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

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The structure of 3-aminobenzoic acid hydrochloride,  $C_7H_7NO_2$ . HCl, has been determined independently in two different laboratories. The compound crystallizes in the triclinic space group P1, 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  $\sim 1.3-1.4$ . Hydrogenbonded 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  $2\theta$  limit of  $132^{\circ}$  ( $d_{\min} = 0.85$  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  $\theta$ - $2\theta$  scan at a speed of  $2^{\circ}$  (in  $2\theta$ ) 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<sup>-1</sup>). 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 pop-The ulation parameters, and a scale factor. minimized was  $\sum w(|F_o| - |F_c|)^2$ , with quantity  $1/w = 2.57 - 0.0054|F| + 0.0019|F|^2;$ latter this 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<sup>-</sup>, and Stewart, Davidson & Simpson (1965) for

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H. The final values for the occupational parameters were  $0.59 \pm 0.05$  for H(8) and  $0.37 \pm 0.05$  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  $-a^*$ ,  $b^*$ ,  $c^*$ ,  $\beta^*$  and  $\gamma^*$  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,  $\alpha^*$ , 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 Ka 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(calc) was greater than the observation threshold of F(obs). In the final cycle the maximum parameter shift was  $0.12\sigma$ . 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  $\alpha$ , and is almost surely caused by the inaccuracy in the procedure of DSM of measuring  $\alpha^*$  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<sub>7</sub>H<sub>7</sub>O<sub>2</sub>N. HCl

Standard deviations in the last significant figure are shown in parentheses.

System: Triclinic	Space	group: P1
$\lambda(\mathrm{Cu} \ K\alpha) = 1.5418$	Å $Z=2$	
	(AS)	(DSM)
а	14·706 (6) Å	14·724 (1) Å
b	5.836 (3)	5.823 (1)
С	4.567 (3)	4.562 (1)
α	96·22 (2)°	95·75 (2)°
β	91.11 (2)	91.20 (2)
γ	98.62 (2)	98.65 (1)
$d_{c}$	1.499 g cm <sup>-3</sup>	1.499 g cm <sup>-3</sup>
d <sub>o</sub>	$1.490 \text{ g cm}^{-3}$	

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  $Å^{-3}$ , beginning at 0.1 e  $Å^{-3}$ . Note that the acid proton is disordered.

# Table 2. Observed and calculated structure factors

Within each group the columns contain h,  $10F_o$  (AS),  $10F_c$  (AS),  $10F_o$  (DSM) and  $10F_c$  (DSM). Reflections marked with an asterisk are 'unobserved' and those marked with 'E' are suspected of being affected by secondary extinction.

h 0 0 1 19	52 68	-6 50 -49 -5 95 94 -4 24 -19 -3 22 20	54 -42 94 76 30 -15 24 21	-16 -15 47 -43	56 66 38 -38	4 156 -161 5 159 167 6 55 -55 7 50 51	154 -144 160 160 56 -56 54 51	-6 97 99 -5 68 -67 -4 55 52 -76 -76	70 80 54 -60 52 48 61 -64	-4 35 40 -3 107 -111 -2 53 55 -1 50 -48	36 38 98 -100 49 53 52 -43	4 84 -83 5 41 42 6 40 -42 7	68 -80 31 34 36 -37 18 18	2 89 -85 3 69 64 8 88 -87 5 221 226	80 -77 65 64 83 -82 180 204	2 34 36	44 -30 32 -46 44 -30	n 2 4   -12 35 -35	
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h J 0 -17 -16 J4 -J2 -15 29 28	39 - 39 36 - 21 34 22	5 55 -55 6 54 51 7 38 -39 8 13 -10 9 20 20 10 74 -75	41 44 38 30 31 -8 31 -8 31 -8 31 -8 31 -8 31 -8 31 -8 31 -8 -8 -8 -8 -8 -8 -8 -8 -9 -8 -9 -8 -9 -8 -9 -8 -9 -8 -9 -8 -9 -9 -8 -9 -8 -9 -8 -9 -8 -9 -8 -9 -8 -9 -8 -9 -8 -9 -8 -9 -8 -9 -8 -9 -8 -9 -8 -9 -8 -9 -8 -9 -8 -8 -8 -9 -8 -9 -8 -8 -8 -8 -8 -8 -8 -8 -8 -8	0 2728 292 1 2868 329 2 174 190 3 179 -193 4 168 171 5 3518-383	326 293 356 324 192 191 181 -193 173 169 350 -368	-) 27 28 -2 66 -64 -1 123 121 0 82 -82 1 107 107 2 20 -22	30 22 61 -49 109 112 72 -71 100 96 19 -21	-9 8 8 -8 98 95 -7 89 92 -6 99 -98 -5 147 151 -4 85 -88	90 83 65 83 109 -94 149 139 96 -83	-15 24 25 -14 10 -10 -13 39 41 -12 14 -15 -11 92 -97 -10 54 53	32 32 35• -14 75 -76 47 43	-11 86 -88 -10 93 92 -9 63 -59 -8 83 79 -7 64 -62	82 -73 87 76 65 -47 75 76 61 -35	-1 54 53 0 107 -105 1 32 35 2 106 -108 3 119 125 4 49 49	97 -94 34 36 97 -105 107 113 54 52	-9 30 -30 -8 28 -25 -7 78 76 -6 48 53 -4 12 -13		-°? -6 -7 -5 -19 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1	38* -10 70 -64 3 44* 3 3 47* -14 2 55 52
-14 78 -76 -13 62 81 -12 65 -66 -11 12 3 -10 68 -68 -9 25 -27	67 -62 70 64 60 -57 65 -56 765 -56 765 -56	11 82 85 12 86 -89 13 35 35 n - 1	59 67 66 -70 28 23	6 66 73 7 161 143 8 177 175 9 63 64 10 22 21	71 67 159 139 186 166 65 53 24 16	3 45 46 5 5 -3 5 86 -85 6 118 117 7 62 -60 8 22 77	49 38 33* 2 73 -74 109 108 60 -55 76 71	-3 163 179 -2 15 -11 -1 113 111 0 179 166 1 169 153 2 39 19	153 150 19 -11 108 106 159 160 144 138 42 42	-9 $45$ $-40-8$ $103$ $103-7$ $17$ $17-6$ $117$ $113-5$ $125$ $-118$	39 -31 91 84 31* 18 105 101 29* 1 108 -106	-0 20 10 -5 135 -138 -4 243 -255 -3 150 156 -2 44 -47 -1 120 121	147 -119 228 -224 158 134 53 -41 126 105	5 36 -30 6 87 87 7 73 -74 6 107 105 9 46 -44 10 40 37	42 - 36 80 62 69 - 74 94 101 48 - 44 41 36	-3 50 62 -2 17 -21 -1 40 43 0 31 32 1 75 -73 2 57 57	65 -61 56 46	-2 20 -20 -1 55 5 0 34 -3 1 55 -5 2 70	55 49 55 49 55 -22 55 -48 50 0 5 48 40
-8 15 -12 -7 112 -108 10 -6 144 137 11 -5 155 -145 1 -4 47 -36	))* -11 00 -98 2) 114 20 -134 44 -38	-14 -13 -12 11 -10 -11 25 -28 -10 9 5	60 -67 53 47 31° -6 22 -25 34° 5	12 21 -15 13 89 88 14 76 -76 15 68 70 16 23 23	23 -18 89 81 73 -69 66 64 22 21	9 10 11 861	42 -35 64 52 76 70	) 245 -230 4 79 79 5 173 -173 6 88 92 7 97 84	203 -209 80 72 158 -155 86 80 90 81	-3 133 127 -2 147 -147 -1 71 70 0 71 -74 1 7° 2	119 114 133 -127 66 58 69 -67 28 1	0 45 43 1 79 67 2 3• -9 3 100 -102 4 66 63 4 142 -148	576 - 45 1077 - 1075 1075 - 1075 1075 - 1075	11 18 14 12 13 h 3 3	33* 18 24 16 71 56	3 75 -75 4 19 17 5 19 19 6 192 188 7 44 46	65 -73 51• 22 51• 13 156 169 45 43	4 21 2 5 43	47* 26 44 - 37 28 30
-2 113 109 11 -1 65 -63 0 195 -195 1 1 53 -46 2 73 -74	11 97 74 56 74 18) 77 50 74 6)	-8 191 201 -7 89 -81 -6 94 91 -5 12 -14 -6 43 -41	155 177 78 -71 84 84 32° -8 38 -34	17 h 1 1 -17 5° -4 -16 50 -50	20 17	-12 -11 -10 -9 24 26 -8 7* 10	20 -19 20 14 28° -10 20 18 32° 7	9 39 -33 10 96 -94 11 122 121 12 106 -111 13 43 42	37 -26 89 -89 97 110 94 -94 42 37	3 28 -32 4 116 118 5 98 -100 6 158 161 7 30 -29	29 -25 110 107 94 -90 138 145 25 -33	6 76 7) 7 28 -27 8 9 8 9 23 -24 10 54 55	75 72 36 -28 35 4 26 -27 54 42	-12 28 -27 -11 13 8 -10 43 -43 -9 20 21 -8 23 -25	40 -34 41* 18 24 -17	9 38 38 10 68 -68 11 33 34 12 13	51 - 38 53 -60 36 37 33 -36	-6 69 7 -5 26 2 -4 26 2 -7 30 -3	5
) 268 278 20 4 137 -141 10 5 103 110 1 6 6 -8 7 57 10 8 36 38	50 -125 50 -125 50 102 50 100 50 1	-3 3% 35 -2 135 -140 -1 276 283 0 143 -146 1 8% 83 2 51 48	35 30 128 -126 250 255 127 -122 68 66 96 45	-15 77 76 -14 18 -20 -13 54 55 -12 13 12 -11 65 65	64 66 33* -15 53 40 32* 7 63 52 29* 1	-7 24 -24 -6 57 59 -5 64 -65 -4 31 2 25	16 -19 50 47 56 -46 39 39 32 24 32 24	14 62 -61 15 12 -15 16 17 B -1 2	50 -40 37• -9 32• -8 33 -36	8 119 -115 9 126 -122 10 26 -25 11 44 43 12 51 -50	105 -104 114 -115 39* -25 52 40 56 -49 69 65	11 04 03 12 20 -22 13 67 67 14 h -2 3	23 -21 65 61 42 -37	-7 6 169 173 -6 169 173 -5 13 -6 -3 74 -73 -2 27 25	151 146 36* -4 34* -15 67 -59 30 20	h 0 4	JJ -27	0 47 -4 1 26 -4 2 46 -4 3 56 5 4 38 -3	51° 33 46 -38 54 47 54 -36
9 101 -100 11 10 120 119 12 11 143 -141 14 12 104 103 10 13 8 -6	12 -93 26 108 33 -131 28 93 42 -4	3 39 34 4 134 132 5 19 -23 6 152 150 7 120 -114	31 27 112 108 17 -17 132 131 93 -92	-9 47 41 -8 80 76 -7 200 -200 -6 114 112 -5 158 -155	47 36 64 65 175 -180 103 103 141 -139	-1 48 -48 -0 11 -70 1 44 -56 2 54 -56 7 64	40 40 40 40 40 40 40 40 40 40 40 40 40 4	-17 -16 -15 13 14 -14 42 -41	17 21 28• -15 33• -7 39 -31	14 h # 2 -15	35 -34 24 14 28 -31	-15 -14 -13 26 27 -12 15 14 -11 52 59	30 21 54 -52 31• 22 34• 14	-1 31 -31 0 11 8 1 77 74 2 25 -26 3 73 75 4 22 -20	32 -28 31• 3 75 65 24 -19 74 64 18 -20	-8 77 78 -7 26 -27 -6 48 47 -5 5* -4 -4 16 20 -1 101 101	66 65 43°-29 43 41 44° 20 44° 20 106 87	5 26 -2 6 58 5 7 8 9	1 49° -27 2 51 55 42° -9 41 46 20 -32
15 5 h + 0 -16	93 93 23 17	9 71 -69 10 74 -7] 11 79 80 12 106 105 13 76 79	63 -55 63 -59 66 86 71 61	-3 187 171 -2 7252 866 -1 396 403 0 3878-418 1 228 241	163 160 269 394 410 407 234 242	5 6 h71	<b>4</b> 9 -48	-12 48 -46 -11 10 11 -10 70 69 -9 70 -70 -8 104 110	48 -42 33° 6 72 58 72 -55 104 90	-13 6 6 -12 11 -12 -11 25 29 -10 0° -10 -9 16 -16	28 27 28 22 36 -7 36 -9	-10 28 -28 -9 25 -22 -8 18 17 - 114 -116 -6 60 61	25 -21 36• -23 33• 15 83 -96 50 50	5 27 25 6 17 -16 7 74 70 8 0° 6 9 50 -51	29 30 24 -14 70 63 35° 5 55 -40	-2 107 -102 -1 21 14 0 82 -82 1 44 46 2 7° 2	109 -96 44* 16 91 -74 56 44 44* 2	-9 -9 -8 -7 -9	3 20 33 35• 6 38• -8
-15 21 -20 -14 14 12 4 -13 71 -72 4 -12 44 39 -11 131 131 13 -10 90 -92 4	40* -14 42* 8 62 -57 42 35 12 102 13 -75	14 52 -55 15 39 43 16 h -3 1	16 35 29 -31	2 3 152 163 4 84 -94 5 188 192 6 154 163 7 40 -40	310 -323 161 162 86 -96 183 184 160 156 18 -43	****	24 27 34 -31 65 -68 44 48 18 -25 10 37	-7 47 -61 -6 199 211 -5 202 -216 -4 76 -76 -3 66 60 -3 66 60	182 197 176 -198 83 -67 61 55 80 -75	-0 55 54 -7 24 -20 -6 30 31 -4 30 -51 -4 15 -5 46	33° -15 32 20 73 -68 32° 12 49 -42	-3 13 -61 -3 59 -61 -2 104 109 -1 76 78 0 37 -32	73 85 55 -59 79 86 66 69 44 -32	11 12 n 4 3	52 -66 26 31	5 96 -94 5 96 -94 6 41 41 7 39 -41 8 24 22	113 111 103 -87 50 39 42 -39 43• 28	-5 26 -2 -4 28 2 -3 20 -1 -2 30 3 -1 33 -3	25 -24 6 42° 28 6 43° -14 2 22 27 5 34 -27
-9 60 59 6 -8 126 -125 11 -7 32 36 -6 78 -70 -5 88 77 6	62 44 11 -100 14 28 72 -60 50 71	-15 -14 8 -12 -13 76 76 -12 75 -72 -11 88 91	84 93 14 -15 63 65 68 -61 81 80	8 284 297 9 166 -170 10 162 162 11 7° -2 12 10 -10	267 271 171 -158 159 166 33° 2 33° 4	i h-74	19 -21 61 76	-1 203 211 0 401g-535 1 150 147 2 126 -123 3 48 -40 5 66 -42	221 197 368 -408 140 148 129 -124 54 -48 56 -47	-2 22 -20 -1 65 -67 0 65 -67 1 130 130 2 40 -38 3 86 88	23 -18 66 -59 64 -54 118 116 40 -39 81 82	1 198 188 2 106 -104 3 96 95 4 102 -95 5 30 31 6 58 -56	172 172 108 -86 99 89 95 -90 40 22 65 -43	-13 -12 -11 -10 5° -1 -9 45 48 -8 2° 6	16 -28 35* 3 39* 12 42* 1 34 36 39* 9	9 36 -34 10 12 -11 11 12 13	42• -1) 39• 11 41 -44 34 31	2 49 -5	433 433 60 51 60 51 50 50 50 50 50 50 50 50 50 50 50 50 50
-3 135 -132 11 -2 193 197 12 -1 150 -147 1 0 124 123 11 1 15 -18	11 -115 70 167 17 -132 19 117 12 -9		14 10 24 24 20 14 189 199 50 -54	13 78 -75 14 78 -75 15 57 58 16 94 -89 17	75 -70 58 46 85 -79 64 67	-7 -6	22 - 37	5 213 -215 6 137 140 7 211 -215 8 124 126 9 82 -80	206 -204 131 133 196 -198 121 114 78 -73	4 48 -47 5 28 -27 6 12) -120 7 74 -71 8 99 97	46 -45 31 -22 108 -110 75 -74 94 90 96 -86	7 38 54 8 302 312 9 39 -37 10 74 74 11 68 -65	43 30 260 279 45 -35 72 64 71 -56	-7 24 22 -6 62 -62 -5 26 25 -4 15 -11 -3 32 -31	19 20 56 -53 27 22 41° -11 30 -27	h 1 4	38 32 41• 24 41• -21		38 -444 5 7 6 30 -27
2 13 122 12 3 123 126 12 4 20 -23 3 5 183 190 15 6 125 -130 12 7 71 72	10 112 13 167 167 19 117 11 71	-3 145 149 -3 82 -83 -2 121 122 -1 25 2 0 40 41 1 146 143	134 135 76 -72 126 114 24* -11 38 36 131 132	-18 -17 -16 78 79 -15 6• 0	15 15 29 -27 59 61 34• -3	-3 53 -53 -3 110 114 -2 63 -62 -1 52 53 -0 54 -55	840000 8400000	10 20 -17 12 117 -119 13 23 -27 14 97 -99 15 64 69	35° -16 98 -103 38° -20 81 -89 55 60	10 60 59 11 12 n 5 2	66 55 44 -35 28 22	1) 28 -24 14 20 -2) 15 16	25 -17 34 -22 65 65 33 -34	-1 $62$ $-620$ $47$ $451$ $33$ $-322$ $47$ $463 7^{\circ} -6$	56 -57 456 -29 476 -29 47 47	-7 2) -22 -55 -5 42 -5 42 -10 -10 -10 -10 -10 -10 -10 -10 -10 -10	40 -10 55 40 41 -35 44 -35	-3 $33$ $-3-2$ $12$ $1-2$ $12$ $1-1$ $22$ $-2-2-2$ $-2-2$ $-2-2$ $-2-2-2$ $-2-2$ $-2-2-2$ $-2$ $-2-2$ $-2$ $-2-2$ $-2$ $-2-2$ $-2$ $-2-2$ $-2$ $-2$ $-2-2$ $-2$ $-2$ $-2$ $-2$ $-2$ $-2$ $-2$	7 19 -27 1 34 11 2 40° -19 2 46 38 8 40° -1 4 50
8 10 44 4 9 39 44 4 10 27 26 3 11 34 -32 3 12 113 108 10	2° -5 12 41 11 24 17 -31 13 94	2 17 -5 3 373 367 4 221 -213 5 33 42 6 110 -104 7 68	20 -4 348 333 194 -188 30 37 90 -90	-15 18 16 -13 45 47 -12 29 -30 -11 181 182 -10 156 -158	19 1) 42 )) 30 -24 142 148 129 -130	1 18 -13 2 9 -0 3 30 -33 4 65 65 5 77 -82	2) -32 57 -54 64 -65	16 17 h 0 2	20 -21	-13 -12 -11 28 30 -10 20 -18 -9 34 13	18 15 27• -7 23 20 33• -16 27 25	h -1 3 -14 38 35 -13 14 14 -12 51 -49 -11 86 84	27 27 34• 9 81 -39 67 66	4 25 25 5 71 71 6 136 -134 7 17 -17 8 9	20 15 61 6) 115 -124 21 -11 42 -37 42 33	-2 28 24 -1 13 12 0 437 -45 1 37 36 2 36 -38 3 48 51	21 44 44 44 56	2 0 C D 2 3 3 4 5 6 1 7	35 -27 37* -20 25 23 27 -31 20 28
15 5 13 150	6 63 12 84	6 55 52 9 18 11 10 205 208 11 178 -179 12 47 49	51 44 13 9 188 172 160 -150 44 35	7 - 0 - 5 - 5 - 5 - 5 - 5 - 5 - 5 - 5 - 5	61 -57 475 124 548 375	0 22 57 7 8 -22 8 41 45 9 34 -37 10	36* 0 36 35 28 -32 24 -31	-16 31 33 -15 18 18 -14 166 -163 -13 20 20 -12 23 -22	)1 29 )3* 16 136 -136 34* 16 13 -16	-8 72 -74 -7 50 3 -6 22 20 0 5 39 -39 -4 25 20	63 -59 36 16 36 -33 35 17	-10 43 -40 -9 99 99 -8 87 -90 -7 47 49 -6 56 58	32 - 37 78 87 72 -80 41 42 46 46 26 -11	-7 31 -33	15 2 25 -26 26 20	4 56 -56 5 21 20 6 39 -34 7 13 -32 8 5 4 9 100 -100	64 - 56 40* 24 43 - 25 27 - 3 41* - 4	0 1	5 25° -40 33 13
-12 21 -21 4 -12 21 -21 4 -10 14 13 4 -9 4 1 4 -8 19 -16 4 -7 100 100 9	12° -15 14 -36 11° 10 12° -11 12° -11 12° -11	10 -5 14 19 -20 15 14 14 16 53 -55 17	47° -17 34° 11 28 -40 25° 26	-J 239 -232 -2 60 58 -1 8 -4 0 61 -56 1 48 -59 2 139 -144 3 60 59	214 -214 49 54 19* 6 55 -52 50 -47 138 -141 57 59	-11 -10 -9 26 -27 -8 65 64 -7 72 -72	27 31 43 -35 30* -23 54 58 63 -64	-14 12 11 -10 24 -23 -9 47 41 -8 32 -27 -7 251 -257 -6 12 7 -5 164 -175	310 -18 400 44 33 -22 213 -238 220 -148	-2 63 84 -1 5 4 0 25 27 1 9 -13 2 29 -26 3 45 45	71 73 18 6 35• 24 39• -4 28 -24 37 37	-4 144 159 -3 85 -95 -2 2078 227 -1 30 22 0 10 8 1 99 -86	124 137 66 -81 179 210 30 19 12* 3 84 -82	-5 31 -32 -3 10 -12 -2 15 -18 -1 31 34 0 34 37 1 19 -19	24 -25 36* -11 21 -10 29 28 20 28 26 -15	10 11 12	)2 )0 26 -21 38 42	2	

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

The values have been multiplied by 10<sup>4</sup>. The thermal parameters are in the form

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

The values of AS are given first.

$\begin{array}{cccccccccccccccccccccccccccccccccccc$		x	У	Ζ	$b_{11}$	b22	b 33	$b_{12}$	b13	b23
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cl	4332 (0)	2249 (1)	3557 (1)	33 (0)	177 (2)	550 (4)	-15(0)	-22(0)	145 (2)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		4331 (1)	2251 (2)	3556 (3)	38 (1)	207 (4)	565 (10)	- 24 (2)	- 36 (2)	146 (4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N	4068 (1)	6935 (4)	913 (5)	19 (1)	163 (7)	545 (14)	-16(2)	-14(3)	134 (8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		4058 (3)	6925.(7)	897 (10)	34 (2)	219 (14)	529 (29)	-18(4)	-4 (6)	100 (16)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(1)	1628 (1)	4538 (4) -	1316 (5)	21(1)	180 (7)	378 (12)	-5(2)	-2(3)	36 (7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	- 、 ,	1620 (4)	4543 (9) -	1318 (13)	29 (3)	207 (17)	465 (35)	-12(6)	-1(8)	53 (18)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(2)	2502 (2)	4752 (4)	5 (5)	25 (1)	168 (7)	412 (13)	-3(2)	1 (3)	79 (7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	. ,	2503 (4)	4759 (9)	19 (13)	33 (3)	203 (17)	428 (36)	-6(6)	- 14 (8)	82 (18)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(3)	3151 (1)	6617 (4) -	- 506 (5)	22 (1)	166 (7)	397 (12)	-4 (2)	4 (2)	56 (7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		3151 (3)	6638 (9) -	- 555 (12)	26 (3)	214 (17)	517 (37)	-8 (5)	8 (8)	68 (20)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(4)	2957 (2)	8257 (4) -	2313 (5)	31 (1)	173 (8)	451 (13)	-8(2)	5 (3)	107 (8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		2951 (4)	8243 (10) -	2329 (13)	37 (3)	213 (19)	532 (38)	-14 (6)	11 (8)	109 (20)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(5)	2089 (2)	7991 (4) -	3648 (6)	39 (1)	203 (7)	466 (14)	4 (2)	-11 (3)	136 (8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		2094 (4)	7975 (10) -	3628 (14)	42 (3)	285 (22)	595 (44)	-4(7)	-23 (10)	167 (24)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C(6)	1424 (2)	6136 (4) -	3176 (6)	27 (1)	238 (8)	464 (14)	-0(2)	-12(3)	83 (8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1425 (4)	6143 (11) -	3156 (13)	32 (3)	342 (22)	461 (37)	-8 (6)	- 22 (8)	126 (22)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C(7)	914 (2)	2577 (4)	-726 (5)	24 (1)	196 (7)	436 (13)	-7(2)	-3(3)	51 (8)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		910 (4)	2578 (10) -	- 730 (13)	31 (3)	228 (19)	538 (41)	-12 (6)	-1(8)	6 (21)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	O(1)	1089 (1)	1314 (3)	1244 (4)	34 (10)	298 (7)	657 (12)	-29 (2)	- 28 (2)	206 (8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1089 (3)	1322 (7)	1239 (9)	46 (2)	312 (15)	688 (30)	- 39 (5)	-37 (6)	190 (17)
157(3) 2261(7) - 2168(10) 38(2) 368(16) 803(30) - 47(4) - 66(6) 214(	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<sup>4</sup>. Parameters without indicated standard deviations were not refined. Values of AS are given first.

	x	У	Z	В
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  $\Delta_j/\sigma_j$  are plotted against the expected values of  $\Delta_j/\sigma_j$  in Fig. 2(*a*) for the positional coordinates and in Fig. 2(*b*) for the anisotropic temperature factors (Hamilton & Abrahams, 1972). The quantity  $\Delta_j$  is the difference between a corresponding pair of parameters from the two structure analyses and  $\sigma_j$  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 deviations 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:



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. 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  $0.2^{\circ}$  (AS) and  $0.5^{\circ}$  (DSM); in C–C–H and C–N–H angles,  $1.7^{\circ}$  (AS), and  $2.5^{\circ}$  (DSM); and in H–N–H and C–O–H angles,  $4^{\circ}$  (AS).

The weighted average of the ring C-C bond lengths,  $1.383 \pm 0.002$  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  $6^{\circ}$ .

The C-N bond length,  $1.461 \pm 0.004$  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



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  $N-H\cdots Cl$ 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  $1\cdot 2^{\circ}$ , about the line  $C(1)\cdots C(4)$  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  $0.4^{\circ}$  (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 (AS)	
0.4046X - 0.5262Y - 0.7388Z = 0.025 (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	-0.050	-0.031
H(1)	0.05	0.04
H(2)	0.06	0.15
H(3)	-0.05	0.00
<b>H</b> (4)	-0.05	-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 MHO(CH<sub>2</sub>COO)<sub>2</sub>, M = Na and K, have been determined from X-ray intensity data. Both compounds are monoclinic, space group  $P_{2_1}/c$ . 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 NaHO(CH<sub>2</sub>COO)<sub>2</sub> and a=7.102 (2), b=10.451 (1), c=8.558 (2) Å,  $\beta=101.44$  (2)° for KHO(CH<sub>2</sub>COO)<sub>2</sub>. 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  $(2, m, \text{ or } \overline{1})$ . 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 potentialenergy 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