GILLIS, J. (1948). *Acta Cryst.* **1**, 76.
GOEDKOOP, J. A. (1950). *Acta Cryst.* **3**, 374.
GOEDKOOP, J. A. (1952). *Theoretical Aspects of X-ray Crystal Structure Analysis*, p. 89. Thesis, Amsterdam.
HARKER, D. & KASPER, J. S. (1948). *Acta Cryst.* **1**, 70.
KARLE, J. & HAUPTMAN, H. (1950). *Acta Cryst.* **3**, 181.
LÖFGREN, T. (1960). *Acta Cryst.* **13**, 429.
MACGILLAVRY, C. H. (1950). *Acta Cryst.* **3**, 214.
ODA, T. & NAYA, S. & TAGUCHI, I. (1961). *Acta Cryst.* **14**, 456.
OKAYA, Y. & NITTA, I. (1952). *Acta Cryst.* **5**, 564.
TAGUCHI, I. & NAYA, S. (1958). *Acta Cryst.* **11**, 543.
WOLFF, P. M. DE & BOUMAN, J. (1954). *Acta Cryst.* **7**, 328.

Acta Cryst. (1962). **15**, 77

The Crystal Structure of Sodium Bicarbonate

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The atomic parameters in sodium bicarbonate are redetermined. The resulting bicarbonate ion structure differs significantly from that found in other salts. The bicarbonate ion was found to have C_{2v} symmetry (excluding the hydrogen atom), with C–O bond distances equal to 1·346, 1·264 and 1·263 Å. The hydrogen bond distance between adjacent bicarbonate ions is 2·595 Å. These dimensions are compared with those in related compounds.

Introduction

The bicarbonate salts are a rather interesting series of compounds which illustrate the effects of crystal packing on the internal structure of covalently bonded molecules. Three such salts which have been studied by X-ray diffraction are potassium bicarbonate (Nitta, Tomiie & Hoo Koe, 1952), sodium sesquicarbonate (Brown, Peiser & Turner-Jones, 1949) and sodium bicarbonate (Zachariasen, 1933). These systems each crystallize by utilizing a different hydrogen bonding scheme and show marked differences in the carbon-oxygen lengths of the anion. The solution of the structure of sodium bicarbonate was obtained, however, by using the assumption that planar trigonal carbonate groups exist in the cyrstal with all carbon-oxygen distances equal to 1·27 Å. This assumption was not valid and only an approximately correct structure resulted. It is the object of the work reported in this paper to collect new diffraction data and to reexamine the atomic parameters of this structure.

Experimental

Small needle-like crystals of sodium bicarbonate were obtained by slow evaporation of the aqueous solution in an atmosphere of carbon dioxide. The resulting crystals were mounted in the usual manner with the axis of rotation corresponding to the needle axis. Several crystals had to be examined before one was found which did not exhibit twinning. The dimensions of this crystal were approximately 0·1 mm. in diameter × 2 mm.

Oscillation and rotation photographs showed the Laue symmetry to be C_{2h}–$2/m$. Systematic absences led to the space group assignment of C_{2h}^5–$P2_1/c$, in agreement with Zachariasen (in his paper Zachariasen used the related unit cell having symmetry C_{2h}^5–$P2_1/n$). The unit cell dimensions obtained, compared with those of Zachariasen, are shown below.

This investigation	Zachariasen ($P2_1/c$)
$a=3{\cdot}51\pm0{\cdot}01$ Å	$a=3{\cdot}53\pm0{\cdot}03$ Å
$b=9{\cdot}71\pm0.01$	$b=9{\cdot}70\pm0{\cdot}04$
$c=8{\cdot}05\pm0{\cdot}01$	$c=8{\cdot}11\pm0{\cdot}04$
$\beta=111°\ 51'$	$\beta=112°\ 25'$
$a:b:c=0{\cdot}361:1:0{\cdot}829$	$a:b:c=0{\cdot}364:1:0{\cdot}836$

The above axial ratios may be compared to the values of $a:b:c=0{\cdot}3582:1:0{\cdot}8253$ determined optically by Groth (1908). Assuming four molecules per unit cell, the calculated density is 2·19 g.cm.$^{-3}$, compared to the experimental density of 2·22 g.cm.$^{-3}$ reported by Groth (1908) and 2·20 g.cm.$^{-3}$ listed in the International Critical Tables (1926).

Multiple film Weissenberg photographs of the $h=0$, 1, and 2 layers were recorded using Cu $K\alpha$ radiation. The intensities of the various reflections were estimated visually in the usual manner with the aid of an intensity strip. Correlation of the intensities of the various sets of film was made by comparison to a photograph which contained fifteen minute exposures of a twenty-five degree portion of each layer; absorption was neglected.

Treatment of data

A Fourier projection down the a axis was calculated using the magnitudes of the structure factors obtained from our intensity data and signs based on

Table 1. *Calculated and observed structure factors*

o k l	F_c	$\|F_o\|$
0.12.0	17.30	16.61
0.10.0	-1.80	<1.67
0 8 0	23.46	21.46
0 6 0	54.18	33.36
0 4 0	3.88	1.65
0 2 0	-15.74	16.67
0.11.1	4.17	4.71
0.10.1	0.13	<1.75
0 9 1	-12.35	11.66
0 8 1	7.31	7.24
0 7 1	-12.14	14.02
0 6 1	8.82	10.15
0 5 1	17.82	19.52
0 4 1	-5.29	6.97
0 3 1	-22.93	23.64
0 2 1	6.14	8.80
0 1 1	-7.76	9.65
0.12.2	-9.67	9.38
0.11.2	-2.97	3.03
0.10.2	-12.06	14.47
0 9 2	10.03	10.81
0 8 2	-8.28	9.55
0 7 2	-13.36	14.16
0 6 2	-24.06	24.39
0 5 2	-4.34	6.72
0 4 2	-28.05	28.82
0 3 2	1.41	3.08
0 2 2	-42.41	34.27
0 1 2	22.46	23.79
0 0 2	-9.70	11.33
0.11.3	7.45	8.43
0.10.3	3.98	4.22
0 9 3	10.20	11.30
0 8 3	-20.80	20.16
0 7 3	5.37	5.54
0 6 3	11.23	12.27
0 5 3	15.81	17.67
0 4 3	19.21	22.50
0 3 3	27.28	28.22
0 2 3	-49.39	38.43
0 1 3	12.12	14.69
0.11.4	9.47	9.30
0.10.4	6.28	6.92
0 9 4	12.94	14.09
0 8 4	3.99	3.72
0 7 4	-21.26	19.13
0 6 4	18.22	18.82
0 5 4	18.55	18.69
0 4 4	9.88	10.79
0 3 4	1.74	<1.56
0 2 4	17.57	18.65
0 1 4	-4.40	6.86
0 0 4	17.23	19.02
0.10.5	3.75	3.56
0 9 5	-14.56	16.31
0 8 5	-6.74	8.56
0 7 5	-1.83	<1.85
0 6 5	8.73	9.18
0 5 5	-19.08	17.23
0 4 5	8.66	9.89
0 3 5	-30.85	28.09
0 2 5	-16.70	18.59
0 1 5	-10.99	10.86
0 9 6	3.10	3.56
0 8 6	-9.18	9.32
0 7 6	-4.66	4.42
0 6 6	-3.85	3.41
0 5 6	-6.52	5.20
0 4 6	0.27	<1.90
0 3 6	0.70	<1.88
0 2 6	6.08	7.05
0 1 6	7.00	7.17
0 0 6	-25.98	21.57
0 7 7	12.48	12.74
0 6 7	-1.14	<1.53
0 5 7	0.35	<1.66
0 4 7	1.20	<1.78
0 3 7	23.05	21.24
0 2 7	-0.87	<1.91
0 1 7	12.84	10.69
0 6 8	-9.01	9.30
0 5 8	4.93	5.52
0 4 8	4.56	5.05
0 3 8	2.63	2.32
0 2 8	7.37	8.13
0 1 8	-10.52	12.36
0 0 8	-24.19	23.63
0 3 9	-8.87	7.43
0 2 9	0.56	<1.20
0 1 9	-7.21	6.56

h k l	F_c	$\|F_o\|$
1.12.0	-8.42	7.63
1.11.0	-0.33	<1.29
1.10.0	-15.44	16.13
1 9 0	-12.71	13.68
1 8 0	-6.88	8.26
1 7 0	9.09	9.85
1 6 0	-20.09	21.09
1 5 0	1.56	3.55
1 4 0	32.78	31.02
1 3 0	-1.73	2.96
1 2 0	-31.23	29.57
1 1 0	-29.85	30.94
1 0 0	-18.58	16.77
1.11.1	4.15	4.32
1.10.1	-8.17	7.91
1 9 1	14.14	13.93
1 8 1	12.30	12.94
1 7 1	0.28	<1.76
1 6 1	-14.25	15.62
1 5 1	16.62	17.00
1 4 1	-20.93	23.04
1 3 1	40.81	36.29
1 2 1	35.65	32.47
1 1 1	3.02	2.84
1.11.2	-2.26	2.56
1.10.2	5.44	5.72
1 9 2	-1.05	<1.65
1 8 2	27.38	23.71
1 7 2	15.51	14.76
1 6 2	-9.29	9.74
1 5 2	-9.27	10.12
1 4 2	21.80	22.47
1 3 2	2.01	2.79
1 2 2	18.26	21.07
1 1 2	11.72	13.34
1 0 2	18.60	17.40
1.11.3	-8.44	4.98
1.10.3	-1.24	<1.07
1 9 3	-2.06	<1.37
1 8 3	0.61	<1.61
1 7 3	-29.63	25.02
1 6 3	5.24	4.91
1 5 3	-14.51	15.40
1 4 3	-1.75	2.41
1 3 3	2.53	5.59
1 2 3	0.34	<1.48
1 1 3	-41.22	37.50
1.10.4	-8.33	6.09
1 9 4	0.19	<1.27
1 8 4	5.64	5.85
1 7 4	-5.43	3.57
1 6 4	-2.15	<1.79
1 5 4	-3.49	3.67
1 4 4	-9.55	9.39
1 3 4	-3.19	3.69
1 2 4	-13.73	15.05
1 1 4	10.07	10.73
1 0 4	17.77	18.49
1 9 5	2.21	1.35
1 8 5	1.15	<1.24
1 7 5	12.07	9.97
1 6 5	9.07	8.56
1 5 5	21.67	18.77
1 4 5	-9.17	8.96
1 3 5	7.84	7.09
1 2 5	2.12	2.56
1 1 5	21.12	19.50
1 8 6	-4.01	2.19
1 7 6	3.53	3.47
1 6 6	2.08	<1.36
1 5 6	-9.16	10.05
1 4 6	-5.97	4.88
1 3 6	0.22	<1.71
1 2 6	-6.01	5.03
1 1 6	24.64	21.61
1 0 6	2.65	2.60
1 6 7	6.35	3.47
1 5 7	-9.79	7.37
1 4 7	-5.07	4.19
1 3 7	-10.64	8.50
1 2 7	-1.37	<1.46
1 1 7	-9.71	8.51
1 2 $\bar{8}$	8.64	5.58
1.12.$\bar{1}$	4.79	4.11
1.11.$\bar{1}$	-5.12	5.43
1.10.$\bar{1}$	13.23	14.30
1 9 $\bar{1}$	0.25	<1.68
1 8 $\bar{1}$	-0.18	<1.69
1 7 $\bar{1}$	-4.00	3.99
1 6 $\bar{1}$	-11.32	14.59
1 5 $\bar{1}$	-14.50	17.55
1 4 $\bar{1}$	23.66	28.44
1 3 $\bar{1}$	5.24	5.86
1 2 $\bar{1}$	-4.06	7.58
1 1 $\bar{1}$	-14.86	15.45
1.11.$\bar{2}$	7.23	8.61
1.10.$\bar{2}$	20.75	23.56
1 9 $\bar{2}$	-9.74	11.08
1 8 $\bar{2}$	15.09	15.70
1 7 $\bar{2}$	-2.46	3.28
1 6 $\bar{2}$	6.30	8.59
1 5 $\bar{2}$	20.56	23.93
1 4 $\bar{2}$	46.00	37.03
1 3 $\bar{2}$	-0.21	<1.01
1 2 $\bar{2}$	66.83	47.95
1 1 $\bar{2}$	-54.41	38.52
1 0 $\bar{2}$	-27.23	22.01
1.11.$\bar{3}$	-5.77	7.32
1.10.$\bar{3}$	1.57	<1.54
1 9 $\bar{3}$	4.91	4.38
1 8 $\bar{3}$	-1.08	<1.72
1 6 $\bar{3}$	-14.68	15.32
1 5 $\bar{3}$	-21.40	24.01
1 4 $\bar{3}$	2.09	1.92
1 3 $\bar{3}$	6.48	7.37
1 2 $\bar{3}$	4.63	6.31
1 1 $\bar{3}$	-8.70	9.76
1.10.$\bar{4}$	-4.73	4.68
1 9 $\bar{4}$	3.53	4.43
1 8 $\bar{4}$	-25.79	24.42
1 7 $\bar{4}$	-0.29	4.40
1 6 $\bar{4}$	-10.16	13.10
1 5 $\bar{4}$	3.07	2.54
1 4 $\bar{4}$	-18.52	20.42
1 3 $\bar{4}$	0.80	1.87
1 2 $\bar{4}$	-16.30	17.44
1 1 $\bar{4}$	-3.04	2.48
1 0 $\bar{4}$	-47.90	44.09
1.10.$\bar{5}$	8.50	9.59
1 9 $\bar{5}$	-1.97	1.57
1 8 $\bar{5}$	-5.91	6.88
1 7 $\bar{5}$	24.61	23.68
1 6 $\bar{5}$	5.20	5.56
1 5 $\bar{5}$	9.95	10.99
1 4 $\bar{5}$	11.91	13.94
1 3 $\bar{5}$	-11.89	13.73
1 2 $\bar{5}$	-13.55	16.38
1 1 $\bar{5}$	33.48	31.87
1.10.$\bar{6}$	7.13	7.82
1 9 $\bar{6}$	4.60	6.07
1 8 $\bar{6}$	-2.81	1.58
1 7 $\bar{6}$	-19.07	19.71
1 6 $\bar{6}$	16.59	17.99
1 5 $\bar{6}$	12.06	13.54
1 4 $\bar{6}$	11.95	11.72
1 3 $\bar{6}$	-3.86	4.72
1 2 $\bar{6}$	11.88	13.53
1 1 $\bar{6}$	-4.98	4.55
1 0 $\bar{6}$	10.49	11.25
1 9 $\bar{7}$	-6.71	7.89
1 8 $\bar{7}$	-10.23	12.91
1 7 $\bar{7}$	8.99	10.08
1 6 $\bar{7}$	7.74	9.76
1 5 $\bar{7}$	-12.34	12.39
1 4 $\bar{7}$	4.75	5.45
1 3 $\bar{7}$	-16.59	16.94
1 2 $\bar{7}$	-14.53	16.33
1 1 $\bar{7}$	-12.78	14.30
1 6 $\bar{8}$	-2.61	2.84
1 5 $\bar{8}$	-3.51	3.48
1 4 $\bar{8}$	-0.86	<1.69
1 3 $\bar{8}$	1.08	<1.75
1 2 $\bar{8}$	-7.35	7.58
1 1 $\bar{8}$	15.47	17.05
1 0 $\bar{8}$	1.56	<1.80
1 5 $\bar{9}$	16.26	17.56
1 4 $\bar{9}$	-5.43	5.77
1 3 $\bar{9}$	2.77	2.93
1 2 $\bar{9}$	1.02	<1.55
1 1 $\bar{9}$	14.12	15.31
1.2.$\bar{10}$	-11.24	13.30
1.1.$\bar{10}$	4.48	4.56
1.0.$\bar{10}$	16.56	18.88

h k l	F_c	$\|F_o\|$
2.10.0	4.99	5.52
2 9 0	-3.75	3.79
2 8 0	-8.52	8.00
2 7 0	8.78	8.61
2 6 0	31.97	29.50
2 5 0	3.74	3.60
2 4 0	2.25	3.09
2 3 0	0.53	<1.31
2 2 0	9.45	12.75
2 1 0	-10.38	11.85
2 0 0	25.10	27.17
2 9 1	-17.19	15.48
2 8 1	10.79	11.15
2 7 1	-5.14	4.12
2 6 1	-10.98	11.39
2 5 1	-13.29	14.71
2 4 1	-4.14	6.04
2 3 1	-33.54	33.35
2 2 1	18.53	21.09
2 1 1	-11.33	12.54
2 9 2	-10.36	9.76
2 8 2	-3.21	3.91
2 7 2	3.19	2.65
2 6 2	-3.31	2.90
2 5 2	0.82	<1.19
2 4 2	-2.84	3.49
2 3 2	-0.56	<1.16
2 2 2	-2.68	3.08
2 1 2	-18.64	19.05
2 8 3	-3.73	3.75
2 7 3	5.32	5.40
2 6 3	-8.24	7.34
2 5 3	16.80	15.29
2 4 3	12.32	12.00
2 3 3	21.19	19.02
2.11.$\bar{1}$	8.02	6.37
2.10.$\bar{1}$	1.13	<0.86
2.9.$\bar{1}$	-2.12	2.08
2 8 $\bar{1}$	-5.73	5.42
2 7 $\bar{1}$	25.29	25.32
2 6 $\bar{1}$	-3.96	3.08
2 5 $\bar{1}$	12.16	13.89
2 4 $\bar{1}$	2.55	2.90
2 3 $\bar{1}$	-11.11	13.75
2 2 $\bar{1}$	-3.74	5.41
2 1 $\bar{1}$	36.13	41.33
2 8 $\bar{2}$	-24.81	22.51
2 7 $\bar{2}$	-2.79	3.97
2 6 $\bar{2}$	-13.53	15.50
2 5 $\bar{2}$	0.90	<1.02
2 4 $\bar{2}$	-11.43	13.44
2 3 $\bar{2}$	-5.02	5.76
2 2 $\bar{2}$	-13.88	16.65
2 1 $\bar{2}$	5.98	6.58
2.10.$\bar{3}$	-4.59	4.78
2 9 $\bar{3}$	0.14	<1.07
2 8 $\bar{3}$	7.95	7.10
2 7 $\bar{3}$	1.03	<1.16
2 6 $\bar{3}$	10.84	12.32
2 5 $\bar{3}$	-12.18	11.99
2 4 $\bar{3}$	-14.16	14.69
2 3 $\bar{3}$	-8.39	8.77
2 2 $\bar{3}$	13.42	12.40
2 1 $\bar{3}$	-1.67	2.34
2.10.$\bar{4}$	9.78	11.64
2 9 $\bar{4}$	9.07	10.78
2 8 $\bar{4}$	7.18	8.74
2 7 $\bar{4}$	5.01	3.93
2 6 $\bar{4}$	18.65	18.73
2 5 $\bar{4}$	-17.20	15.35
2 4 $\bar{4}$	22.85	22.68
2 3 $\bar{4}$	-1.95	2.65
2 2 $\bar{4}$	22.36	22.30
2 1 $\bar{4}$	-47.16	30.60
2 0 $\bar{4}$	19.86	18.75
2.10.$\bar{5}$	-9.03	9.35
2 9 $\bar{5}$	-4.39	5.32
2 8 $\bar{5}$	-3.68	4.15
2 7 $\bar{5}$	1.48	1.16
2 6 $\bar{5}$	9.29	5.73
2 5 $\bar{5}$	-1.38	1.15
2 4 $\bar{5}$	-10.68	9.61
2 3 $\bar{5}$	-12.45	13.23
2 2 $\bar{5}$	-2.82	3.77
2 1 $\bar{5}$	1.62	<0.83
2 9 $\bar{6}$	6.40	6.93
2 8 $\bar{6}$	-2.57	1.90
2 7 $\bar{6}$	-5.51	5.80
2 6 $\bar{6}$	-18.20	17.03
2 5 $\bar{6}$	0.50	<1.18
2 4 $\bar{6}$	-11.85	12.62
2 3 $\bar{6}$	0.60	<1.11
2 2 $\bar{6}$	-18.84	17.86
2 1 $\bar{6}$	10.37	9.70
2 0 $\bar{6}$	-13.66	11.37
2 7 $\bar{7}$	-5.36	5.05
2 6 $\bar{7}$	7.88	7.73
2 5 $\bar{7}$	5.94	7.43
2 4 $\bar{7}$	1.98	1.94
2 3 $\bar{7}$	32.49	20.14
2 2 $\bar{7}$	-5.98	5.36
2 1 $\bar{7}$	-1.83	<1.15
2 7 $\bar{8}$	1.88	3.04
2 6 $\bar{8}$	-6.35	6.42
2 5 $\bar{8}$	-8.78	8.87
2 4 $\bar{8}$	11.98	12.98
2 3 $\bar{8}$	2.43	1.93
2 2 $\bar{8}$	8.56	6.97
2 1 $\bar{8}$	5.17	3.68
2 0 $\bar{8}$	8.74	9.48
2 5 $\bar{9}$	-5.79	6.24
2 4 $\bar{9}$	-2.21	2.06
2 3 $\bar{9}$	-2.37	3.56
2 2 $\bar{9}$	2.90	3.93
2 1 $\bar{9}$	-15.07	16.42
2.2.$\bar{10}$	-4.71	5.44
2.1.$\bar{10}$	-9.98	12.09
2.0.$\bar{10}$	5.51	6.56

Zachariasen's atomic parameters. The resulting electron density pattern was well resolved with no questionable or spurious features. The atomic parameters so obtained differed in all cases by less than 0·1 Å from those of Zachariasen, hence these parameters together with a consistent set of x parameters were used for the initial input in a three dimensional least-squares refinement.

Table 2. *Sodium bicarbonate final atomic parameters*

Corresponding values obtained by Zachariasen (1933) are included in parenthesis

Atom	x	y	z	σx	σy	σz	B
Na	0·4274 (0·430)	0·0047 (0·000)	0·7145 (0·722)	0·0011	0·0003	0·0004	1·10
C	0·2098 (0·245)	0·2370 (0·236)	0·9232 (0·931)	0·0028	0·0007	0·0009	0·90
O_1	0·1896 (0·245)	0·3668 (0·367)	0·9291 (0·931)	0·0018	0·0005	0·0006	0·92
O_2	0·9883 (0·983)	0·1629 (0·169)	0·7946 (0·800)	0·0018	0·0005	0·0006	0·89
O_3	0·4958 (0·505)	0·1707 (0·169)	0·0600 (0·061)	0·0018	0·0005	0·0006	1·01

This refinement was carried out using an I.B.M. 704 program by Sayre, modified by Vand. This program refines all positional parameters and individual isotropic temperature factors. The normal-equation matrix is approximated by including only the cross-terms between parameters of the same atom and unit weights are used throughout. The atomic form factors were stored in tables at intervals of $2 \sin \theta/\lambda$ equal to 1/32 Å^{-1}. Intermediate values are linearly interpolated. The oxygen and carbon form factors were those of McWeeny (1951) and the sodium form factor was that of Viervoll and Øgrim (1949). A total of 374 reflections (329 observed and 45 unobserved) were used in the refinement. The intensities of the unobserved reflections were taken to be one half of the minimum observable value. An initial temperature factor of $B=0{\cdot}5$ was assumed for all atoms. During the least squares refinement the reliability index decreased from $R=0{\cdot}325$ to $R=0{\cdot}108$ while the sum of the squares of the deviations, $\Sigma|F_o-F_c|^2$, decreased from 8,388 to 750. The final calculated and observed structure factors appear in Table 1. The final parameters and their standard deviations appear in Table 2. The final observed electron density projection $\varrho(y, z)$ appears in Fig. 1. All attempts to locate the hydrogen atom failed.

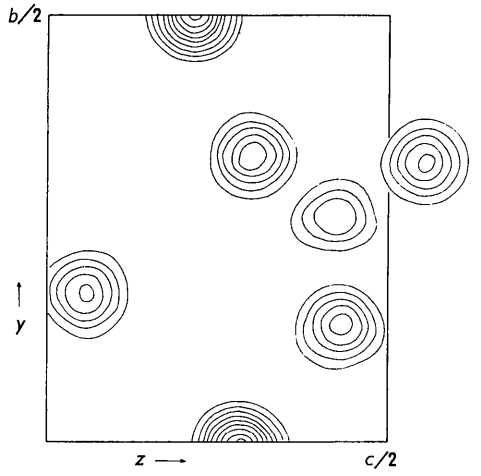

Fig. 1. Final observed electron density projection $\varrho(yz)$.

Discussion of structure

Fig. 2 represents the projection of the structure down the a and b axes. The crystal is seen to consist of layers of anions alternating with cationic layers approximately parallel to the $10\bar{2}$ planes.

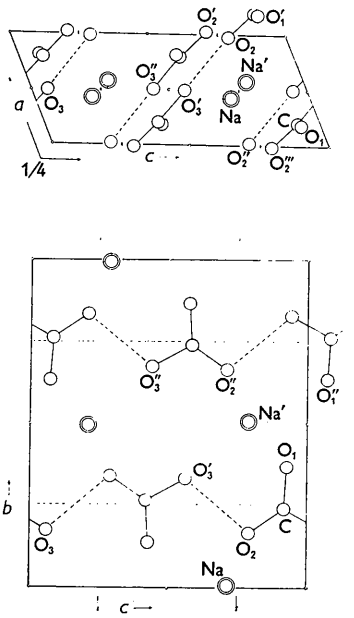

Fig. 2. Projection of the sodium bicarbonate structure down the a and b axes.

Each sodium ion is surrounded by six oxygen atoms in a slightly distorted octahedral arrangement. The various $Na^+ \cdots O$ distances range from 2·389 to 2·471 Å with an average value of 2·438 Å. Zachariasen (1933) reported values for these distances from 2·37 to 2·57 Å with an average value of 2·47 Å, with individual distances differing from our values by about $\pm 0{\cdot}08$ Å. These values of the $Na^+ \cdots O$ distance agree with other values reported in the literature. The following values have been determined; sodium nitrite (Carpenter, 1952), 2·47 and 2·52 Å; sodium thiosulfate pentahydrate (Taylor & Beevers, 1952), 2·38–2·53 Å and in sodium chlorate (Zachariasen,

1929), 2·46 Å. The stereographic projection of the sodium ion coordination sphere in Fig. 3 illustrates the degree of distortion from a regular octahedral arrangement of oxygen atoms.

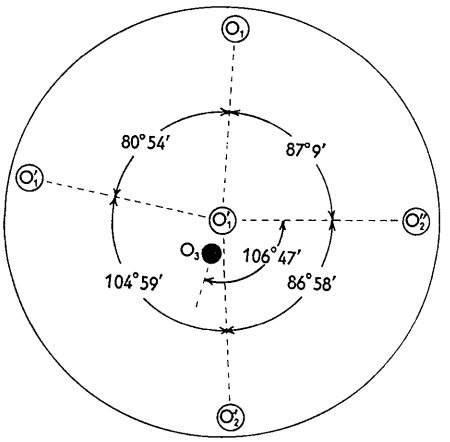

Fig. 3. Stereographic projection of the sodium ion coordination sphere.

The anionic layers consist of infinite chains of hydrogen bonded bicarbonate ions. The dimensions of the bicarbonate ion are given in Fig. 4. Within experimental error the ion exhibits C_{2v} symmetry. The four heavy atoms of each bicarbonate group are planar to within 0·01 Å. The unit normal to this plane is $N = -3{\cdot}1316\mathbf{a}^* - 0{\cdot}8923\mathbf{b}^* + 5{\cdot}9773\mathbf{c}^*$, where **a***, **b***, and **c*** are the three reciprocal cell vectors. This plane is at an angle of 5° 36′ to the $(10\bar{2})$ crystal planes, thus resulting in a slightly pleated hydrogen bonded chain. One of the primary assumptions made by Zachariasen (1933) was that, since the crystal cleavage plane is the $(10\bar{2})$ plane, the hydrogen bonded anions must form sheets parallel to this plane. His other basic assumption was that the CO_3 group is trigonal planar with a C–O bond distance of 1·27 Å. The problem of determining the anionic configuration thus reduced to a four parameter problem, the location of the carbon atom and a single rotation of the CO_3 group about its center. The best fit with observation led to a hydrogen bond distance of 2·55 Å. In detail we have found the following. Only two of the oxygen atoms are involved in hydrogen bonding, the hydrogen atom being covalently bonded to O_3 and electrostatically bonded to O_2. The $O_3 \cdots O_2$ distance of 2·595 Å and the hydrogen bond $C\text{–}O_3 \cdots O_2$ of 112° 56′ are as expected. The bond length of 1·346 Å found for the $C\text{–}O_3$ distance is shorter than the single bond value of 1·43 Å found in paraffinic alcohols and corresponds to 14 % double bond character (Vaughan & Donohue, 1952). In the free ion, both the $C\text{–}O_1$ and $C\text{–}O_2$ bonds would be predicted to have 50% double bond character, or a bond distance of 1·255 Å. The observed values of 1·264 and 1·263 Å, respectively, agree well with this value, and also indicate that the hydrogen bond does not seriously effect the O_2 bonding electrons. The total bond order of the carbon atom is 4·10 and is not significantly different from the expected value of 4·00.

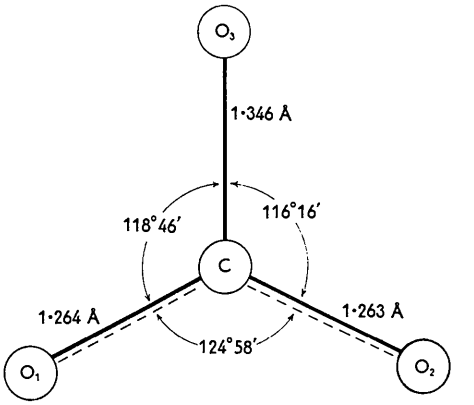

Fig. 4. The bicarbonate ion.

The dimensions of the bicarbonate ion as observed in other salts differ considerably from those reported here for sodium bicarbonate. In potassium bicarbonate (Nitta, Tomiie & Hoe Koo, 1952) the bicarbonate ions form hydrogen bonded dimers as illustrated in Fig. 5. In this case, both the oxygen atoms involved in hydrogen bonding have similar carbon–oxygen distances, namely 1·32 Å and 1·33 Å. The third carbon–oxygen distance of 1·28 Å results in an overall carbon bond order of 3·78. The structure of sodium sesquicarbonate dihydrate (Brown, Peiser & Turner-Jones, 1949) contains two carbonate groups joined by a symmetrical hydrogen bond of length 2·53 Å. These dimers are joined to each other through the two water molecules by somewhat longer hydrogen bonds into infinite chains as shown in Fig. 5. All of the carbon–oxygen bond distances are quite short. The carbon–oxygen bonds of the non-hydrogen bonded oxygen atom and of that which is hydrogen bonded to the water molecule both are 1·23 Å in length, with a calculated double bond character of 68%. The carbon–oxygen bond of the symmetrically hydrogen bonded oxygen atom is 1·26 Å in length, corresponding to 48% double bond character. These values seem remarkably short when compared to the measured carbon–oxygen distance of 1·294 Å found in calcite (Sass, Vidale & Donohue, 1957). The overall bond order for the carbon atom is 4·84.

A somewhat similar dependence of the carbon–oxygen bond length on environment occurs in the monocarboxylic acids. Both formic acid and acetic acid exist in the vapor state as hydrogen bonded dimers and in the solid state as infinite hydrogen bonded chains. The two formic acid C–O bond distances are 1·25 and 1·36 Å in the dimeric vapor (Karle & Brockway, 1944) and 1·23 and 1·26 Å in the solid (Holtzberg, Post & Fankuchen, 1953). Similarly, in the case of acetic acid, the C–O bond distances are 1·25 and 1·36 Å

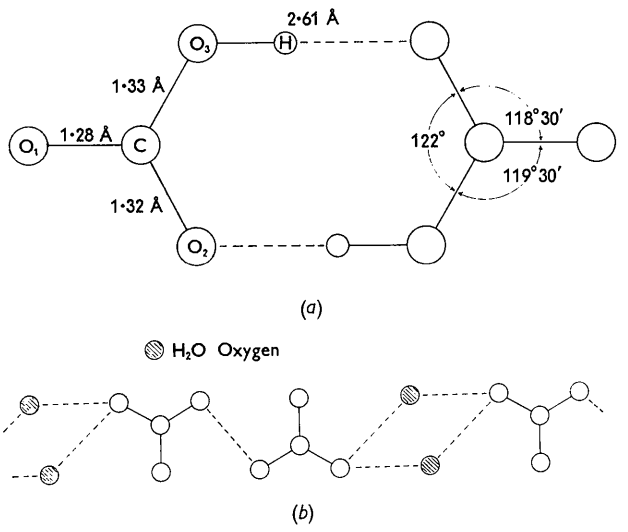

Fig. 5. (*a*) Schematic diagram of the bicarbonate ion in the potassium salt. (*b*) Schematic diagram of the hydrogen bond system in sodium sesquicarbonate.

in the dimeric vapor (Karle & Brockway, 1944) and 1·24 and 1·29 Å in the solid (Jones & Templeton, 1958).

It is tempting to draw comparisons between the dimeric forms of these acids in the vapor state and the dimeric bicarbonate ions in the potassium salt, and similarly between the infinite chain systems of these acids in the solid state with the corresponding bicarbonate chains in the sodium salt. A more valid comparison would result however if data were available for the crystal structures of other carboxylic acids such as propanoic, butyric, valeric, etc. Work on these acids has been started and will be discussed in future papers.

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References

BROWN, C. J., PEISER, H. S. & TURNER-JONES, A. (1949). *Acta Cryst.* **2**, 167.
CARPENTER, G. B. (1952). *Acta Cryst.* **5**, 132.
GROTH, P. (1908). *Chemische Kristallographie* II, 191. Leipzig: Engelmann.
HOLTZBERG, F., POST, B. & FANKUCHEN, I. (1953). *Acta Cryst.* **6**, 127.
International Critical Tables (1926). Vol. 1., 151.
JONES, ROBERT E. & TEMPLETON, DAVID H. (1958). *Acta Cryst.* **11**, 484.
KARLE, J. & BROCKWAY, L. O. (1944). *J. Amer. Chem. Soc.* **66**, 574.
MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.
NITTA, I., TOMIIE, Y. & HOE KOO, C. (1952). *Acta Cryst.* **5**, 292.
SASS, R. L., VIDALE, ROSEMARY & DONOHUE, JERRY. (1957). *Acta Cryst.* **10**, 567.
TAYLOR, PATRICIA G. & BEEVERS, C. A. (1952). *Acta Cryst.* **5**, 341.
VAUGHAN, PHILIP & DONOHUE, JERRY (1952). *Acta Cryst.* **5**, 530.
VIERVOLL, H. & ØGRIM, O. (1949). *Acta Cryst.* **2**, 277.
ZACHARIASEN, W. H. (1929). *Z. Kristallogr.* **71**, 517.
ZACHARIASEN, W. H. (1933). *J. Chem. Phys.* **1**, 634.

Acta Cryst. (1962). **15**, 81

Thermal Expansion of Triglycine Sulphate

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The thermal expansion of triglycine sulphate, which exhibits ferroelectric behaviour, has been investigated both below and above the Curie point by the interferometric method. Along all the directions studied there is an abrupt reversal of sign of the expansion coefficient at the Curie point. Investigations carried out with various rates of heating and cooling have shown that there is no thermal hysteresis. The shortest hydrogen bond in the unit cell of the crystal is found to coincide with the direction of maximum expansion. The results are compared with the X-ray measurements of Ezhkova *et al.* (1959).

Introduction

Triglycine sulphate $(NH_2CH_2COOH)_3H_2SO_4$ crystallizes in the monoclinic system and is found to be ferroelectric at room temperature (Matthias *et al.*, 1956). Morphological and X-ray studies of Matthias *et al.* (1956) and Hoshino *et al.* (1957) have shown that the space group is $P2_1$ in the ferroelectric phase, and above the Curie point of 47 °C. the space group is $P2_1/m$. The crystal belongs to the uniaxial ferroelectric group and the direction of spontaneous polarization is the diad *b*-axis of the crystal. Later workers have given the Curie point to be about 50 °C. (Triebwasser, 1958; Fatuzzo, 1958).