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SOLID STATE STRUCTURE AND CHEMISTRY OF THE CHOLINE HALIDES AND THEIR ANALOGUES. REDETERMINATION OF THE BETAINE HYDROCHLORIDE STRUCTURE, [(CH)<sup>+</sup>NCH<sub>2</sub>COOH]+Cl<sup>-</sup>"

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

December 1969

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The crystal structure of betaine hydrochloride,  $[(\text{CH}_3)_3\text{NCH}_2\text{COOH}]^+\text{Cl}^-$ , 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  $\text{P}2_1/\text{c}$ , with cell parameters  $a = 7.428 \text{ \AA}$ ,  $b = 9.108 \text{ \AA}$ ,  $c = 11.550 \text{ \AA}$ , 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  $0.16 \text{ \AA}$ . The mean C-N bond length is  $1.499 \pm 0.004 \text{ \AA}$  (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  $[(\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{OH}]^+ \text{X}^-$  and betaine  $[(\text{CH}_3)_3\text{NCH}_2\text{COOH}]^+ \text{X}^-$  compounds are of interest because of both the unusual radiation sensitivity of choline chloride (Tolbert, Adams, Bennett, Hughes, Kirk, Lemon, Noller, Ostwald and Calvin, 1953) and the frequent occurrence of these compounds in biological systems. They are components of complex lipids, and they can act as transmethyating 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  $h00$ ,  $0k0$ , and  $00l$  reflections, as measured on a manually operated General Electric XRD-5 diffractometer. The alpha doublet ( $\lambda = 1.5405 \text{ \AA}$  for  $\text{CuK}\alpha_1$ ) 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  $b$  axis, and the  $\beta$  angle was obtained directly from the angle on the  $\varphi$  circle between the  $h00$  and the  $00l$  reflections. The unit cell parameters (at  $23^\circ$ ) are shown in Table 1. The absence of reflections  $h0l$  with  $l$  odd and  $0k0$  with  $k$  odd indicate the space group  $P2_1/c$ . The crystal, which was mounted on the needle axis, measured  $0.09 \times 0.09 \times 0.43$  mm. The four most prominent faces were the  $(100)$ ,  $(001)$ ,  $(\bar{1}00)$  and  $(00\bar{1})$ . The observed density of  $1.314 \pm .005 \text{ g cm}^{-3}$ , which was determined by flotation in a chloroform-ethylene dichloride mixture, agrees well with the value  $1.313 \text{ g cm}^{-3}$  calculated for a molecular weight of 153.5, for  $Z = 4$ , and for a unit cell volume of  $776 \text{ \AA}^3$ .

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  $\theta$ - $2\theta$  scan was employed. The intensities were measured for all reflections lying within half a sphere in reciprocal space corresponding to d-spacings  $\geq 1.006 \text{ \AA}$  ( $2\theta \leq 100^\circ$ ). 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  $\mu$  is  $39 \text{ cm}^{-1}$  (for CuK $\alpha$ ). 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 the background. For  $n$  measurements of the intensity of a particular reflection ( $n$  was always  $\geq 2$ ), 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  $[\sum(I_i - \bar{I})^2]^{1/2}/(n-1)$  and  $[\sum\sigma^2(I_i)]^{1/2}/n$  by using the relationship  $\sigma^2(\bar{I}) = \sigma_L^2(I) + (pI)^2$ , 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  $\text{Cl}^-$ , Cl, O, N and C atoms and those of Stewart, Davidson and Simpson (1965) for the hydrogen atoms. The scattering factor for the  $\text{N}^+$  atom was calculated from the scattering factor of  $\text{N}^{+3}$  (Hurst and Matson, 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  $\sigma(\bar{I})$ :  $\sigma(F^2) = (I_p)^{-1} \sigma(\bar{I})$ ,  $\sigma(F) = [\sigma(F^2)]^{\frac{1}{2}}$  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  $\frac{1}{2}$ ; therefore, the inversion vector  $(2x, 2y, 2z)$  and the screw axis vector  $(2x, \frac{1}{2}, 2(z+\frac{1}{2}))$  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  $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.33$  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 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  $2\theta$  or the intensity. The highest peak on the final difference calculation was 0.11 electrons  $\text{\AA}^{-3}$ .

## 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  $9.4^\circ$  for N-C(1),  $4.3^\circ$  for N-C(2),  $1.6^\circ$  for N-C(3), and  $1.9^\circ$  for N-C(4). The plane of the carboxyl group is at an angle of  $6.7^\circ$  to that of atoms N, C(4), and C(5). The result is that the entire cation conforms within about  $0.1 \text{ \AA}$  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 $\cdots$ Cl angle is  $168 \pm 2^\circ$ , and the O $\cdots$ Cl distance of  $2.955 \pm .002 \text{ \AA}$  is much shorter than, for example, the O $\cdots$ Cl distance of  $3.03 \pm .02 \text{ \AA}$  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
<u>a</u>	$7.428 \pm .002 \text{ \AA}$	$7.45 \pm .02 \text{ \AA}$
<u>b</u>	$9.108 \pm .005$	$9.15 \pm .02$
<u>c</u>	$11.550 \pm .003$	$11.65 \pm .02$
$\beta$	$96.71 \pm .03$	97.0

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

Asterisks indicate zero-weighted data.

OBSERVED AND CALCULATED STRUCTURE FACTORS OF BETAINES HYDROCHLORIDE. PCF(C2C0) = 3CE0

Table with multiple columns containing numerical data for observed and calculated structure factors, including indices like h, k, l and values for F\_obs and F\_calc.



Table 3. Final Atomic Fractional Coordinates and Thermal Parameters with Their Standard Deviations for Hydrogen Atoms in Retainio 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:  $T = \exp[-B(\sin\theta/\lambda)^2]$

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>B</u>
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:

$T = \exp[-\frac{1}{4}\sum\sum B_{ij}h_ih_j/(b_ib_j)]$ , 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.

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 Petaine Hydrochloride

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

<u>Atoms</u>	<u>Distance</u>	<u>Atoms</u>	<u>Distance</u>
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) <sup>..</sup> Cl	2.15(2)
C(1)-H(1)	0.95(2)	O(1) <sup>..</sup> Cl	2.955(2)
C(1)-H(2)	0.92(2)	O(2) <sup>..</sup> N	2.893(2)
C(1)-H(3)	0.91(2)	O(2) <sup>..</sup> C(1)	2.979(3)
C(2)-H(4)	0.93(2)	O(2) <sup>..</sup> C(2)	3.090(3)
C(2)-H(5)	0.93(2)	O(2) <sup>..</sup> H(1)	2.38(2)
C(2)-H(6)	0.95(2)	O(2) <sup>..</sup> H(4)	2.44(2)

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

<u>Atoms</u>	<u>Angles</u>
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) <sup>••</sup> 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  $-x, \frac{1}{2}+y, \frac{1}{2}-z$ .

<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>	<u>Position Number</u> <u>of Atom 2</u>	<u>Atom 2: Translations in</u>		
				<u>x</u>	<u>y</u>	<u>z</u>
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.

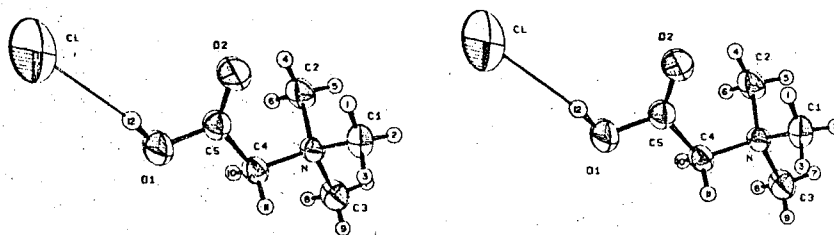
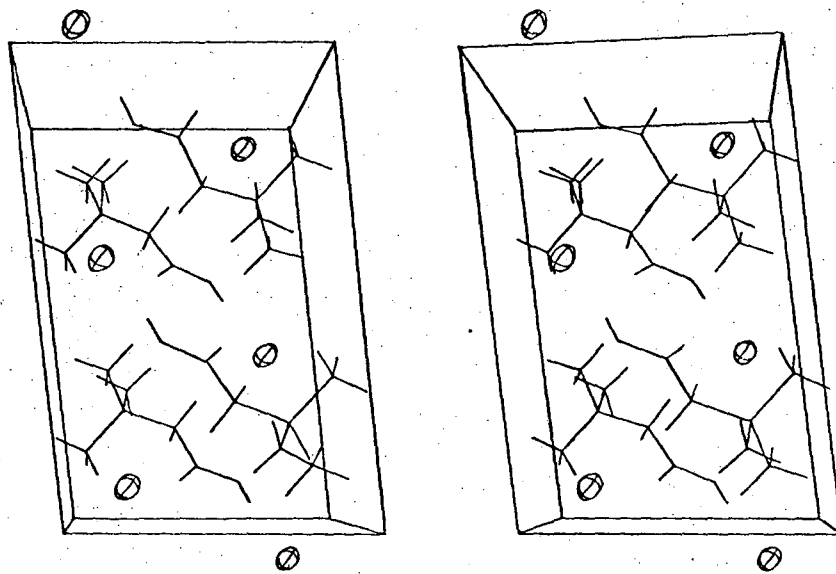


Figure 2. Stereoscopic view of one unit cell of betaine hydrochloride.



EEL 697-254

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