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SOLID STATE STRUCTURE AND CHEMISTRY OF THE CHOLINE HALIDES AND THEIR ANALOGUES. REDETERMINATION OF THE BETAINE HYDROCHLORIDE STRUCTURE, $\left[(CH_3)_3NCH_2COOH\right]^+Cl^-$

Mark S. Fischer, David H. Templeton, and Allan Zalkin

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Lawrence Radiation Laboratory
Berkeley, California 94720

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SOLID STATE STRUCTURE AND CHEMISTRY OF THE CHOLINE HALIDES AND THEIR ANALOGUES. REDETERMINATION OF THE BETAINE HYDROCHLORIDE STRUCTURE, $[(CH_3)_3NCH_2COOH]^+Cl^-$

Mark S. Fischer, David H. Templeton, and Allan Zalkin

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The crystal structure of betaine hydrochloride, $[(CH_3)_3NCH_2COOH]^+ Cl^-$, 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 $P2_1/c$, with cell parameters a = 7.428 Å, b = 9.108 Å, c = 11.550 Å, and $\beta = 96.71^\circ$. 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 of 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 to the hydrogen bonding in choline chloride.

The structures of choline $[(CH_3)_3NCH_2CH_2OH]^+ X^-$ and betaine $[(CH_3)_3NCH_2COOH]^+ X^-$ compounds are of interest because of both the unusual radiation sensitivity of choline chloride (Tolbert, Adams, Bennett, Hughes, Kirk, Lemmon, Noller, Ostwald and Calvin, 1953) and the frequent occurence of these compounds in biological systems. They are compphents 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 and Templeton, 1960), muscarine iodide (Jellinek, 1957) and acetylcholine bromide (Canepa, Pauling and 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 published 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 $\underline{h}00$, $0\underline{k}0$, and $00\underline{\ell}$ reflections, as measured on a manually operated General Electric XRD-5 diffractometer. The alpha doublet (λ = 1.5405 Å for $CuK\alpha_1$) 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 $\underline{b}$ axis, and the β angle was obtained directly from the angle on the φ circle between the $\underline{h}00$ and the $00\underline{\ell}$ reflections. The unit cell parameters (at 23°) are shown in Table 1. The absence of reflections $\underline{h}0\underline{\ell}$ with $\underline{\ell}$ odd and $0\underline{k}0$ with $\underline{k}$ odd indicate the space group $P2_1/c$. The crystal, which was mounted on the needle axis, measured 0.09 x 0.09 x 0.43 mm. The four most prominent faces were the (100), (001), ($\bar{1}00$) and ($00\bar{1}$). The observed density of 1.314 ± .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 $Å^3$.

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 receiving 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 coefficient μ is 39 cm^{-1} (for CuKα). 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: $I = I_{gross} - (t_I/2t_B)(B_1 + B_2)$ and $\sigma^2(I) = I_{gross} + (t_I/2t_B)^2(B_1 + B_2)$, 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 $\sigma(\bar{I})$, the standard deviation of the mean, was calculated from $\sigma_L(I)$ equal to the larger of $[\Sigma(I_i-\bar{I})^2]^{\frac{1}{2}}/(n-1)$ and $[\Sigma\sigma^2(I_i)]^{\frac{1}{2}}/n$ by using the relationship $\sigma^2(\bar{I}) = \sigma_L^2(I) + (pI)^2$, 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 and Mann (1968) for the Cl^-, Cl, O, N and C atoms and those of Stewart, Davidson and Simpson (1965) for the hydrogen atoms. The scattering factor for the N^+ atom was calculated from the scattering factor of N^{+3} (Hurst and Matson, 1959) by using the relationship $f(N^+) = [2f(N) + f(N^{+3})]/3$. For the chlorine atom the anomalous dispersion corrections of Cromer (1965) were used. The function minimized in the least-squares refinements was $R_2^2 = \Sigma \underline{w}(|F_o|-|F_c|)^2/\Sigma \underline{w}|F_o|^2$. In the early stages of refinement, the weights $\underline{w}$ 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 $\sigma(\bar{I})$: $\sigma(F^2) = (Lp)^{-1}\sigma(\bar{I})$, $\sigma(F) = [\sigma(F^2)]^{\frac{1}{2}}$ if $I \leq \sigma(\bar{I})$ and $\sigma(F) = F - [F^2-\sigma(F^2)]^{\frac{1}{2}}$ if $I > \sigma(\bar{I})$. Johnson's ORTEP program (1965) 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 report (1964), 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 map 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 $R = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.33$ 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 2 Å 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 map 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 electrons Å^{-3}.

Results and Discussion

A stereoscopic view of one molecule, which shows the numbering scheme of the atoms, is presented in Figure 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.

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 ± 2°, and the O···Cl distance of 2.955 ± .002 Å is much shorter than, for example, the O···Cl distance of 3.03 ± .02 Å distance in choline chloride (Senko and Templeton, 1960).

The molecular packing is shown in Figure 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.

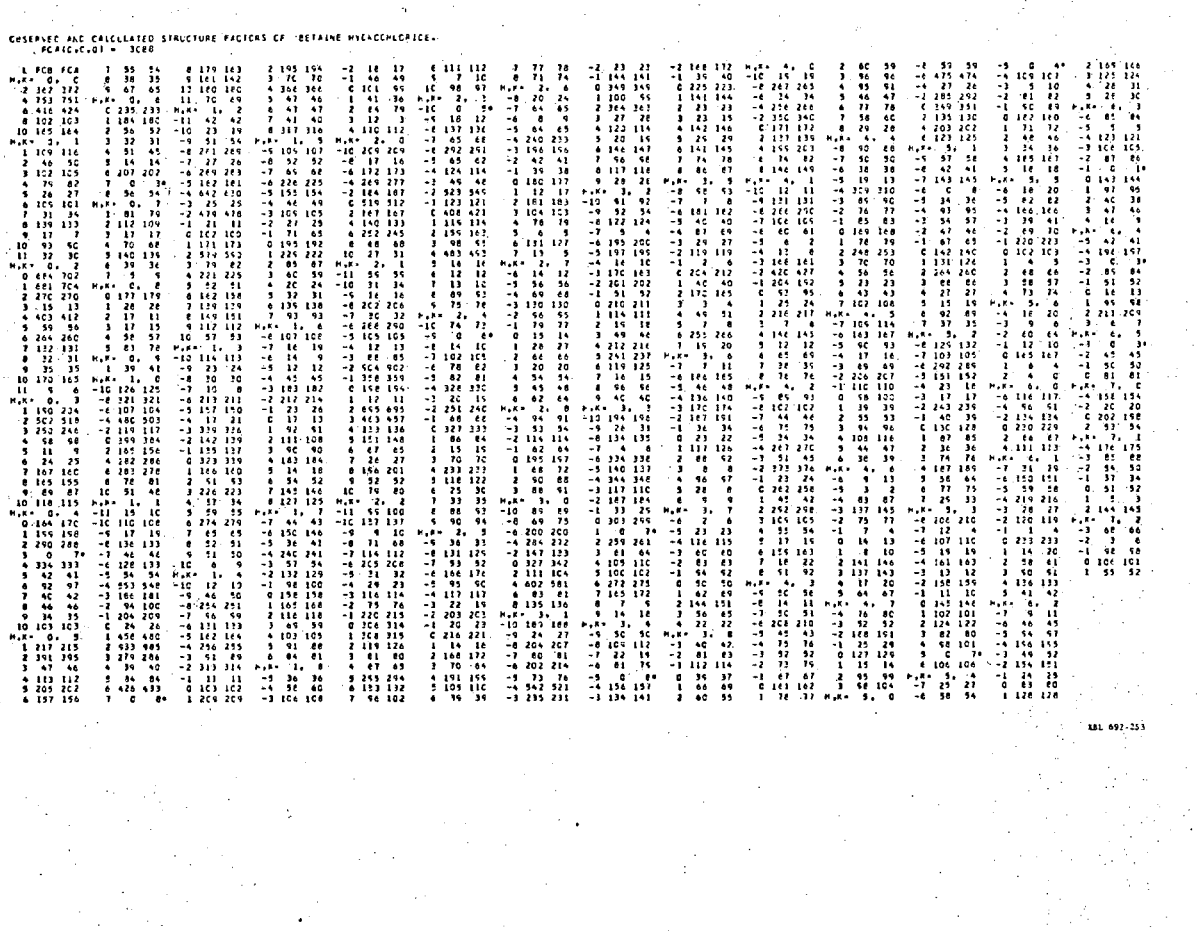
This work has been performed under the auspices of the U.S. Atomic Energy Commission. We thank Dr. R.M. Lemmon for supplying us with his crystals and Prof. M. Calvin for the support of part of this work.

Table 1. Unit Cell Parameters

	This Work	Clastre
a	7.428 ± .002 Å	7.45 ± .02 Å
b	9.108 ± .005	9.15 ± .02
c	11.550 ± .003	11.65 ± .02
β	96.71 ± .03	97.0

Table 2. Observed and Calculated Structure Factor Amplitudes of Betaine Hydrochloride

Asterisks indicate zero-weighted data.



OBSERVED AND CALCULATED STRUCTURE FACTORS OF BETAINE HYDROCHLORIDE.
PCA(C,H,O) = 3C8O

L	FOB	FCA	L	FOB	FCA	L	FOB	FCA	L	FOB	FCA	L	FOB	FCA	L	FOB	FCA	L	FOB	FCA	L	FOB	FCA	L	FOB	FCA	L	FOB	FCA
			7	55	54	8	179	183	2	195	194	-2	18	17	6	111	112	3	77	78	-2	23	23	-2	168	172	H,K=	4, 0	2	80	59	-8	53	59	-5	0	4*	2	169	166
H,K=	0, 0	8	38	35	9	161	142	3	70	70	-1	46	49	5	7	10	8	71	74	-1	144	141	-1	39	40	-10	15	19	3	96	96	-6	475	474	-4	109	107	3	125	124
2	367	372	9	67	65	12	180	180	4	366	366	0	101	99	10	98	97	H,K=	2, 6	0	349	349	0	225	223	-8	267	269	4	95	91	-4	27	26	-3	5	10	4	28	31
4	753	751	H,K=	0, 8	11	70	69	5	47	46	1	41	36	H,K=	2, 7	-8	20	24	1	100	99	1	141	144	-4	34	34	5	46	47	-2	201	202	-2	81	82	5	25	30
6	416	424	0	235	233	H,K=	1, 8	6	47	47	2	84	79	-10	0	5*	-7	64	65	2	364	363	2	23	23	-4	256	266	6	77	78	0	349	351	-1	90	89	H,K=	4, 3
8	102	103	1	184	180	-11	42	42	7	41	40	3	12	3	-9	18	12	-6	8	9	3	27	28	3	23	15	-2	350	340	7	58	60	2	107	110	-6	85	84
10	165	164	2	56	57	-10	23	19	8	317	316	4	110	112	-8	137	136	-5	64	65	4	123	114	4	142	146	0	171	172	8	29	28	4	203	202	1	71	72	-5	5	5
H,K=	3, 1	3	32	31	-9	51	54	H,K=	1, 9	H,K=	2, 0	-7	65	68	-4	240	233	5	20	19	5	25	29	2	127	135	H,K=	4, 4	4	123	125	2	49	46	-4	123	121
1	109	116	4	51	45	-8	271	269	-5	105	107	-10	269	269	-6	292	291	-3	196	196	6	146	147	6	141	145	4	199	203	-8	90	88	H,K=	5, 1	3	34	36	-9	106	105
2	46	50	5	14	14	-7	27	26	-8	57	52	-8	17	16	-5	65	62	-2	42	41	7	56	58	7	74	78	6	34	32	-7	50	50	-5	57	58	4	105	107	-2	87	86
3	102	105	6	207	202	-6	269	263	-7	65	68	-6	172	173	-4	124	114	-1	39	38	8	117	118	8	86	87	8	146	149	-6	38	38	-6	42	41	5	18	18	-1	0	1*
4	79	82	7	0	3*	-5	162	161	-6	226	225	-4	269	277	-1	49	48	0	180	177	9	28	28	H,K=	3, 0	H,K=	4, 1	-5	19	13	-7	143	145	H,K=	5, 5	0	143	144
5	26	27	8	56	54	-4	612	610	-5	155	154	-2	186	187	-2	523	545	1	12	17	H,K=	3, 2	-8	55	53	-10	12	11	-4	379	310	-6	0	8	-6	18	20	1	97	96
6	109	101	H,K=	0, 7	-3	25	25	-4	46	49	0	519	512	-1	123	121	2	181	183	-10	41	42	-7	7	8	-9	131	131	-3	85	90	-5	34	36	-5	82	82	2	40	38
7	31	34	1	81	79	-2	479	478	-3	109	105	2	167	167	0	408	421	3	104	103	-9	52	54	-6	181	182	-8	266	270	-2	76	77	-4	93	95	-4	166	166	3	47	46
8	139	133	2	112	109	-1	21	11	-2	27	25	4	140	133	1	116	114	4	78	79	-8	122	124	-5	42	40	-7	106	105	-1	85	83	-2	54	57	-3	39	41	4	16	9
9	17	7	3	17	17	0	102	100	-1	71	65	4	252	245	2	159	162	5	6	5	-7	5	4	-4	87	89	-6	60	61	0	169	168	-2	47	46	-2	69	70	H,K=	6, 4
10	93	90	4	70	68	1	171	173	0	195	192	6	88	88	3	98	95	6	131	127	-6	195	200	-3	29	27	-5	8	2	1	78	79	-1	67	65	-1	220	223	-5	42	41
11	32	30	5	140	139	2	519	550	1	225	222	10	27	31	4	483	452	7	19	9	-5	197	195	-2	119	119	-4	12	6	2	248	253	0	142	140	0	102	103	-4	194	197
H,K=	0, 2	6	39	34	3	79	82	2	85	87	H,K=	2, 1	5	16	16	H,K=	2, 7	-4	16	10	-1	2	6	-3	168	161	3	70	70	1	131	126	1	4	5	-3	0	3*
0	684	702	7	9	9	4	221	225	3	60	59	-11	56	55	4	12	12	-6	14	12	-3	170	163	0	224	212	-2	420	427	4	50	56	2	264	260	2	68	66	-2	85	84
1	681	704	H,K=	0, 8	9	52	51	4	20	24	-10	31	34	7	13	10	-5	56	56	-2	201	202	1	40	40	-1	204	192	5	23	23	3	88	86	3	58	57	-1	51	52
2	270	270	0	177	179	0	162	158	5	32	31	-9	36	36	8	89	93	-4	69	68	-1	51	52	2	170	165	0	52	55	6	43	43	4	27	27	4	73	74	0	16	13
3	15	13	1	28	28	7	129	129	6	135	138	-8	202	206	9	75	78	-3	130	130	0	210	211	3	3	4	1	25	24	7	102	106	5	15	19	H,K=	5, 6	1	95	98
4	403	412	2	17	11	8	149	151	7	93	93	-7	30	32	H,K=	2, 4	-2	56	55	1	114	111	4	49	51	2	216	217	H,K=	4, 5	0	92	89	-4	18	20	2	211	209
5	59	56	3	17	15	9	112	112	H,K=	1, 6	-6	266	290	-10	74	72	-1	79	77	2	19	18	5	7	8	3	7	6	-7	105	114	7	37	35	-3	9	0	3	6	7
6	264	260	4	58	57	10	57	53	-8	107	108	-5	105	109	-5	0	0*	0	15	14	3	49	46	6	252	266	4	142	143	-6	163	167	H,K=	5, 7	-2	60	64	H,K=	6, 5
7	132	131	5	81	78	H,K=	1, 3	-7	16	19	-4	12	13	-8	14	10	1	28	27	4	212	210	7	19	20	5	12	12	-5	90	93	-8	125	132	-1	12	10	-3	0	3*
8	32	31	H,K=	0, 9	-10	114	113	-6	14	9	-3	88	85	-7	102	105	2	66	66	5	241	237	H,K=	3, 6	4	65	69	-4	17	16	-7	103	105	0	165	167	-2	45	45
9	35	35	1	39	41	-9	23	24	-5	12	12	-2	504	902	-6	78	82	3	20	20	6	119	125	-7	7	11	7	38	35	-3	89	89	-4	292	289	1	6	4	-1	50	50
10	170	165	H,K=	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	76	-2	226	227	-5	151	152	2	4	0	0	81	81
11	9	6	-10	126	125	-7	10	8	-3	183	182	0	158	154	-4	328	332	5	45	48	8	96	96	-5	46	48	H,K=	4, 2	-1	110	110	-4	23	18	H,K=	6, 0	H,K=	7, 0
H,K=	0, 3	-8	321	321	-6	213	211	-2	212	214	1	12	11	-3	20	15	6	62	64	9	40	40	-4	136	140	-5	85	93	0	58	100	-3	17	17	-6	116	117	-4	158	154
1	150	224	-6	107	104	-5	157	150	-1	23	26	2	655	695	-2	251	240	H,K=	2, 8	H,K=	3, 3	-3	170	174	-8	102	102	1	39	39	-2	243	239	-4	96	51	-2	20	20
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4	58	58	0	359	384	-2	142	139	2	111	108	5	151	148	1	86	84	-2	114	114	-8	134	135	0	23	22	-5	34	34	4	108	116	1	87	85	2	66	67	H,K=	7, 1
5	11	9	2	165	156	-1	155	137	3	90	90	6	67	65	2	15	15	-1	62	64	-7	4	8	1	117	126	-4	267	270	5	44	47	2	36	36	-4	111	113	-4	174	175
6	24	25	4	282	286	0	323	339	4	143	144	7	24	27	3	70	70	0	195	197	-6	374	338	2	88	92	-7	51	45	6	36	39	3	74	74	H,K=	6, 1	-3	85	88
7	107	100	6	283	276	1	166	160	5	14	18	8	156	201	4	233	233	1	68	72	-5	140	137	3	8	8	-2	333	376	H,K=	4, 6	4	187	189	-7	31	39	-2	54	50
8	165	155	8	76	81	2	51	53	6	54	52	9	52	52	5	118	122	2	90	88	-4	344	348	4	96	97	-1	23	24	-6	9	13	5	36	64	-6	150	151	-1	37	34
9	89	87	10	51	48	3	226	223	7	145	146	10	79	80	6	75	90	3	88	91	-3	117	110	5	28	0	0	262	250	-5	3	2	6	77	75	-5	59	58	0	51	52
10	118	115	H,K=	1, 1	4	17	14	8	127	125	H,K=	2, 2	7	33	35	H,K=	3, 0	-2	187	184	6	9	9	1	45	42	-4	83	87	7	25	33	-4	219	216	1	5	3
H,K=	0, 4	-11	15	10	5	59	55	H,K=	1, 7	-11	55	100	8	88	92	-10	89	89	-1	33	25	H,K=	3, 7	2	252	298	-3	137	145	H,K=	5, 3	-3	78	27	2	144	145
0	164	170	-10	110	108	6	274	279	-7	44	43	-10	137	137	9	90	94	-8	69	75	0	303	299	-6	2	6	3	105	105	-2	75	77	-6	208	210	-2	120	119	H,K=	7, 2
1	159	158	-9	17	19	7	65	65	-6	150	148	-9	4	10	H,K=	2, 9	-8	200	200	1	0	3*	-5	23	23	4	53	54	-1	7	4	-3	12	4	-1	1	4	-3	88	86
2	290	288	-8	136	133	8	52	51	-5	36	41	-8	71	68	-4	36	33	-4	284	232	2	259	261	-4	116	115	5	17	19	0	14	13	-6	107	110	0	233	233	-2	3	6
3	0	7*	-7	46	46	9	51	50	-4	240	241	-7	114	112	-8	131	125	-2	147	123	3	61	64	-3	60	60	6	159	163	1	8	10	-5	19	19	1	14	20	-1	98	98
4	334	333	-6	128	133	10	0	9	-3	57	54	-6	205	208	-7	93	92	0	327	342	4	109	110	-2	83	83	7	18	22	2	151	146	-4	161	163	2	58	61	0	106	101
5	42	41	-5	54	54	H,K=	1, 4	-2	132	129	-5	31	32	-6	106	176	2	111	104	5	100	102	-3	54	52	8	51	52	2	137	143	-3	13	12	3	40	51	1	55	52
6	92	97	-4	553	548	-10	12	10	-1	98	100	-4	24	23	-5	95	90	4	602	581	6	272	275	0	50	50	H,K=	4, 3	4	17	20	-2	158	159	4	136	133			
7	40	42	-3	106	101	-9	46	50	0	158	158	-3	116	114	-4	117	117	6	83	81	7	165	172	1	42	69	-9	50	56	5	64	67	-1	11	10	5	41	42			
8	46	46	-2	94	100	-8	254	251	1	165	168	-2	75	76	-3	22	19	8	135	136	8	7	9	2	144	151	-8	14	11	H,K=	4, 7	0	145	146	H,K=	6, 2			
9	34	35	-1	204	209	-7	46	50	2	116	118	-1	232	215	-2	203	203	H,K=	3, 1	9	14	18	3	56	65	-7	50	51	-6	76	80	1	107	101	-7	9	11			
10	103	103	0	24	26	-6	131	133	3	69	59	0	306	314	-1	20	13	-10	189	188	H,K=	3, 4	4	22	22	-6	208	210	-3	92	92	2	124	122	-6	46	45			
H,K=	0, 5	1	456	480	-5	162	164	4	103	105	1	308	315	0	216	221	-9	24	27	-9	50	50	H,K=	3, 8	-5	45	43	-2	168	151	3	82	80	-5	54	57			
1	217	215	2	933	985	-4	256	255	5	91	88	2	119	126	1	14	16	-8	204	207	-8	105	112	-3	40	42	-4	75	76	-1	25	24	4	58	101	-4	156	155			
2	391	395	3	279	286	-3	51	49	6	84	81	3	168	172	-7	80	81	-7	22	19	-2	81	83	-3	57	52	0	127	129	5	0	7*	-3	49	52			
3	47	46	4	39	40	-2	313	314	H,K=	1, 8	4	67	65	3	70	64	-6	202	214	-6	81	75	-1	112	114	-2	73	75	1	15	14	4	106	106	-2	154	151			
4	113	112	5	34	34	-1	11	11	-5	36	36	5	255	294	4	191	195	-5	73	76	-5	0	0*	0	36	37	-1	67	67	2	95	99	H,K=	5, 4	-1	14	35			
5	205	202	6	426	433	0	103	102	-4	58	60	6	133	132	5	105	110	-4	542	521	-4	156	157	1	66	69	0	161	162	3	58	104	-7	25	27	0	83	80			
6	157	156	7	0	0*	1	209	209	-3	106	108	7	96	102	6	39	39	-3	235	231	-3	134	141	2	60	55	1	78	77	H,K=	5, 0	-6	58	54	1	128	128			

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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 thermal parameters are in units of square Angstroms. The temperature factor has the form: $T = \exp[-B(\sin\theta/\lambda)^2]$

Atom	x	y	z	B
H(1)	.7362(26)	.1542(25)	.7369(18)	4.6(5)
H(2)	.8486(29)	.2080(21)	.6421(16)	3.3(4)
H(3)	.6466(32)	.2250(20)	.6230(20)	4.1(5)
H(4)	.8855(26)	.3019(24)	.8857(17)	4.0(4)
H(5)	1.0216(28)	.3508(20)	.7967(14)	3.7(4)
H(6)	.9188(27)	.4692(25)	.8622(16)	4.4(5)
H(7)	.9151(28)	.4549(20)	.6139(15)	3.9(4)
H(8)	.8157(26)	.5774(27)	.6754(16)	4.5(5)
H(9)	.7100(30)	.4784(24)	.5804(18)	4.8(5)
H(10)	.6136(25)	.5103(22)	.8037(16)	3.7(4)
H(11)	.5008(23)	.4191(17)	.7108(15)	2.7(4)
H(12)	.3407(27)	.3387(25)	.9524(18)	4.3(5)

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 square Angstroms. The temperature factor has the form: $T = \exp[-\frac{1}{4}\Sigma\Sigma B_{ij}h_i h_j/(b_i b_j)]$, where h_i is the ith Miller index, b_i is the ith reciprocal axis length, and i and j are cycled 1 through 3.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	.21472(6)	.24207(5)	1.09234(4)	3.34(3)	4.38(3)	3.59(3)	-.30(2)	1.17(2)	-.23(2)
O(1)	.37681(18)	.39010(16)	.90178(12)	3.60(7)	4.38(7)	3.99(7)	.52(6)	1.64(5)	.67(6)
O(2)	.58012(19)	.21083(15)	.89939(12)	4.37(7)	3.71(7)	3.95(7)	.59(6)	1.25(5)	.96(5)
N	.76178(16)	.37283(14)	.73148(11)	2.50(6)	2.77(8)	2.77(6)	.03(5)	.40(5)	.17(5)
C(1)	.74561(36)	.22378(24)	.67674(23)	3.48(11)	3.77(11)	3.56(11)	-.04(8)	.85(11)	-.70(9)
C(2)	.91492(28)	.37401(28)	.82812(20)	2.51(9)	4.45(12)	4.18(11)	.16(9)	-.06(8)	-.44(10)
C(3)	.80332(35)	.48153(27)	.64025(22)	3.84(11)	4.11(12)	4.74(12)	.05(9)	1.65(10)	.91(10)
C(4)	.58779(24)	.42035(22)	.77360(16)	2.45(8)	3.09(9)	3.13(9)	.09(7)	.31(7)	-.09(8)
C(5)	.51843(24)	.32588(23)	.86515(14)	2.63(9)	3.45(10)	2.65(9)	-.13(8)	.26(7)	-.30(7)

Table 5. Intramolecular Distances (in Å) in Betaine Hydrochloride

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

Atoms	Distance	Atoms	Distance
N-C(1)	1.496(3)	C(3)-H(7)	0.95(2)
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)

Table 6. Intramolecular Bond Angles (in Degrees) for Betaine Hydrochloride.

Atoms	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)

Table 7. Shortest Intermolecular Distances (in Å) 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)	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

Figure 1. Stereoscopic view of one molecule of betaine hydrochloride.

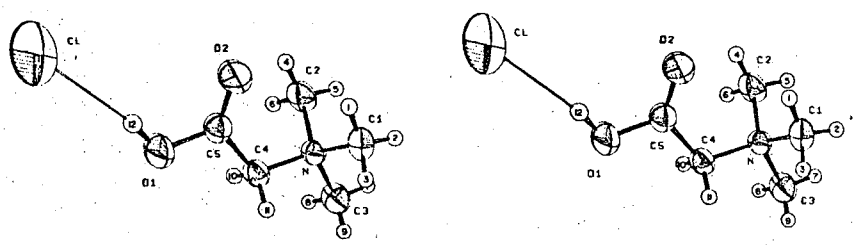
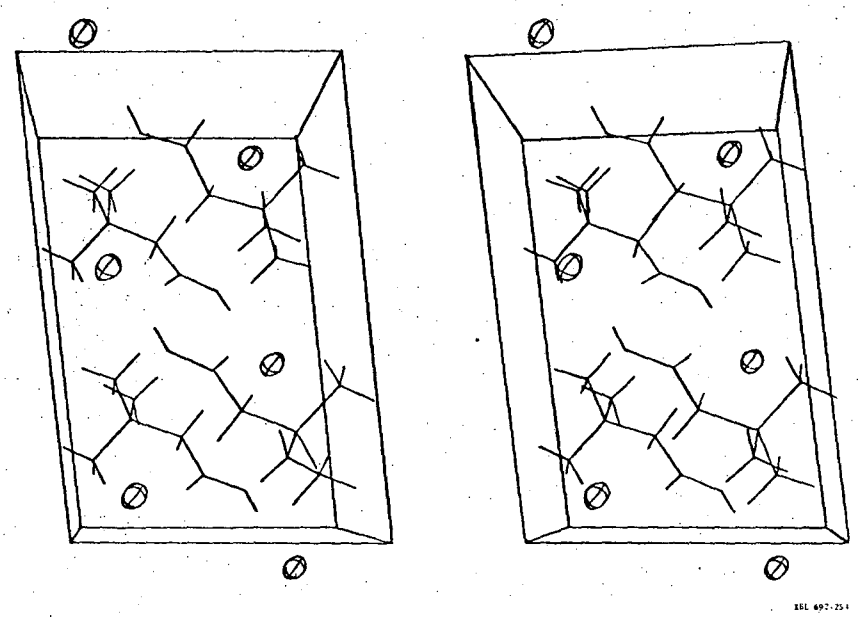


Figure 2. Stereoscopic view of one unit cell of betaine hydrochloride.



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