

The Crystal and Molecular Structure of 3-Aminobenzoic Acid Hydrochloride*

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The structure of 3-aminobenzoic acid hydrochloride, $C_7H_7NO_2 \cdot HCl$, has been determined independently in two different laboratories. The compound crystallizes in the triclinic space group $P\bar{1}$, with two molecules per unit cell and with $a=14.706$ (6), $b=5.836$ (3), $c=4.567$ (3) Å, $\alpha=96.22$ (2), $\beta=91.11$ (2) and $\gamma=98.62$ (2)°. The intensity data were collected with Cu $K\alpha$ radiation and the final R indices are 0.043 (1262 diffractometer data) and 0.096 (1238 photographic data). A comparison of the parameters indicates that their standard deviations have been underestimated by a factor of ~ 1.3 – 1.4 . Hydrogen-bonded dimers are formed through the carboxylic acid groups of centrosymmetrically related molecules; the hydrogen atom is disordered, being approximately equally distributed over the sites associated with the two oxygen atoms.

Introduction

We report here the results of two independent investigations of the crystal structure of 3-aminobenzoic acid hydrochloride. Both investigations were initiated in 1965, with a view toward obtaining further understanding of the influence of polar substituents on the geometry of the benzene ring and of the nature of the C–N bond in various systems. In both cases the original investigation was based on photographic data; subsequently, Arora & Sundaralingam collected new data on an automated diffractometer. Our results, then, afford further opportunity to compare atomic parameters resulting from the two methods of data collection. The agreement is, in general, comforting.

Experimental

1. Arora & Sundaralingam (AS)

Needle-shaped crystals, elongated along c , were obtained by evaporation of a solution of 3-aminobenzoic acid in hydrochloric acid. The initial data were recorded on Weissenberg photographs of layers 0–3 about c and the zero layers about a and b , using Cu $K\alpha$ radiation. Corrections for Lorentz and polarization factors and cross-correlation yielded 580 independent F^2 values. The structure was solved from Patterson and electron-density maps and refined by least-squares calculations to an R index of 0.15.

Additional data, including improved cell dimensions, were subsequently obtained on a Picker four-circle

diffractometer, again using Ni-filtered Cu $K\alpha$ radiation. All reflections out to a 2θ limit of 132° ($d_{\min}=0.85$ Å) were collected from a crystal measuring $0.2 \times 0.2 \times 0.4$ mm, mounted along the c axis. The procedure involved a θ – 2θ scan at a speed of 2° (in 2θ) per min, 30 s background counts at both extremes, and the monitoring of a check reflection at regular intervals throughout the data collection. The check reflection showed a maximum variation of 5% during the period of data collection. The intensities were corrected for Lorentz and polarization effects, but not for absorption ($\mu=39.9$ cm $^{-1}$). Altogether, 1331 independent reflections were scanned, of which 54 had intensities, I , less than $1.4 \sigma(I)$.

Refinement of the heavy atoms alone with anisotropic temperature factors led to an R index of 0.068. A difference map (Fig. 1) then indicated the positions of the hydrogen atoms, and suggested an approximately equal distribution of the carboxyl hydrogen atom between two sites, one on each oxygen atom. Occupancy factors of these two sites were included in subsequent refinement cycles.

Final refinement included, in a single matrix, 138 parameters: coordinates and anisotropic temperature factors for the 11 heavy atoms, coordinates and isotropic temperature factors for the seven ordered hydrogen atoms and the two disordered sites, the two population parameters, and a scale factor. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, with $1/w = 2.57 - 0.0054|F| + 0.0019|F|^2$; this latter expression was chosen so as to lead to a uniform distribution of discrepancies $w(F_o - F_c)^2$. Reflections with $I < 1.4\sigma(I)$ were assigned zero weight, as were 15 intense, low-angle reflections presumably suffering from extinction. Scattering factors were from Hoerni & Ibers (1954) for C, N and O, Cromer & Waber (1965) for Cl^- , and Stewart, Davidson & Simpson (1965) for

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H. The final values for the occupational parameters were 0.59 ± 0.05 for H(8) and 0.37 ± 0.05 for H(9). The final R index ($= \sum ||F_o| - |F_c|| / \sum |F_o|$) was 0.043 for 1262 reflections of non-zero weight.

2. Dancz, Stanford & Marsh (DSM)

Crystals were formed by slow cooling of a solution of 3-aminobenzoic acid in hot, concentrated hydrochloric acid. They were needles, elongated along c and several mm in length; many of them were twinned or cracked. They were stable in air and under irradiation for long periods.

Two crystals were used for the data collection: a short needle mounted along the c axis and an approximately cube-shaped fragment mounted along b . Five reciprocal lattice constants – a^* , b^* , c^* , β^* and γ^* – were obtained from zero-level Weissenberg photographs of the $hk0$ and $h0l$ nets, recorded with the film in the asymmetric (Straumanis) position. The sixth parameter, α^* , was measured on a precession photograph of the $0kl$ net. Intensities were estimated visually from multiple-film equi-inclination Weissenberg photographs of layers 0–3 about c and 0–4 about b , taken with Ni-filtered $Cu K\alpha$ radiation. Each observation was assigned a standard deviation according to the expression given by Sharma & McConnell (1965). Film correlation factors were obtained by a least-squares procedure (Duchamp & Marsh, 1969); intensities were corrected for Lorentz and polarization factors, but not for absorption. The final averaging process yielded intensities and standard deviations for 1497 independent reflections, of which 256 were too weak to be observed above background.

The structure solution was exactly parallel to that of AS: Patterson and electron density maps followed by least-squares refinement. A difference map indicated the positions of all the hydrogen atoms, and again suggested that the proton of the CO_2H group was equally distributed over two sites. Final refinement included, in a single matrix, 112 parameters: coordinates and anisotropic temperature parameters for the 11 heavy atoms, coordinates for the four hydrogen atoms bonded directly to the benzene ring, and a scale factor. The coordinates of the four remaining hydrogen atoms were not adjusted, nor were the temperature factors of any of the hydrogen atoms; the population factors of the two sites H(8) and H(9) were taken as 0.5.

The quantity minimized was $\sum w(F_o^2 - F_c^2)^2$, with weights w taken equal to $1/\sigma^2(F_o^2)$ as derived during the data-reduction process (Duchamp & Marsh, 1969). Unobserved reflections were included only if $F(\text{calc})$ was greater than the observation threshold of $F(\text{obs})$. In the final cycle the maximum parameter shift was 0.12σ . The final R index was 0.096 for 1238 reflections.

Comparison of the results

The unit-cell dimensions and other crystal data are given in Table 1. Agreement between the two sets of

values is only fair. The largest discrepancy is in the values of α , and is almost surely caused by the inaccuracy in the procedure of DSM of measuring α^* directly from a precession film. None of the other discrepancies is more than marginally significant; while we cannot rule out the possibility of small impurities causing real differences in the two batches of crystals, it is more likely that one or both sets of investigators have been slightly optimistic in assigning error estimates.

Table 1. *Crystal data for 3-aminobenzoic acid hydrochloride*, $C_7H_7O_2N \cdot HCl$

Standard deviations in the last significant figure are shown in parentheses.		
System: Triclinic	Space group: $P\bar{1}$	
$\lambda(Cu K\alpha) = 1.5418 \text{ \AA}$	$Z = 2$	
	(AS)	(DSM)
a	14.706 (6) \AA	14.724 (1) \AA
b	5.836 (3)	5.823 (1)
c	4.567 (3)	4.562 (1)
α	96.22 (2) $^\circ$	95.75 (2) $^\circ$
β	91.11 (2)	91.20 (2)
γ	98.62 (2)	98.65 (1)
d_c	1.499 g cm^{-3}	1.499 g cm^{-3}
d_o	1.490 g cm^{-3}	

Observed and calculated structure factors are given in Table 2; the final positional coordinates and temperature factors are given in Tables 3 and 4. The agreement between the two sets of positional parameters is entirely satisfactory, the average discrepancy being 10% larger than the e.s.d.'s of DSM. There is a system-

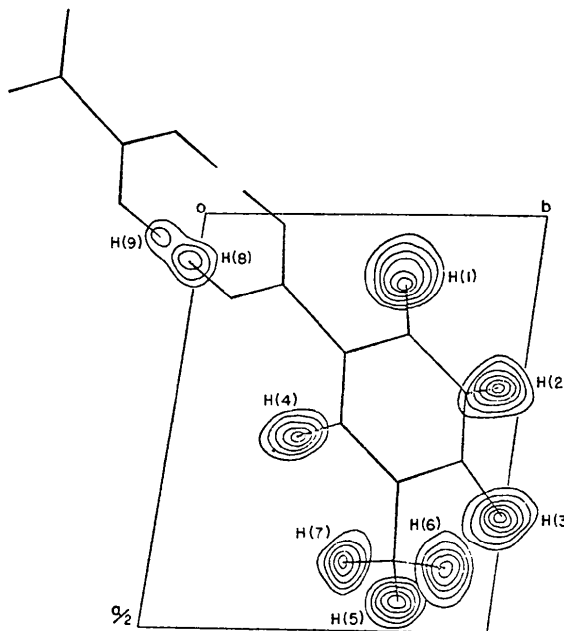


Fig. 1. Difference electron density map of 3-aminobenzoic acid hydrochloride. Contours are at intervals of 0.1 e \AA^{-3} , beginning at 0.1 e \AA^{-3} . Note that the acid proton is disordered.

Table 3. *Heavy-atom parameters and their standard deviations*

The values have been multiplied by 10^4 . The thermal parameters are in the form

$$T = \exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)].$$

The values of AS are given first.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>b</i> ₁₁	<i>b</i> ₂₂	<i>b</i> ₃₃	<i>b</i> ₁₂	<i>b</i> ₁₃	<i>b</i> ₂₃
Cl	4332 (0)	2249 (1)	3557 (1)	33 (0)	177 (2)	550 (4)	-15 (0)	-22 (0)	145 (2)
	4331 (1)	2251 (2)	3556 (3)	38 (1)	207 (4)	565 (10)	-24 (2)	-36 (2)	146 (4)
N	4068 (1)	6935 (4)	913 (5)	19 (1)	163 (7)	545 (14)	-16 (2)	-14 (3)	134 (8)
	4058 (3)	6925 (7)	897 (10)	34 (2)	219 (14)	529 (29)	-18 (4)	-4 (6)	100 (16)
C(1)	1628 (1)	4538 (4)	-1316 (5)	21 (1)	180 (7)	378 (12)	-5 (2)	-2 (3)	36 (7)
	1620 (4)	4543 (9)	-1318 (13)	29 (3)	207 (17)	465 (35)	-12 (6)	-1 (8)	53 (18)
C(2)	2502 (2)	4752 (4)	5 (5)	25 (1)	168 (7)	412 (13)	-3 (2)	1 (3)	79 (7)
	2503 (4)	4759 (9)	19 (13)	33 (3)	203 (17)	428 (36)	-6 (6)	-14 (8)	82 (18)
C(3)	3151 (1)	6617 (4)	-506 (5)	22 (1)	166 (7)	397 (12)	-4 (2)	4 (2)	56 (7)
	3151 (3)	6638 (9)	-555 (12)	26 (3)	214 (17)	517 (37)	-8 (5)	8 (8)	68 (20)
C(4)	2957 (2)	8257 (4)	-2313 (5)	31 (1)	173 (8)	451 (13)	-8 (2)	5 (3)	107 (8)
	2951 (4)	8243 (10)	-2329 (13)	37 (3)	213 (19)	532 (38)	-14 (6)	11 (8)	109 (20)
C(5)	2089 (2)	7991 (4)	-3648 (6)	39 (1)	203 (7)	466 (14)	4 (2)	-11 (3)	136 (8)
	2094 (4)	7975 (10)	-3628 (14)	42 (3)	285 (22)	595 (44)	-4 (7)	-23 (10)	167 (24)
C(6)	1424 (2)	6136 (4)	-3176 (6)	27 (1)	238 (8)	464 (14)	-0 (2)	-12 (3)	83 (8)
	1425 (4)	6143 (11)	-3156 (13)	32 (3)	342 (22)	461 (37)	-8 (6)	-22 (8)	126 (22)
C(7)	914 (2)	2577 (4)	-726 (5)	24 (1)	196 (7)	436 (13)	-7 (2)	-3 (3)	51 (8)
	910 (4)	2578 (10)	-730 (13)	31 (3)	228 (19)	538 (41)	-12 (6)	-1 (8)	6 (21)
O(1)	1089 (1)	1314 (3)	1244 (4)	34 (10)	298 (7)	657 (12)	-29 (2)	-28 (2)	206 (8)
	1089 (3)	1322 (7)	1239 (9)	46 (2)	312 (15)	688 (30)	-39 (5)	-37 (6)	190 (17)
O(2)	157 (1)	2268 (4)	-2162 (5)	30 (0)	358 (7)	762 (13)	-45 (2)	-49 (3)	236 (8)
	157 (3)	2261 (7)	-2168 (10)	38 (2)	368 (16)	803 (30)	-47 (4)	-66 (6)	214 (18)

atic difference in the two sets of temperature parameters, those of DSM being larger by about 0.60 (in units of *B*) for *b*₁₁ and *b*₂₂ and by about 0.45 for *b*₃₃. If this systematic difference is removed, the two sets of individual values again agree almost within the uncertainties of DSM. The systematic difference in the two sets of temperature factors could represent either a difference in the perfection or mosaicity of the two crystals or a systematic error in one set of data or both.

The isotropic temperature factors *B* for the hydrogen atoms as derived by AS seem anomalously small, in all

Table 4. *Hydrogen-atom parameters and their standard deviations*

The coordinate values have been multiplied by 10^4 . Parameters without indicated standard deviations were not refined. Values of AS are given first.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	843 (24)	5833 (57)	-4069 (73)	2.54 (0.69)
	796 (32)	5905 (78)	-4162 (104)	3.0
H(2)	1954 (22)	8895 (60)	-4874 (72)	2.39 (0.65)
	1985 (33)	8801 (85)	-5014 (115)	3.0
H(3)	3457 (20)	9526 (50)	-2530 (60)	1.28 (0.54)
	3412 (33)	9435 (82)	-2625 (106)	3.0
H(4)	2633 (19)	3696 (51)	1267 (62)	1.16 (0.54)
	2630 (34)	3817 (83)	1260 (107)	3.0
H(5)	4528 (21)	7155 (49)	-644 (67)	1.45 (0.56)
	4506	7086	-436	3.5
H(6)	4195 (21)	8508 (60)	2150 (69)	2.03 (0.63)
	4138	8151	2255	3.5
H(7)	4102 (18)	5664 (51)	2016 (60)	0.91 (0.50)
	4123	5643	1826	3.5
H(8)	648 (35)	269 (93)	1696 (96)	0.60 (0.77)
	596	-41	1634	3.5
H(9)	-278 (50)	1332 (133)	-1858 (136)	2.47 (1.27)
	-332	888	-1803	3.5

cases being even smaller than the average *B* of the atoms to which they are bonded. This effect could be due to absorption, or to the use of the hydrogen scattering factors of Stewart *et al.* (1965) which, although an improvement over those of McWeeny (1951), may still be too small for hydrogen atoms attached to carbon.

A more graphic comparison of the two sets of parameters may be obtained from half-normal probability plot analyses (Abrahams & Keve, 1971). The ordered, experimental values of Δ_j/σ_j are plotted against the expected values of Δ_j/σ_j in Fig. 2(a) for the positional coordinates and in Fig. 2(b) for the anisotropic temperature factors (Hamilton & Abrahams, 1972). The quantity Δ_j is the difference between a corresponding pair of parameters from the two structure analyses and σ_j is the standard deviation of this difference, based on the standard deviations of the parameters derived from the least-squares procedures. The temperature parameters were corrected for the systematic differences mentioned above before the calculation of the probability plot shown in Fig. 2(b).

A reasonable straight line may be fitted to each set of points. The slope of the line for the positional coordinates is approximately 1.3, indicating that the standard deviations have, on average, been underestimated by 30%; the slope for the temperature parameters is 1.4, indicating an underestimation of their standard deviations by 40%.

Discussion of the structure

The bond lengths and bond angles for both determinations are shown in Fig. 3. Estimated standard devia-

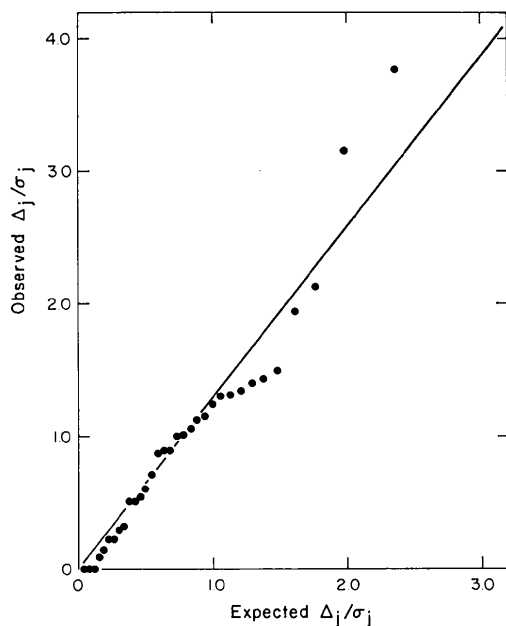
tions in the distances, including a factor of 1.3 as indicated by the half-normal probability plot, are: C-C, C-N and C-O: 0.004 Å (AS), 0.010 Å (DSM); C-H: 0.04 Å (AS), 0.07 Å (DSM); N-H: 0.04 Å (AS); O-H:

0.07 Å (AS); no e.s.d.'s are assigned to the N-H and O-H distances observed by DSM, as these hydrogen atoms were positioned from difference maps and their coordinates were not refined. Corresponding uncertainties in bond angles involving only the heavier atoms are 0.2° (AS) and 0.5° (DSM); in C-C-H and C-N-H angles, 1.7° (AS), and 2.5° (DSM); and in H-N-H and C-O-H angles, 4° (AS).

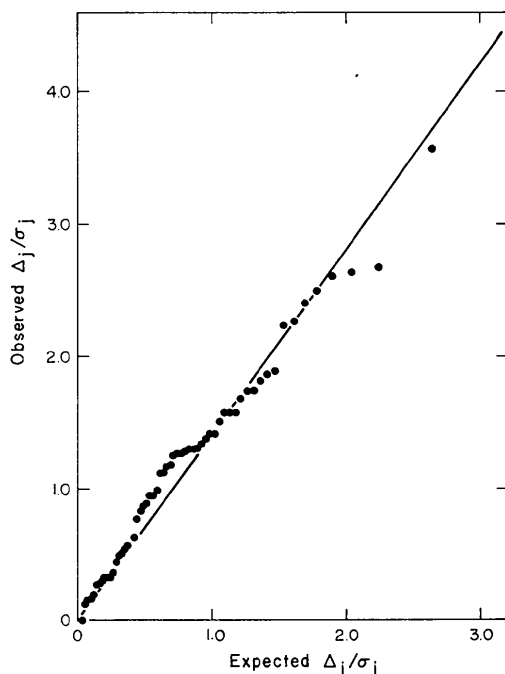
The weighted average of the ring C-C bond lengths, 1.383 ± 0.002 Å, is about 0.01 Å shorter than the value 1.393 Å found in crystalline benzene (Cox, Cruickshank & Smith, 1958). The six distances seem to be equal; on the basis of a significance test (Hamilton, 1964), the proposal that they are equal cannot be rejected at the 0.3 probability level. On the other hand, the interior bond angles show pronounced alternation.

The two C-O bond lengths are equal within experimental error, as are the two C-C-O bond angles. This symmetry, which is a reflection of the disorder in the location of the acidic proton, is in sharp contrast with other carboxylic acid groupings, in which the C-OH and C=O distances usually differ by about 0.08 Å and the C-C-OH and C-C=O angles by about 6°.

The C-N bond length, 1.461 ± 0.004 Å, is appreciably shorter than the value 1.487 given by Marsh & Donohue (1967) as the average value in zwitterionic amino acids; it is also shorter than the value 1.501 Å



(a)



(b)

Fig. 2. Half-normal probability plots for (a) the position coordinates and (b) the anisotropic temperature parameters of the heavy-atoms refined in the two independent structure analyses.

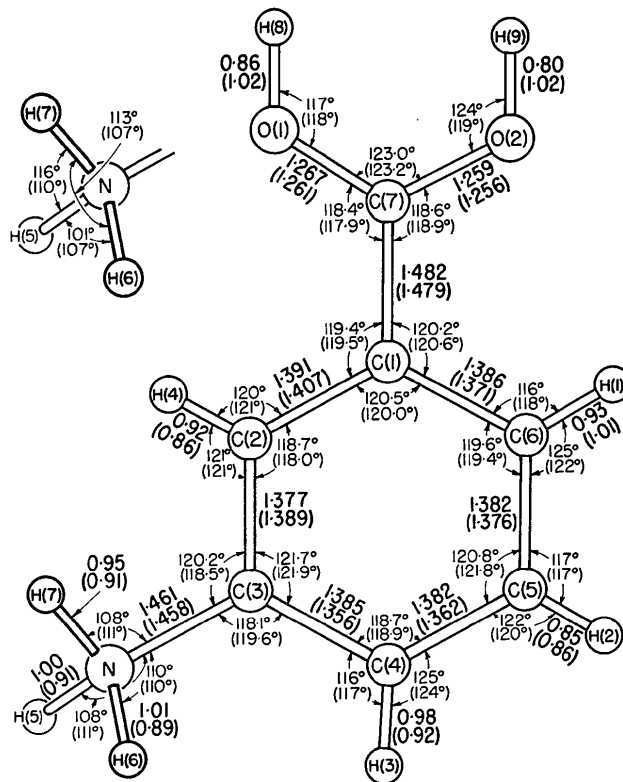


Fig. 3. Bond distances and angles. Values of DSM are in parentheses.

found by Brown (1968) for the zwitterionic molecule in the structure of anthranilic acid, *o*-aminobenzoic acid (a second molecule in that structure exists in the normal, uncharged form). The very strong N-H...Cl bonds, which permit relief of much of the positive charge on the nitrogen atom, plus the aromatic character of the benzene ring apparently leads to a small amount of double-bond character in the C-N bond in the present compound.

The benzene ring itself is slightly but significantly non-planar (Table 5). It is folded, through a dihedral angle of about 1.2°, about the line C(1)...C(4) to form a shallow boat; as a result, while the grouping C(1), C(2), C(6), C(7) is closely planar, the carboxyl carbon atom C(7) is markedly displaced from the best plane of the ring. The carboxyl group is twisted by about 8° relative to the benzene ring; relevant torsion angles are:

C(2)-C(1)-C(7)-O(1)	6.9°
C(2)-C(1)-C(7)-O(2)	-171.9
C(6)-C(1)-C(7)-O(1)	-172.9
C(6)-C(1)-C(7)-O(2)	8.3

The estimated standard deviations in these torsional angles are 0.4° (Stanford & Waser, 1972).

Table 5. *Least-squares plane of the benzene ring and atomic deviations from the plane*

Coefficients are direction cosines relative to the crystallographic axes. The parameters, *X*, *Y*, and *Z*, are in Å measured along the crystallographic axes.

Plane through atoms C(1), C(2), C(3), C(4), C(5) and C(6)

$$0.4095X - 0.5207Y - 0.7373Z = 0.053 \text{ (AS)}$$

$$0.4046X - 0.5262Y - 0.7388Z = 0.025 \text{ (DSM)}$$

	(AS)	(DSM)
C(1)	-0.011 Å	-0.007 Å
C(2)	0.006	0.002
C(3)	0.002	0.006
C(4)	-0.006	-0.008
C(5)	0.002	0.002
C(6)	0.006	0.006
C(7)	-0.042	-0.026
O(1)	-0.216	-0.199
O(2)	0.079	0.107
N	-0.020	-0.031
H(1)	0.05	0.04
H(2)	0.06	0.15
H(3)	-0.02	0.00
H(4)	-0.02	-0.05
H(5)	0.71	0.64
H(6)	-0.84	-0.82
H(7)	0.02	0.09
H(8)	-0.27	-0.21
H(9)	0.00	0.11

Molecular packing and hydrogen bonding

The projection of the structure down the *c* axis is shown in Fig. 4. Hydrogen-bonded dimers are formed through the carboxyl groups of centrosymmetrically

related molecules. This dimer is disordered;* the hydrogen atom occupies, with approximately equal probability, the two sites associated with covalent bonding to O(1) and O(2). The O...O hydrogen bond distance is 2.634 Å, which is in the range normally observed for aromatic carboxylic acid dimers. The ammonium group is involved in three strong hydrogen bonds to chloride ions; the N-H...Cl distances are 3.168, 3.156 and 3.178 Å. In addition the chloride ion is involved in a relatively short contact of 2.73 Å with H(3). Another interesting feature of the structure is the presence of rather short Cl...Cl distances of 3.83 and 3.60 Å.

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* Similar proton disorder in carboxylic acid dimers was inferred from infrared spectroscopy data by S. Hayashi and J. Umemura (Ninth International Congress of Crystallography, Kyoto, Japan, 26 Aug.-7 Sept., 1972, Abstract S239).

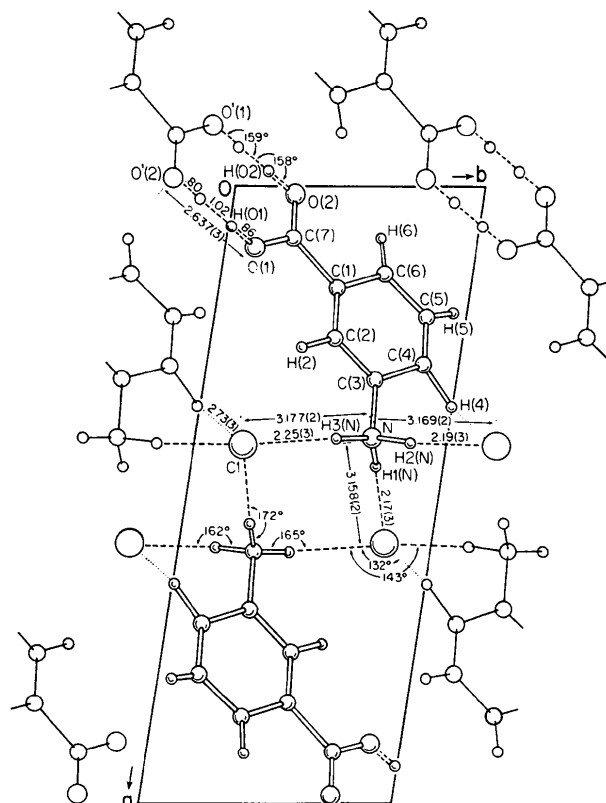


Fig. 4. A view down the *c* axis showing the crystal packing and hydrogen-bonding distances and angles. The hydrogen bonds are indicated by broken lines and short intermolecular distances are shown by dotted lines.

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The Crystal Structure of Sodium Hydrogen Oxydiacetate and Potassium Hydrogen Oxydiacetate

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In a study of the hydrogen bond system in the alkali hydrogen salts of oxydiacetic acid the crystal and molecular structures of $\text{MHO}(\text{CH}_2\text{COO})_2$, $\text{M}=\text{Na}$ and K , have been determined from X-ray intensity data. Both compounds are monoclinic, space group $P2_1/c$. There are four formula units in the cell with $a=6.990$ (1), $b=9.610$ (1), $c=8.434$ (2) Å, $\beta=103.34$ (1)° for $\text{NaHO}(\text{CH}_2\text{COO})_2$ and $a=7.102$ (2), $b=10.451$ (1), $c=8.558$ (2) Å, $\beta=101.44$ (2)° for $\text{KHO}(\text{CH}_2\text{COO})_2$. The structure of the sodium compound was refined to $R=0.074$ from intensities collected by the photographic Weissenberg technique. The intensities for the potassium compound were obtained with a linear single-crystal diffractometer and this structure was refined to $R=0.036$. The two compounds are isostructural, and contain infinite chains of oxydiacetate ions linked by a short hydrogen bond. The chains are cross-linked by the alkali metal ions. The hydrogen bond is probably asymmetric with hydrogen–oxygen distances 1.01 (5) and 1.47 (5) Å in the sodium and 1.05 (3) and 1.44 (3) Å in the potassium compound. The oxygen–oxygen distances are 2.462 (3) and 2.480 (2) Å, respectively.

Introduction

A study of the tris(oxydiacetato)lanthanoidate(III) complexes in the solid state has previously been reported by one of the present authors (Albertsson, 1968, 1970). As X-ray diffraction methods were used, the heavy lanthanoid ions prevented an accurate determination of the geometry of the oxydiacetate ion. To overcome this difficulty an investigation of the well crystallized alkali hydrogen oxydiacetates was commenced. The isostructural sodium and potassium compounds (below denoted NaHOXY and KHOXY) are described in this communication, and a following paper will deal with rubidium hydrogen oxydiacetate. Especially in the potassium and rubidium compounds the interaction between the ligand and the large central ion was expected to be fairly weak. The structural data thus obtained for the ligand could then be compared with the corresponding data for solid complexes with stronger metal–ligand interactions, e.g. the rare earth oxydiacetates (Albertsson, 1972).

The alkali hydrogen oxydiacetates are acid salts formed by a simple symmetric dicarboxylic acid. A series of such compounds has been thoroughly studied by Speakman and coworkers (Macdonald & Speakman, 1972). Its members embody infinite chains of dicarboxylate residues linked end-to-end by short hydrogen bonds across elements of twofold crystallographic symmetry (2, m , or $\bar{1}$). The general features of NaHOXY and KHOXY turned out to be the same but in these two compounds there is no symmetry element between the oxydiacetate ions. We therefore considered it worth while to make a thorough study of the alkali hydrogen oxydiacetates in order to make further contributions to the question of the symmetry of short hydrogen bonds, and the nature of their potential-energy wells.

Experimental

Crystals of NaHOXY and KHOXY were prepared by slow evaporation at room temperature of aqueous solutions of equimolar amounts of oxydiacetic acid and the