

to be stable, while for the light rare-earth elements the hexagonal stacking is stable. In the latter case the rhombohedral form seems to occur as a high temperature modification, which is a situation exactly opposite to that encountered with the two Th₂Co₇ modifications. A survey of the structures occurring and the corresponding lattice constants is given in Table 3. Our values for the rhombohedral form are substantially in agreement with those given by Bertaut *et al.* (1965).

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assistance in the intensity calculations and the X-ray diffraction experiments.

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Solid State Structure and Chemistry of the Choline Halides and their Analogues. Redetermination of the Betaine Hydrochloride Structure, [(CH₃)₃NCH₂COOH]⁺Cl⁻

BY MARK S. FISCHER, DAVID H. TEMPLETON AND ALLAN ZALKIN

Lawrence Radiation Laboratory and Department of Chemistry, University of California, Berkeley, California 94720, U.S.A.

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The crystal structure of betaine hydrochloride, [(CH₃)₃NCH₂COOH]⁺Cl⁻, has been redetermined by X-ray diffraction from the intensities of 782 independent reflections collected on a scanning counter diffractometer. The crystals are monoclinic, space group *P*2₁/*c*, with cell parameters *a*=7.428, *b*=9.108, *c*=11.550 Å, and β=96.71°. The positions of the hydrogen atoms have been found, and the conventional *R* value has been reduced to 0.026. Final atomic positions differ from those given by Clastre by as much as 0.16 Å. The mean C-N bond length is 1.499 ± 0.004 Å (uncorrected for thermal motion). The cation assumes a completely staggered conformation with the acidic hydrogen atom as far away as possible from the nitrogen atom. The hydrogen bonding from the carboxyl group to the chloride ion is relatively strong compared with the hydrogen bonding in choline chloride.

The structures of choline [(CH₃)₃NCH₂CH₂OH]⁺ X⁻ and betaine [(CH₃)₃NCH₂COOH]⁺ X⁻ compounds are of interest because of both the unusual radiation sensitivity of choline chloride (Tolbert, Adams, Bennett, Hughes, Kirk, Lemmon, Noller, Ostwald & Calvin, 1953) and the frequent occurrence of these compounds in biological systems. They are components of complex lipids, and they can act as transmethylating agents. The related acetylcholine is essential to nerve impulse transfer.

Related structures which have been determined previously include choline chloride (Senko & Templeton, 1960), muscarine iodide (Jellinek, 1957) and acetylcholine bromide (Canepa, Pauling & Sörum, 1966). Clastre (1964) has published a preliminary structure report for betaine hydrochloride, in which he refined the *R* value for two of the two-dimensional projections down to 0.18. Bond distances which we calculated from his pub-

lished atomic coordinates implied that the C-N bond lengths ranged from 1.49 to 1.63 Å in length. We undertook this structure investigation to provide an accurate structure, to locate the positions of the hydrogen atoms, and to investigate the packing.

Experimental

Small colorless crystals of betaine hydrochloride were kindly supplied to us by Dr R. M. Lemmon. These were then recrystallized in the form of colorless needles by the evaporation of a water-methanol solution to dryness at room temperature. The unit-cell dimensions were obtained from careful measurements of the Bragg scattering angles for the *h*00, 0*k*0, and 00*l* reflections, as measured on a manually operated General Electric XRD-5 diffractometer. The α doublet (λ=1.5405 Å for Cu Kα₁) was resolved for those reflections of highest

order. The crystal used for both the determination of cell dimensions and the collection of data was mounted on the crystallographic *b* axis, and the β angle was obtained directly from the angle on the ϕ circle between the *h*00 and the 00*l* reflections. The unit-cell parameters (at 23°) are shown in Table 1. The absence of reflections *h*0*l* with *l* odd and 0*k*0 with *k* odd indicate the space group *P*2₁/*c*. The crystal, which was mounted on the needle axis, measured 0.09 × 0.09 × 0.43 mm. The four most prominent faces were the (100), (001), (100), and (001). The observed density of 1.314 ± 0.005 g.cm⁻³, which was determined by flotation in a chloroform-ethylene dichloride mixture, agrees well with the value 1.313 g.cm⁻³ calculated for a molecular weight of 153.5, for *Z*=4, and for a unit-cell volume of 776 Å³.

Integrated intensities were measured with a card controlled, automated General Electric XRD-5 diffractometer. The copper radiation was filtered by a 0.001 inch thick nickel foil placed between the crystal and the re-

Table 1. Unit-cell parameters

	This work	Claestre
<i>a</i>	7.428 ± 0.002 Å	7.45 ± 0.02 Å
<i>b</i>	9.108 ± 0.005	9.15 ± 0.02
<i>c</i>	11.550 ± 0.003	11.65 ± 0.02
β	96.71 ± 0.03°	97.0°

ceiving slit, and a θ - 2θ scan was employed. The intensities were measured for all reflections lying within half a sphere in reciprocal space corresponding to *d* spacings ≥ 1.006 Å ($2\theta \leq 100^\circ$). The intensities of equivalent reflections were averaged to give 794 independent reflections of which 782 were above background. The 32 largest intensities were remeasured at lower X-ray flux to avoid flooding of the counter. Crystal decay, monitored by 24 periodic measurements of six standard reflections, was less than 5%. The calculated linear absorption co-

Table 2. Observed and calculated structure factor amplitudes of betaine hydrochloride
Asterisks indicate zero-weighted data. Values have been multiplied by 9.30; on this scale, *F*(000)=3088.

L FCB PCA	7 55 54	8 119 163	2 195 194	-2 18 17	1 111 112	7 77 78	-2 23 23	-2 168 172	H _{KL} 4, 0	2 60 59	-8 59 59	-5 0 4*	2 169 169
H _{KL} 0, 0	8 58 35	1 161 142	3 70 70	-1 46 49	8 71 74	8 71 74	-1 44 141	-1 39 40	-10 15 19	3 96 96	-8 475 474	-4 109 107	3 125 124
2 312 377	5 58 65	12 180 180	2 304 366	0 121 99	10 90 95	H _{KL} 2, 6	1 340 349	0 225 223	-8 245 245	-8 245 245	-4 27 28	-4 28 31	4 28 31
4 793 751	6 11 70	6 9 9	5 47 46	1 41 36	H _{KL} 2, 4	1 100 55	1 141 144	-6 34 34	5 46 47	-2 285 292	-2 81 82	5 28 30	5 28 30
6 416 424	C 235 233	H _{KL} 1, 2	4 67 47	2 184 79	-1C 0 8*	-7 64 65	2 264 263	2 23 23	-4 265 266	6 77 78	C 245 251	-1 65 69	H _{KL} 4, 3
8 102 103	1 184 180	11 42 42	7 41 40	3 12 3	-5 18 12	-6 8 9	3 27 28	3 23 15	-2 355 360	8 77 78	C 245 251	0 182 180	-8 84
10 165 164	2 56 52	-10 23 19	8 317 316	4 110 112	-8 137 136	-5 64 65	4 120 114	4 142 146	C 171 172	8 29 28	4 203 202	1 71 72	-5 5 5
H _{KL} 2, 1	3 32 31	C 1 5	H _{KL} 1, 5	H _{KL} 2, 5	-1 65 68	-6 74 73	5 20 15	5 20 15	H _{KL} 4, 0	8 29 28	4 203 202	0 182 180	-4 123 121
1 109 116	4 91 45	-8 261 269	-8 105 107	-1C 209 209	-8 292 291	-3 196 196	6 146 147	6 141 145	4 155 203	-8 90 88	H _{KL} 5, 1	3 24 26	-3 102 105
2 46 50	5 14 14	4 27 26	-8 52 52	-8 17 16	-5 65 62	-2 42 41	7 96 98	7 74 78	6 74 82	-7 50 50	-5 57 58	4 165 167	-2 87 86
3 122 125	6 207 002	-6 269 263	-7 65 68	-4 122 173	-4 124 114	-1 38 38	8 117 118	8 86 87	8 144 149	-6 38 38	-8 42 41	5 10 10	-1 0 10
4 70 82	7 0 5*	-5 162 161	-8 226 225	-4 249 277	-3 45 44	0 180 177	9 28 28	H _{KL} 3, 5	H _{KL} 4, 1	-1 16 13	-7 143 145	H _{KL} 5, 5	0 143 144
5 104 101	H _{KL} 0, 7	-5 66 63	-8 155 154	-2 184 187	-2 523 545	1 12 12	H _{KL} 3, 2	-8 98 93	-1C 12 11	-4 309 310	-6 0 8	-8 16 20	1 97 95
7 17 34	8 101 74	-2 479 478	-3 105 105	2 167 167	C 408 421	3 104 103	H _{KL} 1, 2	8 117 118	8 86 87	8 144 149	-6 38 38	-8 42 41	5 10 10
8 139 133	2 112 107	-1 21 11	-2 27 25	4 140 133	1 115 114	4 78 79	-9 52 54	-6 181 182	-8 286 290	-2 76 77	-2 93 95	-4 166 166	3 47 46
9 17 7	3 17 17	0 122 103	-1 71 65	6 252 245	2 155 163	5 6 5	-7 5 4	-4 87 89	-6 60 61	0 109 108	-2 47 46	-2 46 46	H _{KL} 6, 4
10 93 93	4 70 66	1 171 171	0 195 192	8 68 68	2 98 95	6 131 127	-8 195 200	-3 29 27	-5 6 2	1 76 79	-1 67 65	-1 220 223	-5 42 41
11 32 30	5 140 139	2 578 560	3 226 222	10 27 31	4 483 453	7 13 5	-5 197 195	-2 119 119	-4 13 8	2 248 253	0 184 180	0 123 123	-4 194 197
0 484 302	7 5 0	4 221 225	3 60 54	-11 54 59	4 12 12	-6 34 32	-2 176 163	C 204 212	-2 420 427	4 56 56	2 264 260	2 68 66	-2 89 86
1 681 704	H _{KL} 0, 6	5 12 11	4 20 24	-10 31 34	7 13 10	-5 56 56	-2 011 202	-1 40 40	-1 204 192	5 23 23	3 88 86	3 58 57	-1 91 92
2 270 270	0 177 179	6 162 158	5 32 31	-9 16 16	8 89 93	-4 69 64	-1 51 52	2 170 165	C 53 95	6 43 43	4 27 27	4 73 74	0 16 13
3 15 13	1 28 24	4 136 138	-8 102 206	6 75 78	-3 130 130	0 15 14	0 316 211	3 3 4	1 25 16	9 102 108	5 15 19	H _{KL} 5, 6	6 1 91
4 403 412	2 17 11	8 149 151	7 93 93	-7 30 32	H _{KL} 2, 4	-2 96 95	1 116 111	4 4 9	5 7 8	2 232 217	H _{KL} 6, 5	6 92 89	2 211 209
5 98 56	3 17 15	0 112 112	H _{KL} 3, 6	-8 228 290	-1C 74 73	2 19 77	2 19 18	5 7 8	3 1 6	-7 109 114	7 37 35	-3 0 6	3 6 7
6 264 260	4 58 57	4 107 107	-8 107 108	-5 105 105	4 78 82	3 20 20	6 119 125	-7 7 11	4 144 145	-8 163 163	H _{KL} 5, 2	-2 60 64	H _{KL} 6, 5
7 12 13	5 81 78	H _{KL} 1, 3	-7 16 19	-8 14 13	-8 14 1C	1 28 27	4 212 214	7 19 20	5 12 12	-5 9C 93	-8 125 132	-1 12 10	-3 0 3*
8 32 31	H _{KL} 0, 9	-10 114 113	-6 14 9	-3 88 85	-9 102 105	2 66 66	5 241 237	H _{KL} 3, 6	6 65 69	-4 17 16	-7 103 105	-2 165 167	-2 45 45
9 35 35	1 39 41	-9 23 24	-5 12 12	-2 504 902	4 78 82	3 20 20	6 119 125	-7 7 11	7 26 35	-3 65 66	-4 292 289	1 6 4	-1 50 50
10 170 165	H _{KL} 1, 0	-8 30 30	-4 45 45	-1 358 359	-5 82 81	4 54 54	7 16 15	-6 186 185	8 76 74	-2 206 207	-5 152 2 4	0 0 81 01	1 1 1
11 9 6	-6 126 125	-9 10 10	-3 183 182	0 168 194	-4 328 330	5 45 48	8 96 96	-5 46 48	H _{KL} 4, 2	-1 110 110	-4 23 18	H _{KL} 0, 0	H _{KL} 7, 0
1 250 246	-6 107 104	-5 167 150	-1 23 26	2 605 605	-2 251 240	H _{KL} 2, 8	H _{KL} 3, 3	-3 170 174	-8 102 102	1 39 39	-2 243 234	-4 56 51	-2 20 20
2 502 518	-4 480 503	-4 17 21	0 17 13	-8 48 47	-8 48 47	-13 194 198	-2 167 193	-7 44 46	2 167 193	-7 44 46	2 35 53	-1 40 39	-2 154 134
3 250 246	-2 119 117	-3 339 336	1 92 91	4 133 136	C 327 333	-3 93 54	-9 28 31	1 36 34	C 136 136	1 36 34	0 220 220	2 52 54	2 52 54
4 50 50	0 399 384	-2 142 134	2 111 108	9 111 148	1 86 84	-2 114 114	-8 134 135	0 23 22	-5 24 24	4 108 116	1 87 85	2 66 67	H _{KL} 7, 1
5 11 9	2 165 156	-1 125 137	3 90 90	6 67 65	-6 67 65	-1 62 64	-7 4 6	1 113 116	-4 267 270	4 44 47	4 111 113	-4 174 175	4 174 175
6 24 25	4 282 284	0 323 334	4 183 184	7 24 27	3 70 70	0 195 197	-6 334 336	-2 88 82	-3 51 45	6 38 39	3 74 76	H _{KL} 8, 0	-3 89 88
7 167 166	6 283 278	1 166 166	5 14 18	8 156 201	4 233 232	1 68 72	-5 140 137	3 8 8	-2 273 376	H _{KL} 4, 6	4 187 189	-7 31 29	-2 54 50
8 165 155	6 78 81	4 57 53	6 84 82	6 84 82	5 118 122	2 90 88	-4 364 364	4 64 67	-1 23 24	-6 9 13	5 64 64	-6 150 151	-1 37 34
9 89 87	10 51 46	3 220 223	7 145 146	10 90 80	4 255 250	3 88 91	-3 117 110	5 28 8	C 262 258	-5 3 2	6 77 75	-5 59 58	0 51 52
10 118 115	H _{KL} 1, 1	4 57 54	6 127 125	H _{KL} 2, 4	7 39 35	8 89 89	-2 189 184	6 9 9	9 145 42	-4 83 87	H _{KL} 5, 3	-3 78 77	2 144 145
0 164 170	-1C 110 100	6 274 279	-7 44 43	-1C 137 137	5 90 94	-8 0 9 75	0 303 295	-6 2 6	3 105 105	-2 75 77	-8 206 210	-3 112 119	H _{KL} 5, 3
1 155 158	-6 17 19	7 45 45	-6 150 146	-9 10 10	-9 10 10	6 83 81	-1 31 25	7 262 258	-7 2 5	-7 2 5	-7 12 4	-1 1 4	-2 5 6
2 290 288	-8 136 133	8 52 51	-5 36 41	-9 71 68	-5 36 33	-4 286 272	2 290 241	-4 116 115	7 19 0	14 13	-6 107 110	0 233 233	-3 6 6
3 0 0*	-7 46 46	9 51 50	-4 246 241	-1 116 112	-8 131 125	-2 147 133	3 61 64	-3 60 60	6 155 163	1 8 10	-5 19 19	1 14 20	-1 92 98
4 334 333	-6 128 133	1C 0 9	-3 37 36	-6 205 200	-7 53 52	0 327 342	4 105 112	-2 83 83	7 16 22	2 141 146	-4 161 163	2 58 61	0 106 101
5 42 41	-5 54 54	H _{KL} 1, 4	-4 132 129	-5 21 32	-4 166 176	2 111 104	5 105 102	-1 64 52	8 91 92	3 137 143	-3 12 3	3 40 41	1 54 52
6 92 97	-4 553 948	-1C 12 15	-1 98 100	-4 29 23	-1 95 95	4 602 581	6 272 235	0 30 50	H _{KL} 4, 3	4 17 20	-2 156 159	4 136 133	4 136 133
7 45 42	-3 186 181	-9 48 50	0 176 158	-3 116 114	-4 117 117	6 83 81	7 165 172	1 62 64	-5 50 56	5 64 67	-1 11 10	4 41 42	4 41 42
8 46 46	-2 94 100	-8 254 251	1 165 168	-2 75 76	-3 22 19	0 135 136	8 7 9	2 144 151	-8 16 11	H _{KL} 4, 7	7 0 145 144	H _{KL} 6, 2	
9 3 35	-1 204 200	-7 56 59	2 116 118	-2 220 215	-2 203 203	-10 189 188	9 14 12	3 56 65	-7 86 81	-4 76 80	1 102 101	-7 9 11	4 16 15
10 103 103	C 24 26	-6 131 133	3 68 59	4 130 314	1 20 23	-10 189 188	H _{KL} 3, 1	9 14 12	4 22 22	-4 208 210	-3 52 52	-4 60 66	4 60 66
H _{KL} 0, 5	1 458 480	-5 162 164	4 103 105	1 208 319	C 216 221	-9 24 27	-9 50 90	H _{KL} 3, 8	-5 45 43	-2 168 191	3 82 80	-5 64 67	5 64 67
1 217 215	2 533 985	-4 256 255	5 91 88	2 119 126	4 14 16	-8 204 207	-8 105 112	-3 40 42	-4 75 76	-1 25 28	4 98 101	-4 160 155	4 160 155
2 351 355	3 279 286	-3 61 69	6 84 81	3 31 30	-6 84 81	-7 22 10	-7 22 10	-2 81 83	-3 52 52	0 127 129	5 0 0	-4 95 92	4 95 92
3 47 46	4 39 40	-2 313 314	H _{KL} 1, 8	4 67 65	2 70 64	-6 202 214	-6 81 75	-1 112 114	-2 72 74	1 15 14	6 106 106	-2 154 151	2 154 151
4 113 112	6 86												

efficient μ is 39 cm^{-1} (for $\text{Cu } K\alpha$). The data are uncorrected for absorption effects, which may vary by a factor of the order of 1.15 for the extreme cases.

Net intensities I and their standard deviations $\sigma(I)$ were calculated from the expressions: $I = I_{\text{gross}} - (t_I/2t_B)(B_1 + B_2)$ and $\sigma^2(I) = I_{\text{gross}} + (t_I/2t_B)^2(B_1 + B_2)$, where B_1 and B_2 are the number of counts for each background reading and t_I and t_B are the times spent scanning the peak and counting the background. For n measurements of the intensity of a particular reflection (n was always ≥ 2), the intensities were averaged and $\sigma(I)$, the standard deviation of the mean, was calculated from $\sigma_L(I)$ equal to the larger of $[\sum(I_i - \bar{I})^2]^{1/2}/(n-1)$ and $[\sum\sigma^2(I_i)]^{1/2}/n$ by using the relationship $\sigma^2(\bar{I}) = \sigma^2(I) + (p/I)^2$, where p , a constant, was set equal to 0.04 to reduce the weights of the most intense reflections.

The full-matrix least-squares program used was our local unpublished version for the CDC 6600 computer. The atomic scattering factors used during this analysis were those given by Cromer & Mann (1968) for the Cl^- , Cl , O , N and C atoms and those of Stewart, Davidson & Simpson (1965) for the hydrogen atoms. The scattering factor for the N^+ atom was calculated from the scattering factor of N^{3+} (Hurst & Matsen, 1959) by using the relationship $f(\text{N}^+) = [2f(\text{N}) + f(\text{N}^{3+})]/3$. For the chlorine atom the anomalous dispersion corrections of Cromer (1965) were used. The function minimized in the least-squares refinements was $R_2^2 = \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2$. In the early stages of refinement, the weights w were set equal to 1.0, but in the later stages they were set to 0 when $I=0$ and to $1/\sigma^2(F)$ otherwise; $\sigma(F)$ was calculated from $\sigma(I)$: $\sigma(F^2) = (\text{Lp})^{-1}\sigma(I)$, $\sigma(F) =$

Table 3. Final atomic fractional coordinates and thermal parameters with their standard deviations for hydrogen atoms in betaine hydrochloride

The numbers in parenthesis here and in succeeding Tables are the standard deviations of the least significant digit(s). The temperature factor has the form: $T = \exp[-B(\sin \theta/\lambda)^2]$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	0.7362 (26)	0.1542 (25)	0.7369 (18)	4.6 (5) Å ²
H(2)	0.8486 (29)	0.2080 (21)	0.6421 (16)	3.3 (4)
H(3)	0.6466 (32)	0.2250 (20)	0.6230 (20)	4.1 (5)
H(4)	0.8855 (26)	0.3019 (24)	0.8857 (17)	4.0 (4)
H(5)	1.0216 (28)	0.3508 (20)	0.7967 (14)	3.7 (4)
H(6)	0.9188 (27)	0.4692 (25)	0.8622 (16)	4.4 (5)
H(7)	0.9151 (28)	0.4549 (20)	0.6139 (15)	3.9 (4)
H(8)	0.8157 (26)	0.5774 (27)	0.6754 (16)	4.5 (5)
H(9)	0.7100 (30)	0.4784 (24)	0.5804 (18)	4.8 (5)
H(10)	0.6136 (25)	0.5103 (22)	0.8037 (16)	3.7 (4)
H(11)	0.5008 (23)	0.4191 (17)	0.7108 (15)	2.7 (4)
H(12)	0.3407 (27)	0.3387 (25)	0.9524 (18)	4.3 (5)

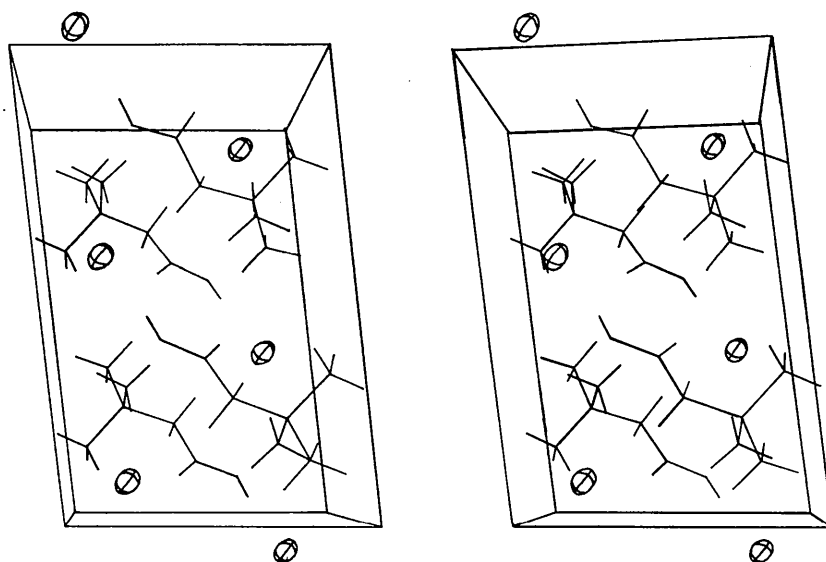


Fig. 2. Stereoscopic view of one unit cell of betaine hydrochloride.

Table 4. Final atomic fractional coordinates and thermal parameters with their standard deviations for Cl, C, N, and O atoms in betaine hydrochloride. The thermal parameters are in units of Å². The temperature factor has the form: $T = \exp[-\frac{1}{4} \sum \sum B_{ij} h_i h_j / (b_i b_j)]$, where h_i is the i th Miller index, b_i is the i th reciprocal axis length, and i and j are cycled 1 through 3.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	0.21472 (6)	0.24207 (5)	1.09234 (4)	3.34 (3)	4.38 (3)	3.59 (3)	-0.30 (2)	1.17 (2)	-0.23 (2)
O(1)	0.37681 (18)	0.39010 (16)	0.90178 (12)	3.60 (7)	4.38 (7)	3.99 (7)	0.52 (6)	1.64 (5)	0.67 (6)
O(2)	0.58012 (19)	0.21083 (15)	0.89939 (12)	4.37 (7)	3.71 (7)	3.95 (7)	0.59 (6)	1.25 (5)	0.96 (5)
N	0.76178 (16)	0.37283 (14)	0.73148 (11)	2.50 (6)	2.77 (8)	2.77 (6)	0.03 (5)	0.40 (5)	0.17 (5)
C(1)	0.74561 (36)	0.22378 (24)	0.67674 (23)	3.48 (11)	3.77 (11)	3.56 (11)	-0.04 (8)	0.85 (11)	-0.70 (9)
C(2)	0.91492 (28)	0.37401 (28)	0.82812 (20)	2.51 (9)	4.45 (12)	4.18 (11)	0.16 (9)	-0.06 (8)	-0.44 (10)
C(3)	0.80332 (35)	0.48153 (27)	0.64025 (22)	3.84 (11)	4.11 (12)	4.74 (12)	0.05 (9)	1.65 (10)	0.91 (10)
C(4)	0.58779 (24)	0.42035 (22)	0.77360 (16)	2.45 (8)	3.09 (9)	3.13 (9)	0.09 (7)	0.31 (7)	-0.09 (8)
C(5)	0.51843 (24)	0.32588 (23)	0.86515 (14)	2.63 (9)	3.45 (10)	2.65 (9)	-0.13 (8)	0.26 (7)	-0.30 (7)

$[\sigma(F^2)]^{1/2}$ if $I \leq \sigma(I)$ and $\sigma(F) = F - [F^2 - \sigma(F^2)]^{1/2}$ if $I > \sigma(I)$. Johnson's (1965) ORTEP program was used for the stereoscopic pictures and as an aid in the thermal analysis.

Structure determination and refinement

Because at the time we were not aware of Clastre's (1964) report, the structure was solved independently. The chlorine-chlorine vectors were evident in a Patterson map, but their interpretation was ambiguous. The y coordinate of chlorine is near $\frac{1}{4}$; therefore, the inversion vector $(2x, 2y, 2z)$ and the screw-axis vector $[2x, \frac{1}{2}, 2(z + \frac{1}{4})]$ both appear in the Harker section at $y = \frac{1}{2}$. The ambiguity escaped notice, and by bad luck the wrong choice was made. As a result, the chlorine z coordinate was assigned a value which was $\frac{1}{4}$ less than the correct one. A Fourier synthesis phased by this chlorine atom indicated eight other atoms. These nine atoms, some of which were later noticed to be at unacceptable bond distances, gave $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.33$ for all the data but $R = 0.09$ for reflections with both k and l even. This result suggested errors of $\frac{1}{2}$ in some y or z coordinates. Addition of $\frac{1}{2}$ to the y coordinates of three atoms gave more reasonable bond distances and decreased R to 0.31, but calculation of interatomic distances showed that molecules related by the inversion center were too close together, with some atoms less than 2Å apart. Therefore, the entire molecule was moved one-fourth of the unit cell in the z direction, at which point R dropped to 0.10.

After the thermal motion of the chlorine atom was approximated by an ellipsoidal anisotropic model, a Fourier difference synthesis revealed the positions of the twelve hydrogen atoms among the highest seventeen peaks. The hydrogen atoms were given individual isotropic temperature factors and all other atoms were given anisotropic temperature factors. The R value dropped to 0.027. The values of $|F_o|/|F_c|$ for the reflections of highest intensity were all less than 1.0. Therefore, an extinction correction of the form $F'_o = F_o (1.0 + cI)$, where $c = 2 \times 10^{-8}$, was applied to give a maximum correction of 5% for the strongest reflection, and R dropped to 0.026.

Up to this point, the atomic scattering factors of Cl⁻ and neutral N had been used. Two other possibilities were tried. The first, with N⁺ and Cl⁻, gave an R value of 0.032, and the second, with both N and Cl neutral, gave an R value of 0.027; the largest shifts in the atomic positions and bond distances were all less than one third of the respective standard deviations. All further discussion will be for N neutral and Cl⁻ atoms. The final weighted R_2 value was 0.034 and the standard deviation of an observation of unit weight was 1.33. The largest shift of any parameter in the final least-squares refinement was less than one per cent of its standard deviation. There was no systematic trend in $|F_o|/|F_c|$ as a function of either 2θ or the intensity. The highest peak on the final difference calculation was 0.11 e.Å⁻³.

Table 5. *Intramolecular distances in betaine hydrochloride*

Standard deviations have been estimated by the method of least squares and are indicated in parentheses.

	Distance		Distance
N—C(1)	1.496 (3) Å	C(3)—H(7)	0.95 (2) Å
N—C(2)	1.498 (3)	C(3)—H(8)	0.96 (2)
N—C(3)	1.504 (3)	C(3)—H(9)	0.92 (2)
N—C(4)	1.497 (2)	C(4)—H(10)	0.90 (2)
C(4)—C(5)	1.500 (3)	C(4)—H(11)	0.91 (2)
C(5)—O(1)	1.316 (2)	O(1)—H(12)	0.82 (2)
C(5)—O(2)	1.193 (2)	H(12)···Cl	2.15 (2)
C(1)—H(1)	0.95 (2)	O(1)···Cl	2.955 (2)
C(1)—H(2)	0.92 (2)	O(2)···N	2.893 (2)
C(1)—H(3)	0.91 (2)	O(2)···C(1)	2.979 (3)
C(2)—H(4)	0.98 (2)	O(2)···C(2)	3.090 (3)
C(2)—H(5)	0.93 (2)	O(2)···H(1)	2.38 (2)
C(2)—H(6)	0.95 (2)	O(2)···H(4)	2.44 (2)

Results and discussion

A stereoscopic view of one molecule, which shows the numbering scheme of the atoms, is presented in Fig. 1. The observed structure factor amplitudes $|F_o|$ as well as the final calculated structure factors $|F_c|$ are listed in Table 2. The final positional and thermal parameters for the hydrogen atoms are given in Table 3 while those for the non-hydrogen atoms are given in Table 4.

The atomic positions found in this investigation differed from those of Clastre (1964) by as little as 0.02 Å for the chlorine atom to as much as 0.16 Å for atom C(2). The mean difference was 0.07 Å, which is more than twenty times the estimated standard deviations in this investigation. Clastre made no statement concerning the precision of his results.

Selected intramolecular distances and angles are listed in Tables 5 and 6 respectively. Because of thermal motion, the observed bond distances tend to be less than the time-average distances between atoms. Our ignorance of the phase relations of thermal motion prevents an unambiguous correction for this effect, but some estimates have been made on the basis of a riding model. For bonds N—C(1), N—C(3), C(5)—O(1) and C(5)—O(2), for which this model seems reasonably consistent with the observed thermal parameters, the corrections fall in the range 0.010 to 0.018 Å.

Table 6. *Intramolecular bond angles for betaine hydrochloride*

	Angles
C(1)—N—C(2)	109.75 (16)°
C(1)—N—C(3)	108.31 (16)
C(1)—N—C(4)	111.70 (15)
C(2)—N—C(3)	108.50 (15)
C(2)—N—C(4)	111.41 (14)
C(3)—N—C(4)	107.04 (15)
N—C(4)—C(5)	116.35 (15)
C(4)—C(5)—O(1)	108.96 (17)
C(4)—C(5)—O(2)	125.97 (17)
O(1)—C(5)—O(2)	125.07 (17)
C(5)—O(1)—H(12)	108.4 (15)
O(1)—H(12)···Cl	168.4 (21)

The orientations of the methyl and methylene groups are very nearly staggered around each of the four C—N bonds, the departures from an entirely staggered conformation being only 9.4° for N—C(1), 4.3° for N—C(2), 1.6° for N—C(3) and 1.9° for N—C(4). The plane of the carboxyl group is at an angle of 6.7° to that of atoms N, C(4) and C(5). The result is that the entire cation conforms within about 0.1 Å to the symmetry of a non-crystallographic mirror plane. The mirror plane passes through (or near) atoms H(12), O(1), O(2), C(5), C(4) N, C(3) and H(7) and relates H(8) to H(9), H(10) to H(11), and the methyl groups C(1) to C(2). The carboxyl group is planar within experimental error.

The carboxyl group is twisted around bond C(4)—C(5) in such a way that atom O(2) is almost as close to and O(1) as far from, the nitrogen atom in the same molecule as is possible. This results in an extended shape for the molecule in which the carboxyl hydrogen atom is remote from the positively charged ammonium group and thus can easily hydrogen bond to the chloride ion. The O—H···Cl angle is $168 \pm 2^\circ$, and the O···Cl distance of 2.955 ± 0.002 Å is much shorter than, for example, the O···Cl distance of 3.03 ± 0.02 Å in choline chloride (Senko & Templeton, 1960).

The molecular packing is shown in Fig. 2, and the closest intermolecular approaches are listed in Table 7. For the bonded hydrogen atoms of this molecule, the center of gravity of the electron distribution as determined by X-ray diffraction is somewhat removed from the equilibrium nuclear position. Therefore, the intramolecular C—H and O—H distances listed in Table 5 are systematically shorter and the intermolecular packing distances in Table 7 involving hydrogen atoms are systematically longer by approximately 0.1 Å than the equilibrium internuclear separation as would be determined by neutron diffraction, for example.

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Table 7. *Shortest intermolecular distances for crystals of betaine hydrochloride*

The equivalent position numbers are 1 for x, y, z ; 2 for $x, \frac{1}{2} - y, \frac{1}{2} + z$; 3 for $-x, -y, -z$; and 4 for $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

Atom 1	Atom 2	Distance	Position number of atom 2	Atom 2: translations in			
				x	y	z	
Cl	H(10)	2.79 (2) Å	3	1	1	2	
	H(11)	2.80 (2)	2	0	0	0	
	H(2)	2.88 (2)	2	-1	0	0	
	H(6)	2.88 (2)	3	1	1	2	
	H(7)	2.89 (2)	2	-1	0	0	
	H(5)	3.02 (2)	2	-1	0	0	
	H(8)	3.18 (2)	3	1	1	2	
	H(3)	3.20 (2)	2	0	0	0	
	H(9)	3.21 (2)	4	1	-1	1	
	H(4)	3.26 (2)	1	-1	0	0	
	H(8)	3.42 (2)	4	1	-1	1	
	C(1)	O(1)	3.270 (3)	4	1	-1	1
		O(2)	3.348 (3)	2	0	0	-1
C(2)	O(1)	3.440 (3)	1	1	0	0	
C(4)	O(2)	3.459 (3)	4	1	0	1	
O(1)	O(1)	3.396 (3)	3	1	1	2	

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The Crystal and Molecular Structure of 4-Formylpyridine Thiosemicarbazone

BY R. RESTIVO AND GUS J. PALENIK

Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada

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4-Formylpyridine thiosemicarbazone, $C_7H_8N_4S$, forms pale yellow, acicular, monoclinic crystals. The space group is $P2_1/n$ and there are four molecules in the unit cell of dimensions $a = 7.238$, $b = 13.949$, $c = 8.419$ Å and $\beta = 90.9^\circ$. The structure was solved from a minimum Patterson function and refined by Fourier syntheses and full-matrix least-squares methods. The final residual, R , for the 1339 observed reflections measured with a diffractometer is 0.055. The C-S bond distance of 1.678 (2) Å is comparable with that found in similar compounds. The N-N bond length of 1.365 (6) Å is interpreted in terms of resonance of the side chain with the pyridine ring. The molecules are linked by N-H...S hydrogen bonds into dimer-like units which are held together by N-H...N hydrogen bonds.

Introduction

Thiosemicarbazones possess a wide range of biological activity depending on the parent aldehyde or ketone. Hagenbach & Gysin (1952) reported that 4-formylpyridine thiosemicarbazone (4FPYTSC) showed tuberculostatic activity; subsequently, Jones, Slack, Squires & Wooldridge (1965) reported that it showed antiviral activity as well. However, French & Blanz (1966)

showed that 4FPYTSC shows no carcinostatic activity whereas they found that 2-formylpyridine thiosemicarbazone was a tumor inhibitor. Apparently the position of the thiosemicarbazone group on the pyridine nucleus dictates the biological activity of formylpyridine thiosemicarbazones. Whether the differences in biological activities are related to electronic or steric effects is debatable. Therefore, a crystal structure study of 4FPYTSC was undertaken as part of a broad pro-