Acta Cryst. (1949). **2**, 167

The Crystal Structure of Sodium Sesquicarbonate

By C. J. Brown

Research Laboratories, Imperial Chemical Industries Limited (Dyestuffs Division),
Hexagon House, Blackley, Manchester 9, Great Britain

H. S. Peiser and Miss A. Turner-Jones

Research Department, Imperial Chemical Industries Limited (Alkali Division),
Winnington, Northwich, Cheshire, Great Britain

(*Received* 8 *February* 1949)

The crystal structure of sodium sesquicarbonate (trona) has been determined completely. The crystals are monoclinic, space group $C2/c$, with cell dimensions $a = 20{\cdot}41 \pm 0{\cdot}03$; $b = 3{\cdot}49 \pm 0{\cdot}01$; $c = 10{\cdot}31 \pm 0{\cdot}01$ A.; $\beta = 106^\circ\ 20' \pm 10'$. The approximate atomic co-ordinates were found by means of a two-dimensional Patterson synthesis followed by the systematic comparison of structure amplitudes. These co-ordinates have been refined by means of three-dimensional Fourier syntheses, using 650 experimental structure amplitudes. The carbonate ion is found to be planar, with 120° angles, within experimental error; the C–O distances are $1{\cdot}23 \pm 0{\cdot}02$; $1{\cdot}23 \pm 0{\cdot}02$ and $1{\cdot}26 \pm 0{\cdot}02$ A., the last oxygen being bonded by a hydrogen bridge of 2·53 A. to an oxygen of another carbonate ion, forming what might be called a complex $[HC_2O_6]^{3-}$ anion. The water molecule has hydrogen bonds of lengths $2{\cdot}72 \pm 0{\cdot}03$ and $2{\cdot}77 \pm 0{\cdot}03$ A. to oxygen atoms of carbonate ions.

Introduction

Sodium sesquicarbonate, $Na_2CO_3.NaHCO_3.2H_2O$, is native to Africa as the mineral trona, and is also manufactured commercially in Great Britain. Its crystal structure is of interest for a number of reasons. First, crystal data on carbonates in general are remarkably scarce, and in particular the only alkali carbonates whose structures are known are sodium bicarbonate, $NaHCO_3$ (Zachariasen, 1933), sodium carbonate monohydrate, $Na_2CO_3.H_2O$ (Harper, 1936), and potassium silver carbonate, $KAgCO_3$ (Donohue & Helmholz, 1944). Secondly, the only structure in which the dimensions of the carbonate ion have been determined with precision is that of calcite, $CaCO_3$ (Elliott, 1937), and additional data on the length of the C–O bond in carbonates would be welcome. Thirdly, the two types of hydrogen bond are present together in sodium sesquicarbonate, and further information concerning the lengths of these would be of value.

Morphology and optical data

The crystals of sodium sesquicarbonate used in this investigation were prepared synthetically, and were monoclinic prisms with pronounced development of the orthodomes (101) and $(10\bar{1})$, resulting in elongation along [*b*]. There is perfect cleavage parallel to (100) and good cleavage parallel to $(10\bar{1})$.

The refractive indices given by Larsen & Berman (1934) are $\alpha = 1{\cdot}412$, $\beta = 1{\cdot}492$ and $\gamma = 1{\cdot}540$. An unpublished determination by C. W. Bunn gave $\alpha = 1{\cdot}418$, $\beta = 1{\cdot}492$ and $\gamma = 1{\cdot}543$. The α-vibration direction is parallel to [*b*], and the γ-vibration direction makes an angle of 83° with [*c*]. The optic axial angle $2V = 72^\circ$, and the dispersion is rather strong, with $r < v$.

X-ray experimental technique

The dimensions of the unit cell were obtained from single-crystal rotation photographs by measurement of the layer lines. The angle β was derived by calculation from the unit lengths of the *a*, *c*, [101] and [103] axes. $a = 20{\cdot}41 \pm 0{\cdot}03$; $b = 3{\cdot}49 \pm 0{\cdot}01$; $c = 10{\cdot}31 \pm 0{\cdot}01$ A.; and $\beta = 106^\circ\ 20' \pm 10'$. The density required for four units of $Na_2CO_3.NaHCO_3.2H_2O$ per unit cell is 2·13 g.cm.$^{-3}$, while experimental values recorded in the literature range from 2·112 to 2·147 g.cm.$^{-3}$

Systematic extinctions are $\{hkl\}$ absent for $(h+k)$ odd, and $\{h0l\}$ absent for l odd, leading to the alternative space groups Cc or $C2/c$. As the crystals showed no evidence of polar character, the latter was provisionally adopted. Since it has led to a reasonable structure which could be satisfactorily refined, the space group $C2/c$ may be considered to be definitely established for this substance.

X-ray intensities were obtained in the first place by means of single-crystal oscillation photographs about [*b*], and subsequently by Weissenberg moving-film photographs about [*a*] (zero and eight layers), [*b*] (zero and first layer), and [*c*] (zero and four layers). The equi-inclination method was used for the layer-line photographs. The multiple-film technique devised by Robertson (1943) was used with slight modification; three films were loaded into the camera and exposed, then a further three films were loaded and given an exposure eight times as long as the first three. The absorption factor for normal incidence with this batch of film was found in a separate experiment to be almost exactly two, using Cu $K\alpha$ radiation. In this way, sets of films covering the same range of spots were obtained having relative exposures of 1 : 2 : 4 : 8 : 16 : 32. The [*b*] oscillation and [b] Weissenberg photographs were used in conjunction in intensity estimation. The estimation of all the spots was carried out visually; a certain value was ascribed to a spot of medium intensity on each set of photographs, and then all the other spots on the same set were related to the first one by comparison between the photographs of different relative exposure times. The appropriate correction factors for angular velocity and film absorption as determined by Cox & Shaw (1930) were applied to the intensities from the oscillation photographs, and the corresponding values determined by Tunell (1939) were applied to the Weissenberg photographs, as well as the Lorentz and polarization factors. The various sets of photographs were placed on the same relative intensity scale by working out the ratio between pairs of common spots, and then multiplying each set by the appropriate ratio. The relative intensity scale was converted to the absolute by comparison of the experimental structure amplitudes with the calculated, and then multiplying by the ratio. In this way experimental structure amplitudes were obtained for 650 planes. Unfortunately, this technique has left some 70 planes having spacings between $\frac{1}{2}\lambda$ and 1·20 A. unobserved, but appropriate allowance has been made for these planes in the subsequent work. The linear absorption coefficient for sodium sesquicarbonate is 36 cm.$^{-1}$, and since very small crystals were used, no allowance has been made for absorption.

Preliminary deductions regarding the structure

The space group $C2/c$ possesses an eightfold general position, and since the unit cell contains four units of $Na_2CO_3.NaHCO_3.2H_2O$, it may be concluded that 8 Na, 8 CO_3 and 8 H_2O probably lie in general positions, while the other 4 Na and 4 H atoms must occupy special positions. The possible fourfold special positions for these sodium and hydrogen atoms are either on twofold axes at $(0, y, \frac{1}{4})$, etc., or on sets of symmetry centres at $(0, 0, 0)$, etc., $(0, \frac{1}{2}, 0)$, etc., $(\frac{1}{4}, \frac{1}{4}, 0)$, etc., or $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$, etc., in the nomenclature of the *International Tables*. The correct assignment of these positions to the sodium and hydrogen atoms could not be made in the early stages of the analysis, but it subsequently emerged that the sodium lies on the twofold axes at $(0, y, \frac{1}{4})$, $(0, -y, \frac{3}{4})$, $(\frac{1}{2}, \frac{1}{2}+y, \frac{1}{4})$ and $(\frac{1}{2}, \frac{1}{2}-y, \frac{3}{4})$. Similarly, the hydrogen was found to lie on the centres of symmetry at $(0, 0, 0)$, $(0, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

The existence of a short axis ([b] = 3·49 A.) indicates that probably a projection of the structure along this axis will be free from overlapping atoms. Further, the fact that the direction of least refractive index is parallel to [b] indicates that probably the carbonate ions will lie in a plane roughly perpendicular to this axis, in the same way as in the structure of sodium bicarbonate.

Cleavage data indicate that there should be planes of weak cohesion parallel to (100) and (10$\bar{1}$). The direction of greatest optical density is inclined to [c], and therefore to (100) by 83°, and since the angle between (100) and (10$\bar{1}$) is 77° it seems fairly probable that the strongly bound complex anions will lie in strips roughly parallel to (10$\bar{1}$). These would be separated from one another by strips of sodium ions, so that the cleavage planes would be occupied mainly by sodium ions.

The Patterson synthesis

A two-dimensional Patterson synthesis was computed, using values of F^2 for the $\{h0l\}$ zone in the formula

$$P(x, z) = \Sigma\Sigma F^2(h0l) \cos 2\pi(hx + lz).$$

The resultant vector map is shown in Fig. 1.

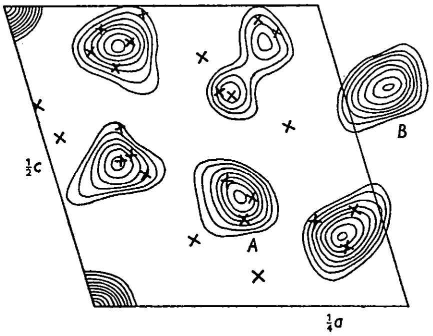

Fig. 1. Patterson two-dimensional projection on (010). The crosses represent interatomic vectors calculated from the final set of co-ordinates.

Since one set of sodium ions lies on general positions (x, y, z), etc., and the other set on special positions which project as symmetry centres, it is apparent that the Patterson vector $(2x, 2z)$, due to the separation of two general sodium ions, will be paired by a vector (x, z) due to the separation of a general sodium ion from a special sodium ion. Examination of the vector map showed several possibilities for pairs of vectors having co-ordinates (x, z) and $(2x, 2z)$, but structure-amplitude agreement and other considerations indicated that the only reasonable choice was to take the peak A as (x, z) and the peak B as $(2x, 2z)$. The x and z co-ordinates of peak B are 0·288 and 0·382 respectively, and thence the values of x and z for the general sodium ion are 0·144 and 0·191 relative to the special sodium ion. It was subsequently determined that the special sodium ion lay at $(0, y, \frac{1}{4})$ on a twofold axis, hence the x and z co-ordinates of the general sodium ion were given by the Patterson synthesis as $x = 0·144$ and $z = 0·441$.

No attempt was made to interpret the other peaks in the Patterson vector diagram at this stage of the work, but as the final structure must account for the Patterson peaks, the complete set of interatomic vectors involving sodium and oxygen atoms has been calculated, and is represented by small crosses in Fig. 1.

Trial determination of the other atomic positions

As the x and z co-ordinates of the two sodium atoms had been deduced from the space group and from the

Patterson synthesis, it remained to find positions for the carbonate ion and the water molecule. This was done by the systematic comparison of structure amplitudes. The list of experimental F's (Tables 5 and 6) shows a number of outstandingly high values. Those in the region of 100 or more in the $\{h0l\}$ zone include (204), (402), (606), (80$\bar{6}$), (10.0.$\bar{2}$) and (14.0.0); these were used for the comparisons. For the sodium atom in the special position, the contribution to the structure amplitude for planes having $l=4n$ is positive, while for planes having $l=4n+2$ it is negative. Similarly, it was found that the structure-amplitude contributions from the sodium atom in the general position were positive for (204) and (14.0.0), while they were negative for (402), (606), (80$\bar{6}$) and (10.0.$\bar{2}$), thereby reinforcing the contribution from the other sodium atom. It was therefore regarded that the phases of these six large structure amplitudes were determined by the contributions from the two sodium atoms, since it would have been most improbable for the contributions from the carbonate ion and the water molecule to outweigh those of the sodium atoms for these particular planes. Next, a diagram of the projection of the unit cell was drawn, on which the appropriate maxima for these six planes were represented by lines. The most probable positions of the remaining five atoms were in the region of the intersections of these lines. Four regions were very clearly indicated on the diagram, and, as three of these regions formed an equilateral triangle, it was assumed that the carbonate ion was located there, and that the water molecule was in the fourth region. It was hardly to be expected that the carbon atom would show up by this method owing to its relatively lower scattering power, but for preliminary phase determination of structure amplitudes it was assumed to be at the centre of the equilateral triangle. Co-ordinates for all the atoms were then written down, and the structure amplitudes for about 50 planes (i.e. those having h up to 14 and l up to 6) were calculated. The agreement was reasonably good, and enabled a start to be made with the process of refinement by means of Fourier syntheses.

Two-dimensional Fourier syntheses

The first Fourier projection along [b] was computed, using approximately 50 terms. Refinement of the atomic co-ordinates proceeded successfully, and after three syntheses, using successively more terms, the refinement was judged to be complete. There were no changes of sign caused by the final synthesis. The resulting electron-density contour map is shown in Fig. 2. The computation was carried out in the usual way using the original type of Beevers-Lipson strips. By virtue of the space group having $\{h0l\}$ present only for h even and l even, it was possible, by halving the values of h and l, to sum the electron density at intervals of $\frac{1}{120}$th of the cell edge. This was an advantage in the case of this structure, because of the rather great length of [a] (20·41 A.), and there would have been some uncertainty in drawing the contours had the summation been carried out at the usual intervals of $\frac{1}{60}$th.

The fractional co-ordinates measured from the electron-density contour map (Fig. 2) are listed in Table 1.

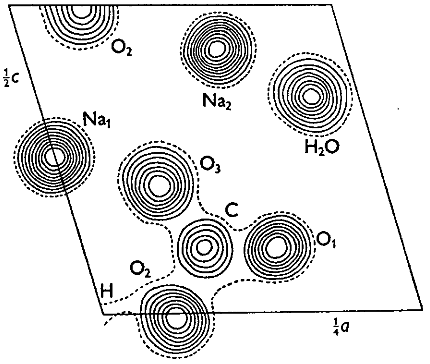

Fig. 2. Two-dimensional Fourier projection on (010). Contours are at intervals of 1 e.A.$^{-2}$, the 1-electron contour being shown by the broken lines.

Table 1. *Fractional co-ordinates from Fig.* 2

Atom	x	z
Na_1	0	0·250
Na_2	0·151	0·427
C	0·094	0·104
O_1	0·150	0·103
O_2	0·056	0·992
O_3	0·074	0·206
H_2O	0·214	0·350

Determination of the y co-ordinates

The first approximation to the y co-ordinates of the atoms was made by trial. From the [b] Fourier projection it appeared that, in order to maintain reasonable radii for the sodium ions, the y co-ordinate of O_3 would need to be 0·5 from that of Na_1, and the same argument applies also to the y co-ordinates of Na_2 and H_2O. It was further expected that the carbonate ion would be roughly planar, and nearly parallel to (010), since [b] is so short. With these various considerations in mind, possible y co-ordinates were tried until reasonable agreement was obtained for about 50 $\{hkl\}$ planes, having $k=1$. There was the further point to be noted that final choice had not been made between the various sets of special positions for the sodium and hydrogen ions, and each of these had to be tried until the best agreement was reached.

Three-dimensional Fourier syntheses

The fifty terms obtained by trial of y co-ordinates were used in computing portions of a three-dimensional Fourier synthesis along lines parallel to [b] at the values of x and z obtained from the two-dimensional projection. It was found that the maxima on these lines were sharp, and by taking these maxima as new y co-ordinates, and then repeating the process of structure-amplitude calculation and Fourier synthesis, refinement was achieved fairly rapidly. After three stages of this refinement process all the $\{hkl\}$ terms were involved in a final set of line syntheses; the results are shown in Fig. 3, and the measurements from these graphs are given in Table 2.

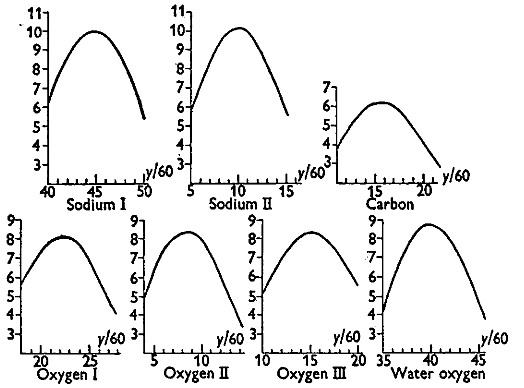

Fig. 3. Electron density along lines parallel to [*b*] through atoms as given by three-dimensional Fourier syntheses. Electrons shown as ordinates.

Table 2. *Fractional co-ordinates from Fig.* 3

Atom	y
Na_1	0·748
Na_2	0·165
C	0·262
O_1	0·373
O_2	0·139
O_3	0·257
H_2O	0·669

Finally, all the structure amplitudes were inserted as terms of a three-dimensional Fourier synthesis which was computed in sections parallel to (010) at the values of y given in Table 2. The result is shown in Fig. 4, plotted as a composite electron-density map. The x and z co-ordinates obtained by measurement of the centres of these peaks are given in Table 3.

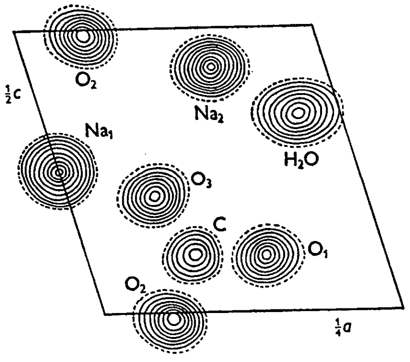

Fig. 4. Composite three-dimensional Fourier synthesis sections. The 1-electron contour is shown by the broken lines, and the other contours are at 1-electron intervals.

Table 3. *Fractional co-ordinates from Fig.* 4

Atom	x	z
Na_1	0	0·250
Na_2	0·154	0·428
C	0·091	0·102
O_1	0·149	0·099
O_2	0·055	0·990
O_3	0·074	0·206
H_2O	0·213	0·346

It is seen that these figures do not differ from those given by the two-dimensional Fourier projection by more than 0·004 in any one case, and the average difference is only 0·0016. With regard to the 70 {*hkl*} planes whose X-ray intensities were not observed owing to the limits of the experimental technique, it was found that when their calculated *F*'s were inserted in this final three-dimensional synthesis, none of the y co-ordinates was changed by more than 0·01, which is well within the experimental error. This was considered sufficient justification for not taking these additional planes into account.

The atomic co-ordinates

There was some uncertainty as to whether the x and z co-ordinates given by the three-dimensional synthesis would be better than those given by the two-dimensional projection. Certainly the three-dimensional synthesis had a larger number of terms, 650 as against the 140 used in the projection, and consequently the resolution was higher, but it was possible to compute it only at intervals of $\frac{1}{60}$th of the cell edge with the facilities available, whereas the projection was computed at intervals of $\frac{1}{120}$th. For this reason it was decided to take the mean of the x and z co-ordinates given by the two syntheses as the final values, and these, together with the final y co-ordinates, are listed in Table 4.

Table 4. *Final co-ordinates*

Atom	x	y	z
Na_1	0	0·748	0·250
Na_2	0·152	0·165	0·428
C	0·093	0·262	0·103
O_1	0·150	0·373	0·101
O_2	0·056	0·139	0·991
O_3	0·074	0·257	0·206
H_2O	0·214	0·669	0·348

Fig. 5 depicts the whole of the contents of the unit cell in diagrammatic fashion. Sufficient heights of atoms out of the plane of projection are indicated to show the environment of the sodium ions.

Structure-amplitude agreement

The atomic scattering factors used in computing the structure amplitudes were those given in the paper on the crystal structure of sodium bicarbonate (Zachariasen, 1933), where the value of *B* in the temperature factor appears to have been $1{\cdot}5\times10^{-16}$ A.^{2} There were no changes of phase of any of the terms following the final three-dimensional Fourier synthesis. The value of the error $\frac{\Sigma\,|F_{\text{exp.}}-F_{\text{calc.}}|}{\Sigma F_{\text{exp.}}}$ is 0·192 for the {*h*0*l*} terms only, and 0·276 for all the {*hkl*} terms. The values of the experimental and calculated structure amplitudes for the {*h*0*l*}, {*hk*0} and {0*kl*} zones are given in Table 5 to show the agreement obtained; in Table 6 are given the experimental *F*'s for the {*hkl*} planes, together with the calculated phases. Fig. 6 gives a general indication of the agreement obtained between the calculated and experimental *F*'s {*hkl*}.

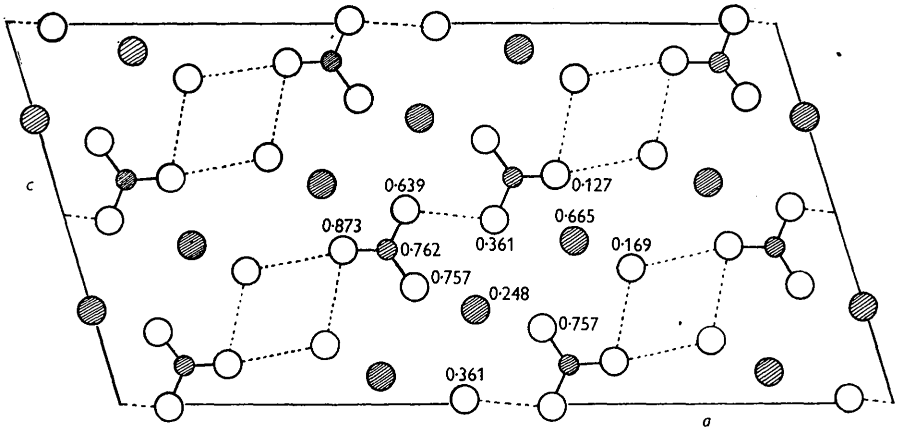

Fig. 5. Diagrammatic representation of contents of unit cell. Sodium and carbon atoms shaded; all others are oxygens. Hydrogen bonds are shown by broken lines.

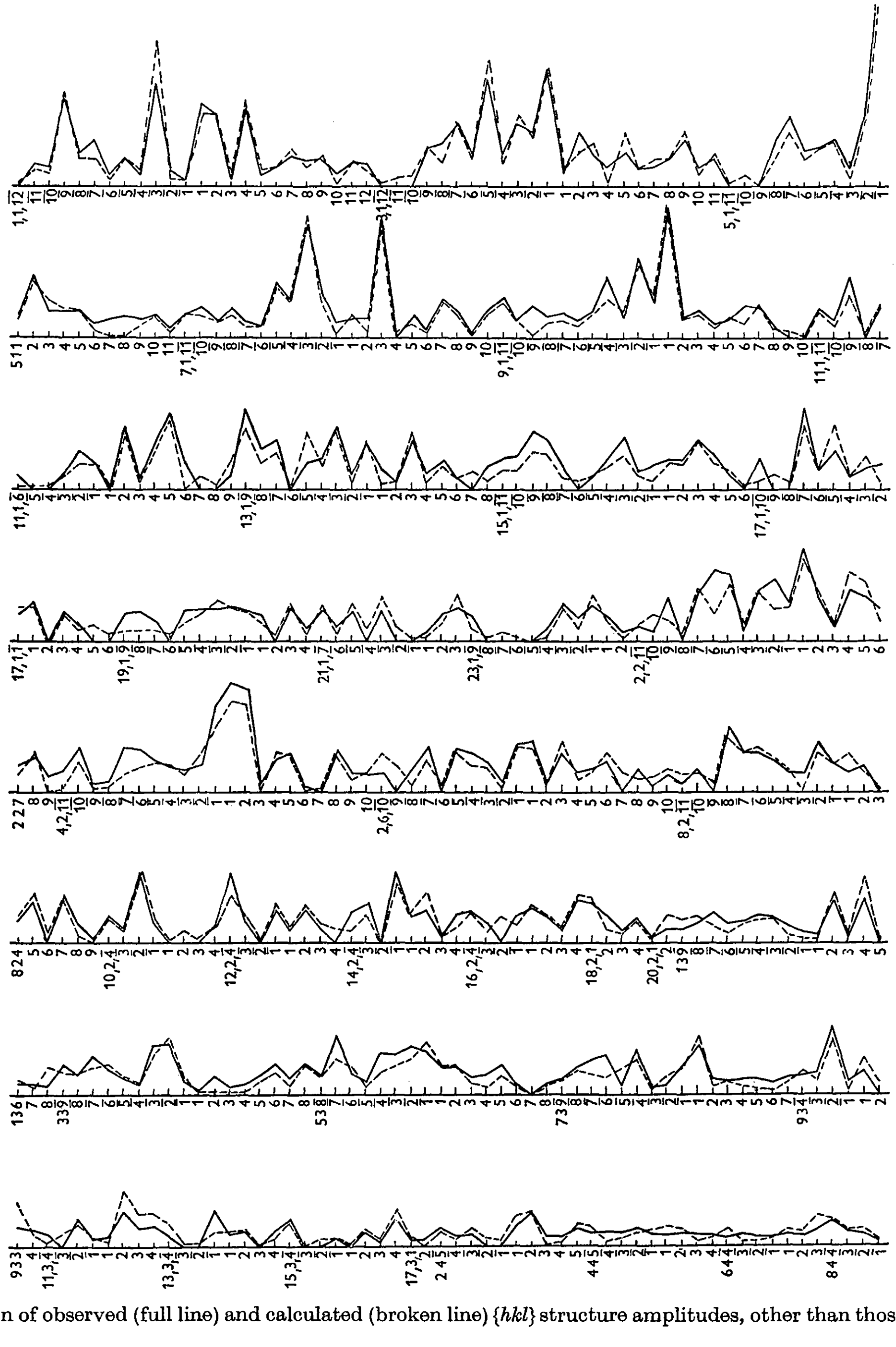

Fig. 6. Comparison of observed (full line) and calculated (broken line) $\{hkl\}$ structure amplitudes, other than those given in Table 5.

Table 5. *Observed and calculated structure amplitudes*

hkl	$F_{\text{exp.}}$	$F_{\text{calc.}}$
000	—	+456
002	20	+23
004	17	−11
006	50	−56
008	11	+6
0,0,10	20	+19
0,0,12	16	+22
$2,0,\overline{12}$	26	+30
$2,0,\overline{10}$	43	+41
$20\bar{8}$	14	−6
$20\bar{6}$	28	−36
$20\bar{4}$	69	+60
$20\bar{2}$	0	0
200	39	+38
202	31	−40
204	139	+142
206	23	+13
208	43	+58
2,0,10	0	−3
2,0,12	16	−30
$4,0,\overline{12}$	20	−13
$4,0,\overline{10}$	54	−53
$40\bar{8}$	25	+23
$40\bar{6}$	75	+74
$40\bar{4}$	29	+35
$40\bar{2}$	18	+6
400	54	−61
402	140	−153
404	96	+76
406	25	+28
408	48	+45
4,0,10	17	−16
4,0,12	13	+19
$6,0,\overline{12}$	11	+11
$6,0,\overline{10}$	51	−46
$60\bar{8}$	31	−30
$60\bar{6}$	39	−41
$60\bar{4}$	8	+1
$60\bar{2}$	26	−21
600	27	+30
602	63	+54
604	22	−22
606	88	−94
608	20	+10
6,0,10	7	−10
$8,0,\overline{12}$	24	+10
$8,0,\overline{10}$	0	−10
$80\bar{8}$	37	+37
$80\bar{6}$	123	−108
$80\bar{4}$	72	−72
$80\bar{2}$	25	−35
800	34	−23
802	10	−10
804	26	+31
806	18	−9
808	19	−19
8,0,10	23	−29
$10,0,\overline{10}$	48	−34
$10,0,\bar{8}$	47	+39
$10,0,\bar{6}$	12	+13
$10,0,\bar{4}$	40	+47
$10,0,\bar{2}$	158	−139
10,0,0	59	−50
10,0,2	57	−48
10,0,4	27	−24
10,0,6	15	+12
10,0,8	10	+14
10,0,10	20	−18
$12,0,\overline{10}$	15	0
$12,0,\bar{8}$	20	+7
$12,0,\bar{6}$	68	−66
$12,0,\bar{4}$	60	+59
$12,0,\bar{2}$	15	−10
12,0,0	44	+46
12,0,2	45	−39
12,0,4	28	−23
12,0,6	53	−50
12,0,8	12	−18
$14,0,\overline{12}$	36	+39
$14,0,\overline{10}$	26	+18
$14,0,\bar{8}$	0	−8
$14,0,\bar{6}$	51	−46
$14,0,\bar{4}$	9	−11
$14,0,\bar{2}$	12	−10
14,0,0	124	+100
14,0,2	44	−22
14,0,4	16	+8
14,0,6	10	−5
14,0,8	0	+2
$16,0,\overline{12}$	15	+14
$16,0,\overline{10}$	19	+7
$16,0,\bar{8}$	0	+10
$16,0,\bar{6}$	42	+35
$16,0,\bar{4}$	55	+61
$16,0,\bar{2}$	35	−33
16,0,0	36	−32
16,0,2	33	−26
16,0,4	78	+62
16,0,6	0	+12
$18,0,\overline{10}$	30	−33
$18,0,\bar{8}$	39	+34
$18,0,\bar{6}$	37	+50
$18,0,\bar{4}$	19	+22
$18,0,\bar{2}$	15	+14
18,0,0	19	+18
18,0,2	16	−12
18,0,4	33	+28
18,0,6	0	−7
$20,0,\bar{8}$	24	+7
$20,0,\bar{6}$	23	−26
$20,0,\bar{4}$	14	−11
$20,0,\bar{2}$	0	+5
20,0,0	61	+46
20,0,2	47	+46
20,0,4	4	0
$22,0,\bar{8}$	23	+28
$22,0,\bar{6}$	34	−36
$22,0,\bar{4}$	10	−4
$22,0,\bar{2}$	10	+1
22,0,0	7	−6
22,0,2	4	−9
$24,0,\bar{4}$	19	+31
$24,0,\bar{2}$	18	−25
24,0,0	8	−8
$26,0,\bar{4}$	13	+10
110	25	+22
310	45	+26
510	23	−20
710	7	+4
910	32	−38
11,1,0	10	−5
13,1,0	7	+2
15,1,0	0	+1
17,1,0	14	+12
19,1,0	6	+4
21,1,0	14	+6
23,1,0	5	−6
220	38	−29
420	4	+8
620	12	−4
820	0	+2
10,2,0	18	−6
12,2,0	22	−34
14,2,0	32	−43
16,2,0	0	+10
18,2,0	6	−5
20,2,0	15	−14
22,2,0	6	−2
130	20	−18
330	12	−2
530	13	+12
730	22	−17
930	19	+34
11,3,0	14	+6
13,3,0	11	−5
15,3,0	0	−2
17,3,0	0	−11
19,3,0	1	−4
240	16	+21
440	9	+8
640	10	−18
840	7	+2
10,4,0	18	+34
020	108	−110
021	20	−17
022	36	+25
023	13	−14
024	12	−7
025	0	−2
026	23	+31
027	10	−14
028	0	−3
029	13	+4
0,2,10	0	−8
0,2,11	33	+30
040	0	−3
041	10	+10
042	21	−31
043	11	+10
044	16	+9
045	0	−1

Discussion of the structure

The crystal structure of sodium sesquicarbonate is a simple ionic one. Each sodium ion is surrounded by six oxygen atoms, some belonging to the carbonate ion, and some to the water molecule; the co-ordination of one sodium ion is octahedral, and the other sodium ion is at the centre of a slightly distorted trigonal prism. The nearest neighbour environments of these two sodium ions are shown in Fig. 7. The mean Na–O distance is thus 2·45 ± 0·02 A., which is slightly greater than that obtained from the sum of the atomic radii given by Pauling (2·35 A.), Wasastjerna (2·33 A.), Goldschmidt (2·30 A.) and Zachariasen (2·44 A.). Comparable values obtained in similar crystal-structure determinations are: sodium bromate (2·38 A.), sodium nitrate (2·40 A.), sodium sulphate (2·41 A.), sodium formate (2·44 A.), sodium chlorate (2·46 A.), sodium bicarbonate (2·47 A.), sodium nitrite (2·48), sodium chromate (2·52 A.) and sodium carbonate monohydrate (2·57 A.).

Table 6. *Observed structure amplitudes with calculated phases*

hk \ l	$\bar{12}$	$\bar{11}$	$\bar{10}$	$\bar{9}$	$\bar{8}$	$\bar{7}$	$\bar{6}$	$\bar{5}$	$\bar{4}$	$\bar{3}$	$\bar{2}$	$\bar{1}$	1	2	3	4	5	6	7	8	9	10	11	12
1.1	0	+17	+15	−68	+26	−36	+10	−22	−10	+80	+13	+5	−63	+56	−5	+61	−10	+15	−23	−20	+22	−10	−19	+18
3.1	0	0	0	−30	+33	+48	+24	−81	−25	−48	−41	−91	+10	+41	+24	−14	+24	+13	−15	+21	−36	+14	−20	
5.1		0	0	0	−33	+54	−28	−30	+37	+14	+54	−198	+18	−48	−20	−21	−22	−11	−14	0	+15	+18	−7	
7.1		−19	−24	−14	−24	−13	−10	−44	−29	+90	−33	−12	+14	+14	−95	0	−14	−5	−28	−21	−3	−20		
9.1		+31	+13	−25	+16	−19	−13	−22	−47	−15	−63	−27	+102	+14	−21	+10	+14	−24	−22	−9	0	0		
11.1		+22	−13	+47	0	+24	−9	0	0	+12	+30	−20	0	−48	−9	−37	+60	0	0	0	+9			
13.1				−62	−32	+39	0	+22	+25	+50	+11	+36	−16	+6	−38	−12	+21	−9	0	−17				
15.1		+24	+26	−45	+39	+17	0	−10	−23	+40	−13	−19	+24	+23	+39	+26	+11	0						
17.1			+23	0	0	+63	+16	−29	+10	−17	+17	−21	+30	0	+24	−13	0	0						
19.1				−21	−24	0	0	−24	+25	+25	+27	−24	+20	0	−26	+10								
21.1						−24	+12	−23	0	+24	0	0	+6	+20	−25									
23.1				−18	0	0	0	0	−9	−28	−17	−26	+18	+6										
2.2		+10	−7	−33	0	−36	+55	−52	−6	−38	+48	+29	+72	+33	−9	−38	−34	+25	−22	−27	+11			
4.2		−17	+35	+7	−8	−35	−34	−25	−19	−17	+21	−69	−86	+82	−5	−25	+30	−4	0	−32	−14	+14		
6.2			+14	0	+17	+32	0	+34	−30	−23	+7	−37	−39	−7	−29	−14	−17	+23	0	−17	−4	+12		
8.2		+5	+17	0	−47	−30	+30	−24	+14	+14	+38	+22	+14	−20	0	−17	−32	0	−36	+15	0			
10.2									−22	−11	+54	+16	0	0	0	+14								
12.2									−54	+17	0	−25	−10	+25	+9	0								
14.2									−24	+29	0	+55	+20	+25	+4	−22								
16.2									−24	−15	0	+20	+27	+17	+9	−33								
18.2													−30	+20	+9	−19								
20.2													+3	−10										
1.3				+10	−15	−23	+15	+16	+21	−20	−13	−8	+6	−32	+4	−33	0	−10	+9	+7				
3.3				+24	−16	−31	−20	+13	+9	−38	+40	+11	−4	−15	−6	−8	−15	−24	−13	−24				
5.3					+15	−45	+16	+10	−32	−31	−37	+33	−20	+21	−13	+15	−22	+7	0	−8				
7.3				−12	+20	−26	+29	+6	+34	−5	+5	+20	−36	−11	+10	+11	−12	+9	+13					
9.3									+15	−17	+52	−10	−13	0	+16	−13								
11.3									−10	0	−22	+6	+7	+27	+14	+16								
13.3									−8	0	0	+26	+10	−12	0	+12								
15.3									+21	0	0	+7	0	−11	−3	−22								
17.3													−4	0										
2.4								+14	−8	+9	0	0	−15	−25	−7	−7	+13							
4.4								+10	+11	+10	+13	+9	+8	−9	−8	+8								
6.4									+7	+8	+6	+6	+8	−8	+12									
8.4									+20	−11	−8	−4	−5	+13	−6									
10.4											+8	0												

The carbonate ion is planar within experimental error. Two of the C–O interatomic distances are 1·23 ± 0·01 A., while the third is 1·26 ± 0·01 A. The third oxygen whose C–O distance is slightly greater than that of the other two is the one involved in the short hydrogen bond, and this longer C–O distance was therefore to be expected. The angles between the C–O bonds do not differ from 120° by more than 1°. The distance of the carbon atom out of the plane formed by the three oxygen atoms is 0·017 A., which gives an indication of the accuracy with which the lightest atom has been located in the structure. The values of the C–O distances are somewhat shorter than that which has previously been regarded as the best, viz. 1·313 A. in calcite (Elliott, 1937), although 1·27 A. was found in sodium bicarbonate, and 1·22 and 1·25 A. in sodium carbonate monohydrate.

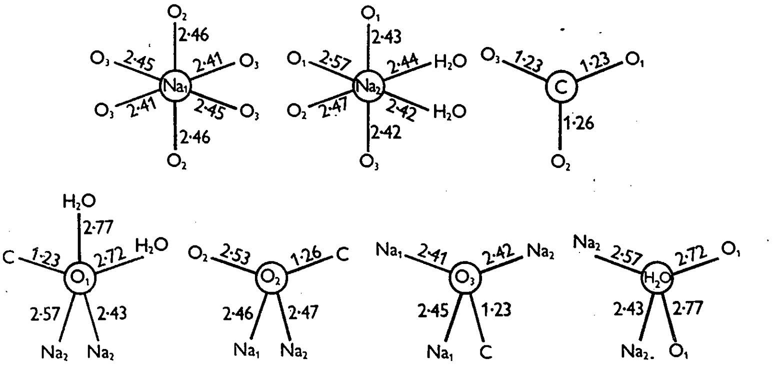

Fig. 7. Diagram of bond-lengths and nearest-neighbour distances (in A.).

Pairs of carbonate ions are linked together by a short hydrogen bridge of the 'acid-salt' type, of length 2·53 ± 0·02 A. This length is comparable with that observed in sodium bicarbonate (2·55 A.), potassium dihydrogen phosphate (2·54 A.), potassium hydrogen phenylacetate (2·55 A.) and oxalic acid dihydrate (2·52 A.). The angle which this hydrogen bond makes with the C–O bond is 111°. These pairs of carbonate ions linked by a hydrogen ion may be regarded as forming a complex anion $[HC_2O_6]^{3-}$, with the hydrogen ion occupying a space-group symmetry centre. This system has also been observed in the structures of potassium hydrogen phenylacetate and potassium hydrogen *p*-hydroxybenzoate (Speakman, 1948), which crystallize in the same space group *C*2/*c*. The true relation of the hydrogen to the centre of symmetry may be either statistical or time-average. An explanation of the precise function of the hydrogen is outside the scope of this paper, but it may be mentioned that it is generally considered at the present time that such a hydrogen ion would be in a state of vibration between two equilibrium positions on either side of the symmetry centre.

The water molecule is situated between two carbonate ions in such a way that two hydrogen bonds of the 'hydroxyl' type are formed; one is of length 2·72 ± 0·03 A., and the other 2·77 ± 0·03 A. These are comparable with the lengths found in ice (2·76 A.), in alcohols (2·70 A.), resorcinol (2·70 A.) and in various metallic hydroxides such as AlO(OH) (2·70 A.) and FeO(OH) (2·71 A.). The two hydrogen bonds subtend an angle of 120° at the oxygen atom of the water molecule, and make angles of 108 and 147° with the C–O bonds of the carbonate ions. The distances apart of unbonded water oxygen atoms are 3·31 and 3·21 A. It is not thought that any significance attaches to the slight difference in length (0·05 A.) of these two long hydrogen bonds. Probably spatial considerations cause the difference, as the longer of the two bonds makes the angle (147°) which shows the greater departure from the tetrahedral value.

It is seen that the oxygen atom of the water molecule is surrounded roughly tetrahedrally by four atoms, two sodiums and two oxygens. As commonly observed in hydrate structures, the water oxygen is surrounded in this way by two cations and two anions, and in this matter sodium sesquicarbonate obeys the usual rule.

Fig. 7 illustrates the nearest neighbour arrangement for each of the atoms in the structure.

The authors desire to express their thanks to Mr C. W. Bunn for his interest and encouragement in this work.

References

Cox, E. G. & Shaw, W. F. B. (1930). *Proc. Roy. Soc.* A, **127**, 71.
Donohue, J. & Helmholz, L. (1944). *J. Amer. Chem. Soc.* **66**, 295.
Elliott, N. (1937). *J. Amer. Chem. Soc.* **59**, 1380.
Harper, J. P. (1936). *Z. Krystallogr.* **95**, 266.
Larsen, E. S. & Berman, H. (1934). *Bull. U.S. Geol. Surv.* no. 848.
Robertson, J. M. (1943). *J. Sci. Instrum.* **20**, 169.
Speakman, J. C. (1948). *Nature, Lond.*, **162**, 695.
Tunell, G. (1939). *Amer. Min.* **24**, 448.
Zachariasen, W. H. (1933). *J. Chem. Phys.* **1**, 634.