

## A Neutron-Diffraction Study of Sodium Sesquicarbonate

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Fourier projections, on the (010) plane, of the neutron scattering density of  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$  have been obtained from single-crystal intensity data at room temperature. The length of the O–H bonds in the water molecules is  $1.01 \pm 0.02$  Å, with the hydrogen atoms displaced slightly from the line of the O–O bonds, so as to make the H–O–H angle approximately tetrahedral. The contours of the hydrogen atom at the centre of symmetry are markedly anisotropic, being extended along the O–O bond, and they are discussed in relation to possible ‘half-hydrogen’ positions on either side of the centre.

### Introduction

Sodium sesquicarbonate,  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ , which occurs naturally as the mineral trona, offers an attractive subject for study by neutron diffraction using single-crystal methods. The X-ray investigation of the structure by Brown, Peiser & Turner-Jones (1949) revealed two points of particular interest on which information could be expected to be obtained with neutrons: first, the detail of the ‘short’ hydrogen bond across the centre of symmetry between  $\text{CO}_3$  ions and, secondly, the detailed configuration of the atoms in the water molecules—in particular the length of the O–H bonds in these molecules.

The symmetry of sodium sesquicarbonate is monoclinic, with space group  $C2/c$  and

$$a = 20.41 \text{ \AA}, \quad b = 3.49 \text{ \AA}, \quad c = 10.31 \text{ \AA}, \quad \beta = 106.3^\circ.$$

The number of parameters to be determined by neutrons is such that the substance provides a convenient advance in the development of Fourier-synthesis methods of data analysis, following the substances of higher symmetry such as  $\text{KHF}_2$  and  $\text{KH}_2\text{PO}_4$  which have been studied previously with neutrons (Peterson & Levy, 1952; Bacon & Pease, 1953, 1955; Peterson, Levy & Simonsen, 1953, 1954). From a practical point of view the three main starting requirements for a successful neutron-diffraction analysis with present-day techniques are satisfied: thus, first, the co-ordinates of all atoms other than hydrogen are already known from the X-ray work; secondly, the information sought for should be revealed by a Fourier projection, rather than three-dimensional analysis; and, thirdly, crystals of sufficient size for adequate intensity measurement can be obtained, elongated along the projection axis, i.e. the unique monoclinic axis in this particular case.

### Experimental details

The crystals used were cut from a naturally occurring block of the mineral kindly provided by Mr R. Brooks. The one used for the majority of the measurements

had dimensions approximately 3 mm.  $\times$  4 mm.  $\times$  1.1 cm., the last being in the direction of the  $y$  axis. This crystal was selected as being effectively a single crystal throughout its volume from the evidence of its narrow and symmetrical rocking curve for neutron reflection. A series of  $225 h0l$  reflexions was measured, mainly with a neutron wavelength of 0.81 Å, corresponding to a minimum interplanar spacing of about 0.5 Å. Most of these reflexions were measured using our powder-type neutron spectrometer (Bacon, Smith & Whitehead, 1950), but a proportion of them was studied on a much smaller spectrometer specially designed for single crystals (Bacon & Dyer, 1955) which was being brought into use about this time.

With a crystal of the size mentioned, with linear dimensions in the horizontal plane of about 4 mm., there is considerable secondary extinction for the most intense reflexions. The 400 reflexion, which is the most intense of all, was reduced by extinction to about 60% of its true value. The correction for secondary extinction was made on the basis of measurements at three different wavelengths, as described by Bacon & Pease (1953), and this was done not only with the large crystal generally employed but also with a number of other smaller samples. In general the experimental procedure was similar to that used in the above paper; all the measurements were made at room temperature.

### Results

At the outset of the work it was interesting to see how much information could be obtained from two Fourier line-projections, using only the intensity data provided by the  $h00$  and  $00l$  reflexions, up to (42,0,0) and (0,0,20). Utilising the X-ray knowledge of the positions of all the atoms other than hydrogen, line-difference-projections were obtained by synthesis of the quantity  $(F_o - F_{\text{NaCO}})$  along the  $x$ ,  $z$  axes respectively.  $F_o$  is the experimentally determined value of the structure factor and  $F_{\text{NaCO}}$  is the calculated contribution of the sodium, carbon and oxygen atoms. The projections

served to locate the hydrogen atoms as roughly occupying the shaded areas shown in Fig. 1.

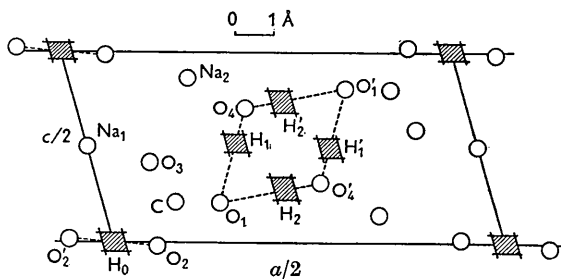


Fig. 1. A plan on (010) of a quarter of the unit cell of sodium sesquicarbonate, with shaded areas to indicate the positions of the hydrogen atoms deduced from line projections of  $(F_o - F_{\text{NaCO}})$  on the  $x, z$  axes. The shaded areas are defined by the intersection of bands parallel to the  $x, z$  axes of width equal to the half-peak widths of the atoms in the line projections and centred on the positions of the peaks.

The Fourier projection of neutron scattering density on the (010) plane, obtained by using all the  $h0l$  intensity data, is shown in Fig. 2(a). The contours for hydrogen are, of course, negative, corresponding to a difference in phase of  $180^\circ$  for the neutron scattering by hydrogen nuclei in comparison with that of almost all other nuclei. The precise details of the contours are much affected by series-termination errors, which are more important for neutrons than for X-rays since the higher Fourier terms fall off in value only on account of thermal vibrations and there is no supporting effect from a decrease of atomic scattering factor with increasing Bragg angle  $\theta$ , as there is for X-rays. However, the peak heights of the atoms in the projection served to determine the values of the Debye temperature factor  $B$  in the expression  $F = F_o \exp(-B \sin^2 \theta / \lambda^2)$

for the individual atoms and these were used in ensuing calculations instead of the general value  $B = 1.5 \times 10^{-16} \text{ cm.}^2$  which was used in the X-ray work. It was clear also that the only atomic co-ordinates whose X-ray values were seriously disputed by the neutron data were those of the oxygen atoms in the water molecules, notable their  $z$  co-ordinates. The amended data obtained in this way were used to calculate the function  $(F_o - F_{\text{NaCO}})$  for the various reflexions. The Fourier projection of this function represents the scattering density due to hydrogen atoms alone, with imperfections due to experimental intensity errors and to incorrect assumptions regarding the positions and thermal vibrations of the other atoms. From a study of the projection in the neighbourhood of the latter their parameters can be refined by the following procedure. From the assumed co-ordinates and temperature factors and a knowledge of the minimum interplanar spacing used in the Fourier synthesis we can calculate the effective atomic projection of each atom by using equation (3a) given by Bacon & Pease (1953). If to this derived projection of, for example, an oxygen atom we add whatever intensity occurs at the corresponding location in the projection of  $(F_o - F_{\text{NaCO}})$ , then we shall have a corrected oxygen atom, free from series-termination errors, from which a revised set of parameters can be found. By carrying out successive projections of  $(F_o - F_{\text{NaCO}})$  in this way the 'background' in these projections is progressively improved. Fig. 2(b) shows the final result after a series of four such projections. The two small 'non-hydrogen' peaks which still remain near Na, C, O positions, namely those near  $O_3$  and  $O_4$ , are thought to be due to inaccuracies in the experimental data rather than to incorrect subtraction of these oxygen atoms. In order to show more clearly

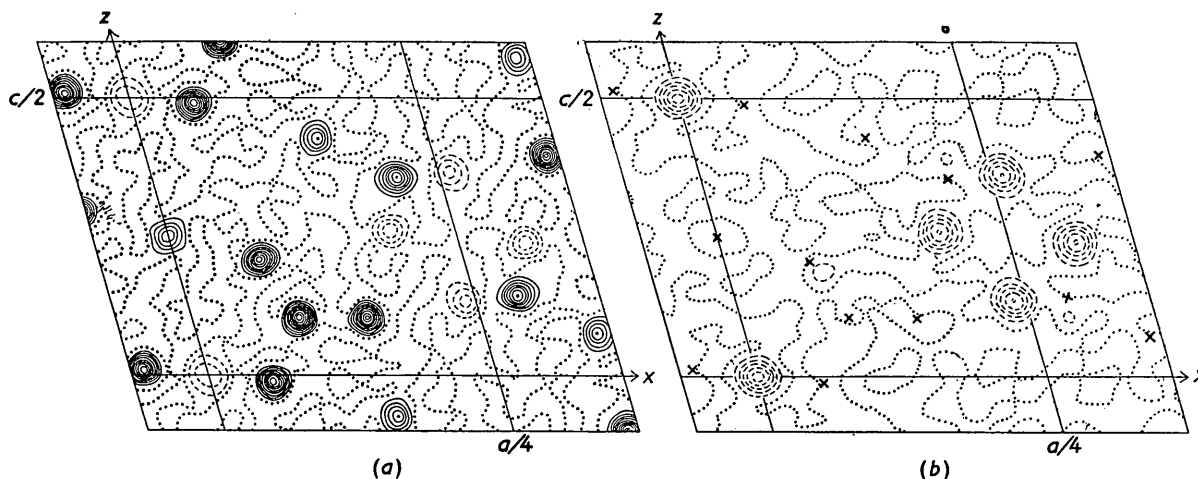


Fig. 2. (a) The Fourier projection on (010) of the neutron scattering density in sodium sesquicarbonate, obtained by synthesis of  $F_o$  for 225  $h0l$  reflexions. Contours are drawn at intervals of 100 units, with the positive contours shown by full lines and the negative contours by broken lines. Zero contours are shown dotted. The atoms can be identified from Fig. 1.

(b) The Fourier projection on (010) of hydrogen atoms only, obtained by synthesis of the function  $(F_o - F_{\text{NaCO}})$ . Contours are drawn at intervals of 50 units, i.e. twice as frequently as for Fig. 2(a). Negative contours are shown by broken lines and zero contours are dotted. The positions of the sodium, carbon and oxygen atoms are indicated by the crosses.

Table 1. Atomic parameters from X-ray and neutron data

Atom	$x/a$		$z/c$		$B \times 10^{16} \text{ (cm.}^2\text{)}$	
	X-rays	Neutrons	X-rays	Neutrons	X-rays	Neutrons
Na <sub>1</sub>	0	0	0.25	0.25	1.5	1.5
Na <sub>2</sub>	0.152	0.152	0.428	0.428	1.5	1.5
C	0.093	0.093	0.103	0.103	1.5	1.1
O <sub>1</sub>	0.150	0.151	0.101	0.102	1.5	1.25
O <sub>2</sub>	0.056	0.055	-0.009	-0.012	1.5	
O <sub>3</sub>	0.074	0.074	0.206	0.207	1.5	
O <sub>4</sub> (water)	0.214	0.212	0.348	0.356	1.5	
H <sub>0</sub>	—	0	—	0	—	3.9
H <sub>1</sub>	—	0.192	—	0.259	—	3.9
H <sub>2</sub>	—	0.240	—	0.137	—	

detail of the projection, particularly the background, the density interval between contours in Fig. 2(b) is only a half of that used in Fig. 2(a). The final parameters deduced in this way are shown in Table 1, which also includes for comparison the data obtained by Brown *et al.* (1949) with X-rays. The nomenclature of the atoms is consistent with that used by these latter workers, and will be clear from our Fig. 1. The estimated accuracy of the atomic positions, as determined by neutrons, is  $\pm 0.02 \text{ \AA}$  for hydrogen and  $\pm 0.01 \text{ \AA}$  for the other atoms. The background contours of the difference projection offer no justification for the use of anisotropic temperature factors for the carbon, oxygen and sodium atoms.

The reliability index,  $\Sigma(|F_o - F_c|) \div \Sigma F_o$ , calculated from our final parameters, was 11.0%.

Table 2. Bond lengths from X-ray and neutron data

Bond	X-rays (Å)	Neutrons (Å)
O <sub>1</sub> -O <sub>4</sub>	2.72 ± 0.03	2.76 ± 0.02
H <sub>1</sub> -O <sub>4</sub>	—	1.03 ± 0.03
O <sub>1</sub> -O <sub>4</sub> '	2.77 ± 0.03	2.78 ± 0.02
H <sub>2</sub> -O <sub>4</sub> '	—	0.99 ± 0.03
O <sub>2</sub> -O <sub>2</sub> '	2.53 ± 0.02	2.50 ± 0.02

Table 2 gives the three O-O bond lengths in the structure and the O-H bond lengths in the water molecules, together with the values of the former given by the X-ray work. In calculating the bond lengths deduced by neutrons it is assumed that the  $y$  coordinates of the oxygen atoms as found by X-rays are correct and that the hydrogen atoms H<sub>1</sub>, H<sub>2</sub> are in the plane defined by O<sub>1</sub>, O<sub>4</sub>, O<sub>1</sub>'.

### Discussion

The topics of most interest on which conclusions can be drawn from the foregoing study are the lengths of the O-H bonds in the molecules of water of crystallization and the detail of the hydrogen atom at the centre of symmetry. If we consider that the two independent values of  $1.03 \pm 0.03$  and  $0.99 \pm 0.03 \text{ \AA}$  for the two bonds are not significantly different, we can note that the mean value of  $1.01 \pm 0.02 \text{ \AA}$  is the same as that found by Peterson & Levy (1953) for the O-H bond in deuterated ice, where the O-O bond

length of  $2.76 \text{ \AA}$  is practically identical with the long bond in sodium sesquicarbonate.

It will be seen from both the direct projection, Fig. 2(a), and the difference projection, Fig. 2(b), that the O-H-O bonds which join an oxygen atom in a water molecule to an oxygen in a carbonate group are not quite linear. The two hydrogens in a water molecule are brought a little closer together than a linear arrangement would allow. Calculation shows that this achieves a more nearly tetrahedral arrangement of atoms around the water-molecule oxygen, the angle H<sub>1</sub>-O<sub>4</sub>-H<sub>2</sub>' being equal to  $107^\circ$ . Bearing in mind the estimated error in the location of H<sub>1</sub>, H<sub>2</sub>', it can be shown that this angle is not significantly different from the tetrahedral angle of  $109^\circ$ , in contrast with the significantly larger value of  $114^\circ$  for the angle O<sub>1</sub>-O<sub>4</sub>-O<sub>1</sub>'.

The distribution of scattering density for the hydrogen atom at the origin, H<sub>0</sub>, is markedly anisotropic. In the difference projection of Fig. 2(b), where the contours should be free of errors caused by diffraction ripples from the oxygen atoms O<sub>2</sub>, O<sub>2</sub>', the major axis of the elliptically shaped contours lies quite closely along the line O<sub>2</sub>O<sub>2</sub>'. The anisotropic distribution is to be contrasted with the case of KHF<sub>2</sub>, where Peterson & Levy (1952) showed that the hydrogen atom was located centrally between the two fluorine atoms with no distinguishable anisotropy. However, the F-F bond length in KHF<sub>2</sub> is only  $2.26 \text{ \AA}$ , in contrast with  $2.50 \text{ \AA}$  in KH<sub>2</sub>PO<sub>4</sub>, where it was shown by Bacon & Pease (1953) that the distribution of contours was consistent with the existence of a double potential well whereby the proton could take up either of two positions which were distant from one or other of the two oxygen atoms by  $1.07 \text{ \AA}$ . The anisotropy in our Fig. 2(b) for sodium sesquicarbonate is distinctly less than for KH<sub>2</sub>PO<sub>4</sub>, even when allowance is made for the fact that the bond direction O<sub>2</sub>-O<sub>2</sub>' is inclined at about  $20^\circ$  to the plane of the projection. We conclude, in fact, that if our distribution about the origin represents the summation of two spherically symmetrical half-hydrogens placed either side of the origin, in disordered arrangement, then the O-H distances for these two positions are  $1.12 \pm 0.02 \text{ \AA}$ . Fig. 3 illustrates this conclusion from a more practical view-point, by comparing the distribution of scattering density which we find along the bond in sodium sesquicarbonate with what would be

observed if the O-H distance found in  $\text{KH}_2\text{PO}_4$  was maintained. It does appear that the difference is

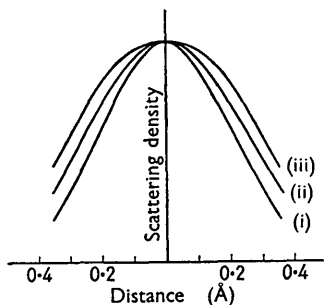


Fig. 3. Curves (i), (ii) show the variation of neutron-scattering density at right-angles to and along the  $\text{O}_2\text{-O}_2'$  bond, for the hydrogen atom at the centre of symmetry. Curve (iii), which is to be contrasted with (ii), shows what the distribution along the bond in projection would be if the O-H distances were the same as in  $\text{KH}_2\text{PO}_4$ .

significant when the possible experimental errors are considered. However, it is clear that data must be collected on a series of compounds before any general conclusions can be drawn about the existence, or otherwise, of a position of minimum energy on each side of a centre of symmetry. We are at present studying potassium hydrogen bis-phenylacetate by neutron diffraction as a further example: here the

O-O bond is believed to be a little longer, 2.55 Å (Speakman, 1949).

We are grateful to Mr R. Brooks, of Imperial Chemical Industries Limited (Alkali Division), Winnington, who provided us with the crystals of sodium sesquicarbonate, and to Mr R. F. Dyer, of the Atomic Energy Research Establishment, who carried out much of the experimental work.

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## Short Communications

*Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.*

*Acta Cryst.* (1956). **9**, 85

**Crystallographic data for certain alkaloids. V. Some delphinium alkaloids.** By F. M. LOVELL, *Viriamu Jones Laboratory, University College, Cardiff, Wales*

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The cell dimensions and space groups of the *delphinium* alkaloids given in Table 1 were obtained from oscillation and Weissenberg photographs ( $\text{Cu K}\alpha$  radiation). The densities were determined by flotation. The accuracy of the cell dimensions is of the order of 1% and  $\beta$  angles are accurate to within  $1^\circ$ .

### Delpheline, $\text{C}_{25}\text{H}_{39}\text{O}_6\text{N}$

The Laue symmetry is *mmm* and the only systematic absences are those with odd indices along each axis. The space group is therefore uniquely determined as  $P2_12_12_1$ .

### Delpheline hydriodide, $\text{C}_{25}\text{H}_{39}\text{O}_6\text{N} \cdot \text{HI}$

The Laue symmetry in  $2/m$  and the systematic absences indicate that the space group is either  $P2_1/m$  or  $P2_1$ . There are two molecules in the unit cell and the molecule

is optically active (Henry, 1949). The space group is therefore  $P2_1$ .

### Dehydrodelpheline, $\text{C}_{25}\text{H}_{37}\text{O}_6\text{N}$

The Laue symmetry is  $2/m$  and the systematic absences indicate that the space group is either  $P2_1$  or  $P2_1/m$ . The optical activity of the molecule requires that the space group be  $P2_1$ .

### Oxodelpheline, $\text{C}_{25}\text{H}_{37}\text{O}_7\text{N} \cdot \text{H}_2\text{O}$

The Laue symmetry is *mmm* and the systematic absences determine the space group uniquely as  $P2_12_12_1$ . The empirical formula given for this material was  $\text{C}_{25}\text{H}_{37}\text{O}_7\text{N} \cdot \frac{1}{2}\text{H}_2\text{O}$  (Cookson & Trevett, 1954). There are no twofold general positions in  $P2_12_12_1$  and the ob-