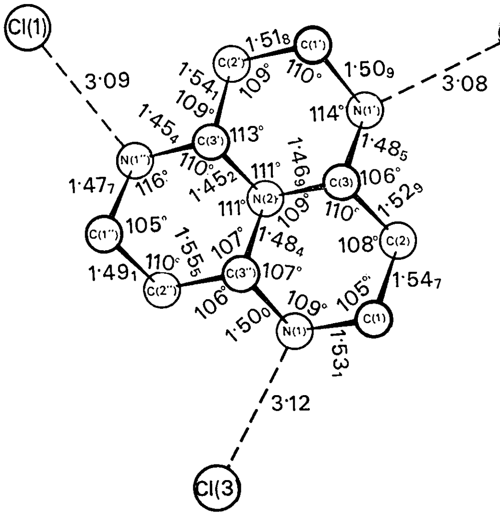


Fig. 4. Bond distances and angles.

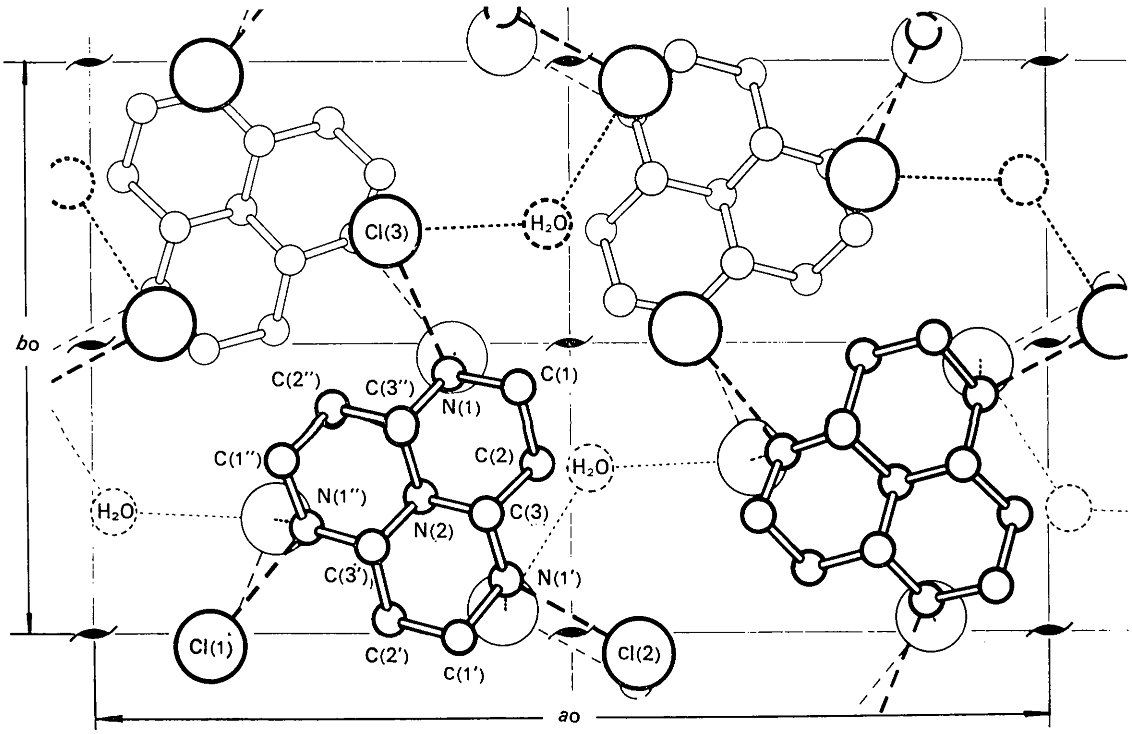


Fig. 5. Drawing of the structure, viewed along the *c* axis.

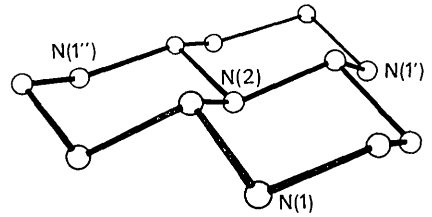


Fig. 6. General view of the $C_9H_{18}N_4$ molecule showing puckered ring structure.

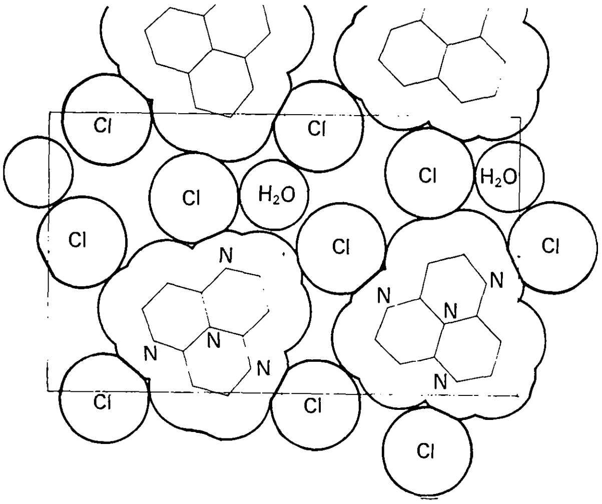


Fig. 7. Packing drawing of molecules in one layer, viewed along the c axis.

range from $1{\cdot}51_8$ to $1{\cdot}55_5$ Å with a mean value $1{\cdot}539 \pm 0{\cdot}015$ Å. The pyramidal C–N bonds to the central nitrogen ranged from $1{\cdot}45_2$ to $1{\cdot}48_4$ Å with a mean value $1{\cdot}46_8 \pm 0{\cdot}014$ Å; the other five C–N bonds ranged from $1{\cdot}45_4$ to $1{\cdot}50_9$ Å with a mean value of $1{\cdot}48_6 \pm 0{\cdot}016$ Å.

The symmetrical puckered ring structure of the $C_9H_{18}N_4$ molecule is shown in Figs. 4, 5, and 6. The packing arrangement of the molecules and hydrogen bonding within one layer viewed along [001] are shown in Fig. 7. The average plane of the $C_9H_{18}N_4$ molecule is almost parallel to the *ab* plane. The Cl^- ions are not quite symmetrically arranged, *i.e.* they deviate from an equilateral triangular arrangement. This was first observed in the Patterson function. The H_2O molecule is closer to two of the Cl^- ions ($Cl(2)-O = 3{\cdot}36_1$ Å and $Cl(3)-O = 3{\cdot}31_5$ Å) than it is to the third Cl^- ion ($Cl(1)-O = 3{\cdot}54_7$ Å). Presumably the two closer Cl^- ions form hydrogen bonds with the H_2O molecule with the resulting distortion of the Cl^- arrangement.

The nitrogen atoms in the ring (with the exception of the central nitrogen) are each hydrogen bonded to two nearest neighbor Cl^- ions, one approximately in the plane of the molecule at $\sim 3{\cdot}1$ Å and the other at about the same distance below the molecule. The molecules are packed essentially in layers parallel to the *ab* plane and are joined into two separate strings of molecules along the *b* axis through the hydrogen bonds between the H_2O and two Cl^- ions. The interaction between layers is largely hydrogen bonding between the nitrogen atoms N(1), N(1') and N(1'') and the Cl^- ions below.

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