

# NEUTRON DIFFRACTION STUDIES OF ORGANIC MOLECULES

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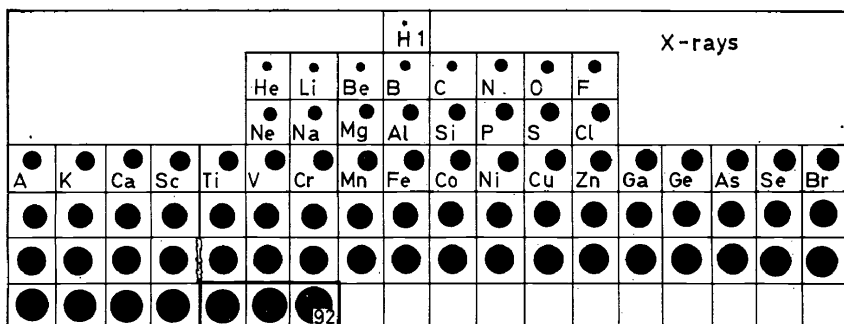
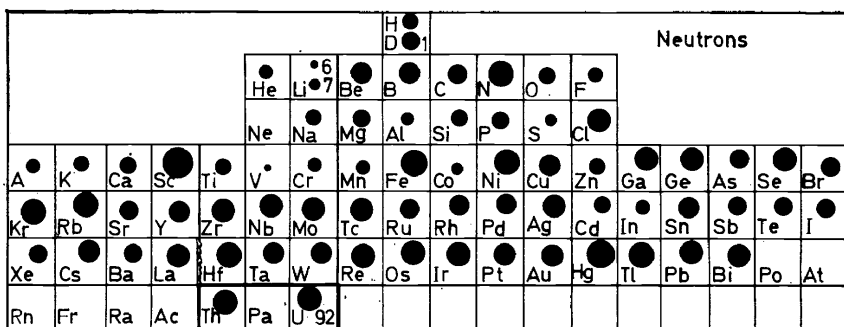
## INTRODUCTION

Within another year or so neutron diffraction will have been an active technique for a quarter of a century, and by then will have reached parity with x-ray diffraction as an accurate technique for studying the atomic arrangements in solids. Having achieved parity for general accuracy it will remain pre-eminent, from the point of view of the study of organic molecules, by virtue of its greatly superior ability to locate hydrogen atoms and its freedom from the pitfalls caused by uncertainties of electron distributions around and between atoms. In this paper we shall survey the capabilities of the technique at the present time, emphasizing some of the topics of particular interest and then looking in more detail at a typical example of a molecular study which is in progress at the moment.

The principles of the technique are by now well-known. From the present point of view its virtues arise from particular properties of the neutron and the way in which neutrons are scattered by atoms. Unlike quanta of electromagnetic radiation it is possible for neutrons (neutrons of thermal energy in fact) to have both a wavelength roughly equal to the interatomic separation in solids and an energy about equal to that of the characteristic vibrations within an ionic or molecular solid. As a result of this, neutrons can be used to obtain information about both atomic coordinates and the dynamics of the solid. With electromagnetic radiation on the other hand it is possible to use x-rays to obtain the coordinate information and infrared to examine the vibrations. *Figure 1* which represents in diagrammatic form the scattering amplitudes of the elements for neutrons and x-rays indicates the significance of the appreciable scattering amplitude of hydrogen for the former radiation.

The particular progress of neutron diffraction over the past five years has depended on two inter-related factors. The steady rise in the intensity of neutron beams which can be obtained from reactors, amounting to about a ten-fold increase each decade, has resulted in a proportional decrease in the amount of material required for investigation. So far as organic molecules are concerned we are almost entirely dependent on single-crystals for worthwhile structural studies and the increase in neutron intensity has greatly widened the range of materials for which suitable crystals can be grown. Of equal importance is the fact that the reduced crystal volume is sufficiently small for a crystal of roughly spherical shape to be used without

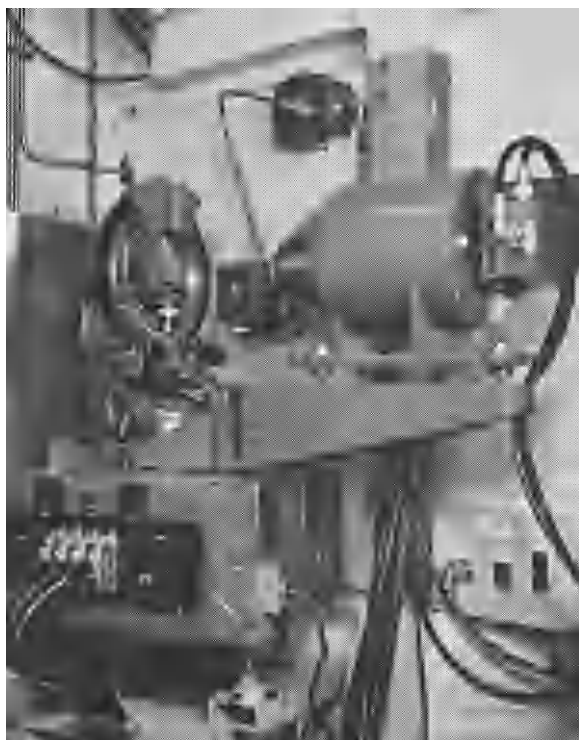
## Scattering of radiations by atoms



The coloured areas are proportional to the amplitude of the scattered wave. For neutrons the scale of the drawing is ten times larger than for x-rays.

Figure 1. A representation of the scattering amplitudes of the elements for neutrons and x-rays, arranged according to position in the Periodic Table. In the case of neutrons the amplitudes for H,  $^7\text{Li}$ , Ti and Mn are negative, involving an additional phase change of  $180^\circ$

the linear dimension being so large that secondary extinction effects are very troublesome. A linear dimension of 2 mm is usually adequate. Thus the early restriction to the use of cylindrical crystals, resulting in the possibility only of two-dimensional projections of scattering density, has now disappeared. The consequence of this is that with just one single-crystal it becomes possible to use automated three-dimensional methods, giving greatly increased accuracy and considerably enhanced speed of working. The last few years have therefore witnessed rapid development of automatic single-crystal diffractometers. An example of an instrument in use at the Atomic Energy Research Establishment, Harwell is shown in Figure 2. So far, most of these instruments have been used at reactors which give peak thermal fluxes of  $10^{13}$ – $10^{14}$  neutrons  $\text{cm}^{-2}\text{sec}^{-1}$  but a few reactors are now in use or under construction with fluxes up to  $10^{15}$  which improve considerably further the prospects for molecular-structure analysis.



*Figure 2.* A single-crystal diffractometer at the A.E.R.E. Harwell (reproduced by permission of the United Kingdom Atomic Energy Authority)

### EXAMPLES OF CURRENT STUDIES OF HIGH ACCURACY

A good example of the kind of problem which can now be attacked with neutrons is provided by the work of Brown and Levy<sup>1</sup> at Oak Ridge on sucrose and glucose. In the former study 2800 independent measurements of the intensities of spectra were made in order to determine about 400 parameters. It is perhaps worth noting that this is a relatively simple proposition compared with the x-ray analysis of myoglobin<sup>2</sup> in which 17000 reflections were measured, with the aim of determining the 21500 parameters needed to define the structure completely or 11340 parameters if the hydrogen atoms were left out of the reckoning altogether. In the neutron analysis of sucrose the coordinates of the carbon and oxygen atoms were determined to an accuracy of 0.003 Å and the hydrogen atoms to 0.007 Å. *Figure 3* indicates the shape of the model of sucrose viewed along the *a* axis, with the structural formula of the molecule placed in the same orientation, to give an idea of the complexity of this study. The two intramolecular bonds are of particular interest. Quite apart from the precision of the information concerning the hydrogen atoms, the general accuracy of the neutron determinations is as satisfactory as for an x-ray study of a

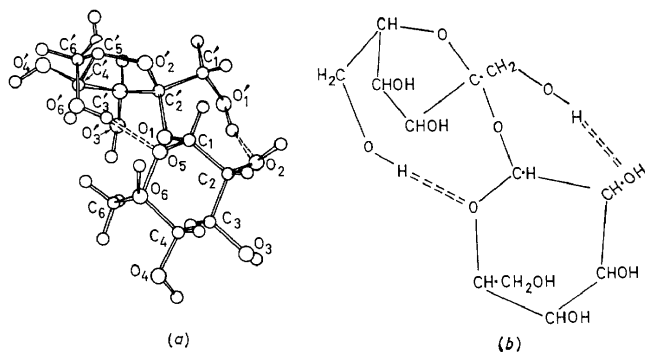


Figure 3. The atomic structure of the sucrose molecule (a) as revealed by the neutron diffraction analysis of Brown and Levy<sup>1</sup> with (b) the conventional structural formula in the same orientation. The broken lines indicate the intramolecular hydrogen bonds

crystal of comparable complexity. Perhaps the most ambitious project which has been achieved so far is the study of the monocarboxylic acid derivative E<sub>2</sub> of vitamin B<sub>12</sub> by Moore, Willis and Hodgkin<sup>3</sup>. The complexity here is an order of magnitude greater than for sucrose and there are 228 atoms in the asymmetric unit of the structure. In the first stage of the investigation 1500 reflections, going down to a spacing of 1.3 Å, were used to determine 820 parameters. The accuracy is therefore inevitably less than for sucrose where the reflection/parameter ratio was 7:1. Nevertheless some convincing chemical information was forthcoming from the analysis. Figure 4 shows the neutron scattering density over the corrin nucleus and emphasizes the point that for neutrons the cobalt atom at the centre is the 'lightest' atom in the

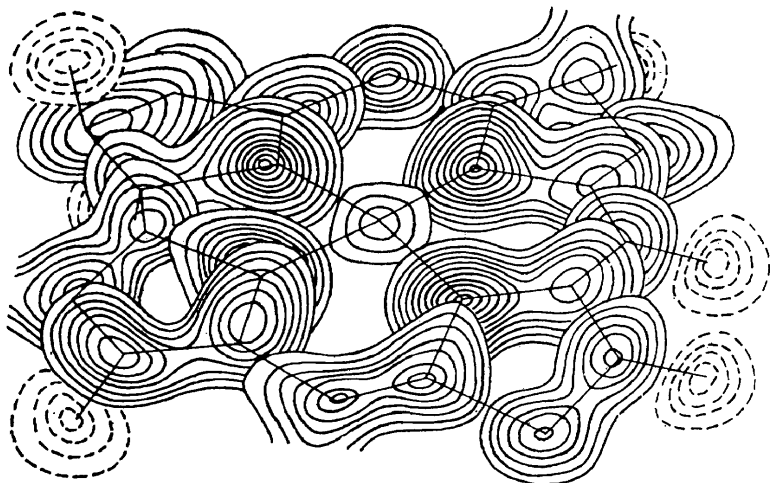


Figure 4. The contours of neutron scattering density over the corrin nucleus of the acid derivative of vitamin B<sub>12</sub> (Moore, Willis and Hodgkin)<sup>3</sup> *Nature Lond.* 214, 130 (1967) [courtesy of *Nature*]

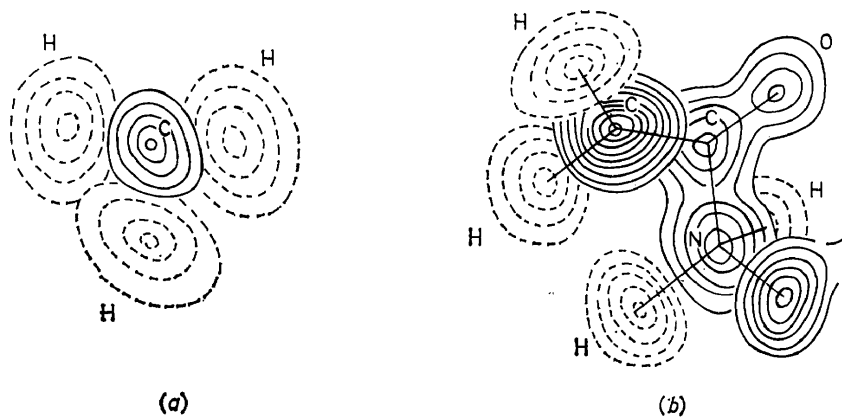


Figure 5. Details of (a) a methyl group, indicating non-rotation and (b) a group conclusively identified as  $(\text{CO.NH}_2)$  in the  $\text{B}_{12}$  derivative [courtesy of *Nature*]

molecule, with a scattering length of only  $0.25 \times 10^{-12}$  cm, whereas nitrogen, with  $b = 0.94 \times 10^{-12}$  cm, is the heaviest. Figure 5 indicates two other details from the analysis: at (a) we see one of the methyl groups, which is clearly *not* in free rotation about the single bond which links it to the ring carbon atom, and at (b) one of the acetamide groups. In the latter case the magnitudes of the contours do establish conclusively the nature of this group, showing that the atoms are indeed  $\text{CO.NH}_2$  and cannot be  $\text{COOH}$  which remained a possible configuration from earlier x-ray work. This work has been developed by measuring a further 1000 reflections in the range of spacings from  $1.3\text{--}1.0$  Å and a considerable improvement in the refinement of the atomic positions is to be expected.

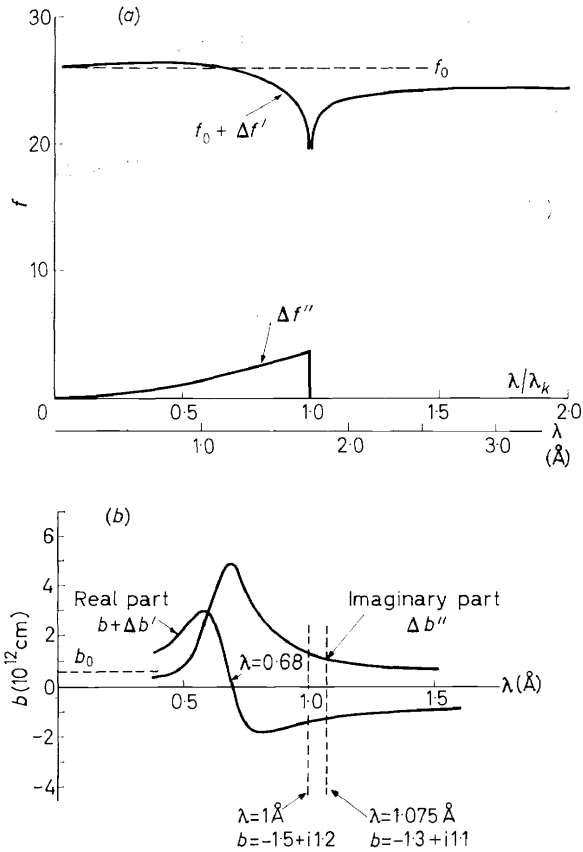
More recently Duckworth<sup>4</sup> has carried out a very accurate 3-dimensional analysis of hexamethylene tetramine, a very simple cubic structure of a symmetrical and almost spherical molecule which gives a good idea of the ultimate precision which is obtainable at present. By making very careful corrections for absorption, secondary extinction and thermal motion the following bond lengths and standard deviations have been deduced: for C—H,  $1.0942 \pm 0.0060$  and for C—N,  $1.4615 \pm 0.0034$  Å.

### SOME TOPICS OF PARTICULAR INTEREST

Most of the opportunities for neutron diffraction in solving chemical problems associated with molecular structure arise from the differences in the scattering amplitudes of the elements, compared with x-rays, which were summarized in Figure 1. At the same time advantage can be taken of the differences in scattering amplitude for different isotopes of certain elements, in particular for hydrogen where the negative  $b$  value of  $-0.372$  for ordinary hydrogen is in marked contrast to the positive value,  $+0.66$  for deuterium. There are however several factors of a different kind which are of significance and have lately attracted a good deal of interest.

### Anomalous scattering

First, it is found that 'anomalous scattering' effects, which occur in the neighbourhood of an absorption resonance, are in a few cases much larger than what occurs for x-rays. In *Figure 6 (a)* is plotted, as a typical example, the variation of scattering amplitude with x-ray wavelength in the neighbourhood of an absorption resonance.



*Figure 6.* A comparison of the parameters for anomalous scattering in the cases of x-rays and neutrons. At (a) is shown the real and imaginary contributions to the scattering amplitude  $f$  for Fe, as a function of the wavelength of the x-rays. (b) shows corresponding data for the cadmium isotope  $^{113}\text{Cd}$  for neutrons

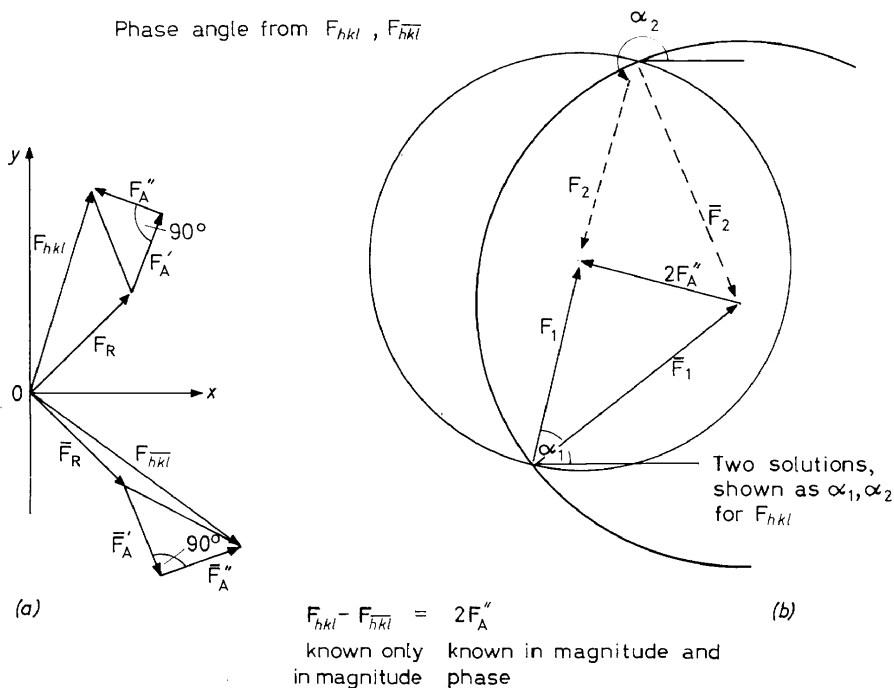
neighbourhood of the absorption edge for iron. The normal atomic scattering factor  $f_0$ , which is a real quantity, is replaced by

$$f = f_0 \times \Delta f' \times i \cdot \Delta f''$$

Near the absorption edge the magnitudes of  $\Delta f'$  and the imaginary component  $\Delta f''$  are about equal and amount to about 20 per cent of the value of  $f_0$ . For x-rays this is a quite general effect which occurs near the absorption edges of the electron shells. A rather similar effect occurs with neutrons for

a few nuclei which have nuclear resonances near to thermal energy. The nuclei are  $^{10}\text{B}$ ,  $^{113}\text{Cd}$  and  $^{149}\text{Sm}$ , and the important feature is that the anomalous effects are much larger than for x-rays. The lower curves in *Figure 6* refer to  $^{113}\text{Cd}$  and it will be seen that at the resonance wavelength of  $0.68 \text{ \AA}$  the coefficient of the imaginary term  $\Delta f''$  is 7.6 times as great as the usual, real, value which the scattering amplitude has at wavelengths well away from the resonance position. The virtue of this large value of imaginary component in the scattering amplitude is that it provides a method of phase-determination in non-centrosymmetric structures. The method rests, as was demonstrated by Bijvoet for x-rays, on a breakdown of Friedel's Law which states that reflections  $hkl$  and  $\bar{h}\bar{k}\bar{l}$  are normally of equal intensity. The technique for determining the phase angle for structures which incorporate an anomalously scattering atom is indicated in *Figure 7*. The basic problem is to solve the equation  $\mathbf{F}_{hkl} - \mathbf{F}_{\bar{h}\bar{k}\bar{l}} = \mathbf{F}_A''$  where each of the structure factors  $\mathbf{F}$  is a vector.  $\mathbf{F}_{hkl}$ ,  $\mathbf{F}_{\bar{h}\bar{k}\bar{l}}$  refer to the contribution from the whole unit cell, for the oppositely directed reflections  $hkl$  and  $\bar{h}\bar{k}\bar{l}$ , and these are known in magnitude but *not* in phase. On the other hand  $\mathbf{F}_A$ ,

Phase angle from  $F_{hkl}$ ,  $F_{\bar{h}\bar{k}\bar{l}}$



*Figure 7.* Diagram (a) indicates how the reflections  $hkl$ ,  $\bar{h}\bar{k}\bar{l}$  will have different structure factors in non-centrosymmetric structures which contain an anomalously scattering atom. (b) illustrates the two possible solutions to the equation which defines the phase angle for  $F_{hkl}$ , or for  $F_{\bar{h}\bar{k}\bar{l}}$ . The ambiguity can be resolved by making measurements at two different wavelengths

which is the contribution from the anomalously scattering atom, will be known in both magnitude and phase if, as is often the case, the coordinate

positions of this atom are already known. This equation can be solved graphically, giving two possible solutions, as indicated in *Figure 7* but these can be distinguished by carrying out measurements at two different wavelengths, one on each side of the resonance position. This has been discussed by Dale and Willis<sup>5</sup> with a view to determining the structure of crystals of insulin containing the cadmium isotope  $^{113}\text{Cd}$ . Some preliminary measurements have been made but the observed intensities with crystals measuring 1.5 mm have been surprisingly small. In considering the possibilities of this method of phase determination by introducing an anomalous scatterer, calculations show that there is an optimum value for the ratio of the numbers of normal and anomalous atoms. If the number of atoms in the unit cell is too large then the presence of just one or two anomalous scatterers will produce an insignificant difference between the values of the structure factors  $F_{hkl}$  and  $F_{\bar{h}\bar{k}\bar{l}}$ . On the other hand the resonance scattering is always accompanied by resonance absorption and this sets a lower limit to the number of ordinary atoms in the unit cell. The permissible range is greater if hydrogen-containing crystals are partially deuterated.

### Thermal motion and bond-lengths

Many hydrogen atoms, particularly in aromatic compounds, are situated on the outsides of molecules and this means that when rotation or oscillation of molecules occurs then the motion of the hydrogen atoms is both large and anisotropic. This fact adds importance to the value of neutrons in determining molecular structure because it means that the accurate location of hydrogen atoms, and the even greater precision for deuterium atoms, at large radial distances leads to accuracy in defining the molecular motion. At the same time the large thermal motion leads to an appreciable difference between the equilibrium value of a bond length and its apparent value in a plot or assessment of scattering density. The coordinates of the atom as deduced by least-squares or a Fourier analysis are simply the centre of gravity of the diffuse atomic positions and this is not the same as the equilibrium position. The result is that the bond length to the hydrogen atom, for example the C—H bond from a benzene ring, is apparently shortened. The amount of shortening will depend on the type of correlation which exists between the motion of the two atoms concerned, that is between the C, H motions in the example which we have just mentioned, or between the O, H atoms in a hydroxyl group. Unfortunately the correlation between the motions of the neighbouring atoms cannot be determined directly and will only emerge when a correct model has been devised of the motion of the structure as a whole, compounded as it necessarily will be of rotational and translational movements of the molecule as a rigid body together with motion which is due to bending and stretching of individual bonds. In some cases the apparent shortening of the bonds is surprisingly large, although it can always be reduced by carrying out the diffraction investigations at reduced temperature. The effect has been discussed at length by Busing and Levy<sup>6</sup>, originally in connection with these authors' analysis of calcium hydroxide. *Figure 8* indicates how for  $\text{Ca}(\text{OH})_2$  the correction to the O—H bond length at room temperature could range from 0.016 Å, for correlated parallel movements of the oxygen and hydrogen atoms, to 0.125 Å for an



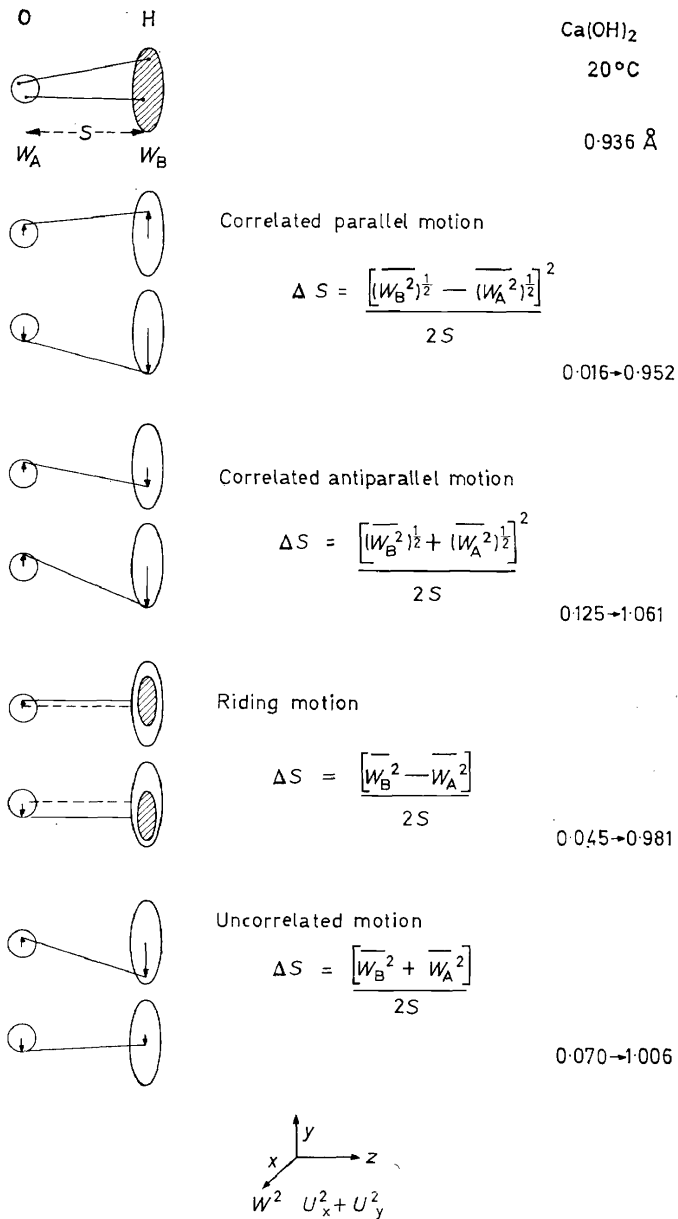


Figure 8. A summary of possible correlations of motion for two atoms, such as the O, H atoms in the hydroxyl groups of Ca(OH)<sub>2</sub>. The numbers on the right of the diagram show the values of the bond-length correction (and the corrected lengths) which would be appropriate in each case, using the observed data for W<sub>A</sub>, W<sub>B</sub> in Ca(OH)<sub>2</sub>

assumption of antiparallel motion. A likely type of motion for the light hydrogen atom in the OH group is the 'riding motion' in which the displacement of the hydrogen atom relative to the oxygen atom is independent of the particular position in which the oxygen atom happens to be. This state of affairs produces an intermediate degree of bond-shortening, amounting to 0.045 Å. It is interesting to note that there is a substantial correction to the position of the terminal hydrogen atom which appears at the bottom of the sucrose molecule in *Figure 3*. The motion of this atom is large because it is not restrained in position by any hydrogen bonding. If we assume that it 'rides' on the oxygen atom O<sub>4</sub> then we can calculate that the equilibrium value of the O—H bond length is increased from 0.89 Å to 0.94 Å.

We have considered at some length this problem of apparent bond shortening due to thermal motion in order to emphasize the difficulties and dangers in drawing conclusions, and in making subsequent chemical inferences, from differences of bond length in comparable compounds. An example is the familiar one of trying to establish a unique correspondence between O—H and O—O separations in hydrogen bonds or in perhaps drawing a conclusion that any such correspondence depends on whether the bonds are bent or straight. We can but conclude that very precise measurements must be made on a wide selection of compounds, and preferably at reduced temperatures also, before any general conclusions can be safely drawn. Ideally the situation would be met if the experimental accuracy in the determination of atomic coordinates, bond lengths, bond angles and thermal motion could be increased by a factor of ten, but failing this for the time being it seems clear that definitive results can only be obtained by a much more comprehensive neutron survey of substances than has been possible so far. It is a pity from this point of view that the number of opportunities for engaging in this kind of research is so restricted by the small number of high-flux reactors which are available. There are many quite basic chemical problems which still await a thorough experimental pronouncement until more adequate data have been obtained. Among these are the question of a centred symmetrical hydrogen atom in short hydrogen bonds, the distinction between a nuclear position and the centre of gravity of an electron cloud in bonds such as O—H and the problem of buckled bonds in overcrowded hydrogen systems such as 18-annulene. Significant pointers have been obtained on these problems but generally the information is not conclusive.

Conventional measurements of diffraction patterns, representing the elastic scattering of a beam of monochromatic neutrons, produce essentially a static or 'time-averaged' picture of the atomic structure. At the same time however information is forthcoming about the displacement of the atoms from their mean positions (the so-called 'thermal motion' of the atoms) as a consequence of the reduction of spectral intensities which these motions will necessarily cause. The usual method of data analysis is to regard each atom in the asymmetric unit of the structure as independent and requiring nine parameters to specify completely its position and motion. Three of these give the coordinates of its equilibrium position and the other six define the magnitude and orientation of the triaxial ellipsoid which

describes its thermal motion. By least-squares analysis a set of such parameters is determined for each distinct atom and the accuracy of these is dependent on the ratio of the number of independent experimental measurements to the total number of unknown parameters. The accuracy will of course depend also on the absence of any errors in the experimental measurements. At this stage in the analysis, when one is presented with a picture of the thermal motions of individual atoms, the problem is to correlate these into a coherent pattern of vibrations which is satisfactory from both a physical and chemical point of view. The resultant motion will be compounded, as we have already mentioned, of motions of the molecule as a whole and relative motions of atoms within the molecule. It is not easy to deduce these precisely, depending as they often do on measuring a difference between roughly equal quantities. The alternative approach<sup>7</sup> is to refine the parameters of motion in terms of translational and rotational motion of the molecules as rigid bodies, supplemented by intramolecular vibrations. We emphasise that the truth and accuracy of the final conclusions will depend on the model of motion which has been initially assumed.

### Inelastic scattering

In recent years increasing use has been made of neutron spectroscopic methods of directly measuring the frequencies of vibrations. We have already mentioned that this depends on the inelastic scattering of neutrons, in which the size of a quantum of energy of vibration is deduced as the gain or loss of energy of the neutron in the scattering process. This technique is particularly simple in the case of hydrogen-containing materials and in comparison with infrared spectroscopy has the advantage of distinguishing those motions in which hydrogen atoms take part. This arises because the large incoherent scattering of hydrogen, amounting to 80 barns, which is a troublesome complication in ordinary diffraction patterns, is now employed to advantage. A simple example in *Figure 9* from the early work of Boutin<sup>8</sup> shows the type of information which is forthcoming. The two curves in this figure compare the scattering measurements of solid hydrogen fluoride, at  $-120^{\circ}\text{C}$ , and potassium hydrogen fluoride at  $25^{\circ}\text{C}$ . In the former there is a sharp peak at an energy gain of 67 mV, compared with the much larger value of 147 mV for the latter. These peaks correspond to vibrations which depend on the strength of the hydrogen bond in the two substances and indicate the much stronger bond in  $\text{KHF}_2$ , in agreement with the increase in length of the F—F bond from 2.26 Å in  $\text{KHF}_2$  to 2.49 Å in solid HF. In more complicated molecules it will often happen that there is overlap between peaks in the neutron spectrum which arise from more than one vibration, associated with different groups in the molecule. White<sup>9</sup> has shown how it is possible to separate these by partial substitution of hydrogen by deuterium, which does not display any large incoherent scattering. In the case of  $\text{CH}_3\text{OH}$  for example, in which the spectrum is a superposition of effects due to the  $\text{CH}_3$  and OH groups, it is possible to render each of these, in turn, inoperative by substituting its hydrogen atoms with deuterium. It is possible to achieve a similar result, in a cheaper manner, by substituting fluorine for the hydrogen and this has been demonstrated in some studies of acetic acid and trifluoroacetic acid.

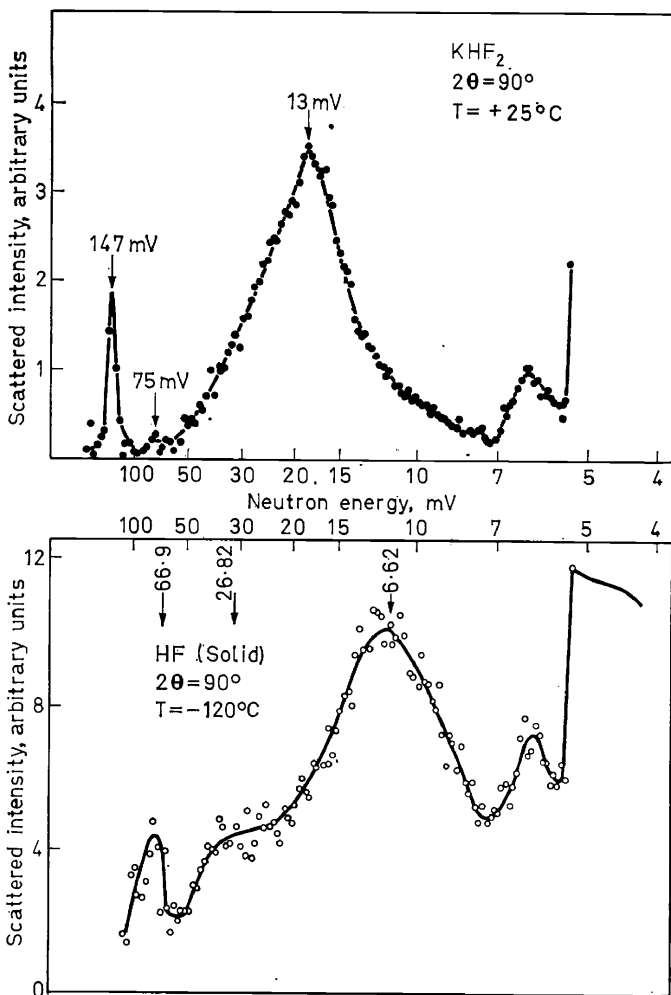


Figure 9. A comparison of the spectra of inelastically scattered neutrons from solid HF and KHF<sub>2</sub>, contrasting the higher energy peaks which correspond to energy gains of 67 mV and 147 mV respectively (from Boutin *et al.*<sup>8</sup>)

### A NEUTRON STUDY OF SALICYLIC ACID

We shall conclude this paper with a preliminary account of a neutron investigation of salicylic acid which is at present being carried out<sup>10</sup>. This provides a good example of the way in which the neutron measurements can be used to develop further the conclusions of x-ray work and also gives some idea of the accuracy of current methods of analysis. The structure of salicylic acid was determined using x-rays in 1953 by Cochran<sup>11</sup> from two-dimensional projections on the 001 and 010 planes. A combination of counter and photographic methods gave structure factors for 140 hk0 reflections and 40 h01 reflections. An intention by the present author to

carry out a neutron analysis shortly afterwards was thwarted by inability to grow crystals which were sufficiently large to make use of the low neutron intensities which were then available. In 1964 the results of a three-dimensional analysis using photographic data were published by Sundaralingam and Jensen<sup>12</sup> who measured 732  $hkl$  reflections. This confirmed the general lines of Cochran's structure and with higher precision in fixing the hydrogen atoms was able to give more reliable figures for the length of the C—H bonds. Nevertheless with an average value of 0.973 Å these were still recorded as much shorter than would be expected. Subsequently we have been able to grow from the melt a crystal with linear dimensions of about 2 mm which is of adequate size for a neutron flux of a few times  $10^{13}$ . We have measured 650 reflections and are analysing these on both conventional lines and in terms of a rigid-body analysis. For illustrative purposes we have used our  $hk0$  structure factors to project two versions of the structure on the

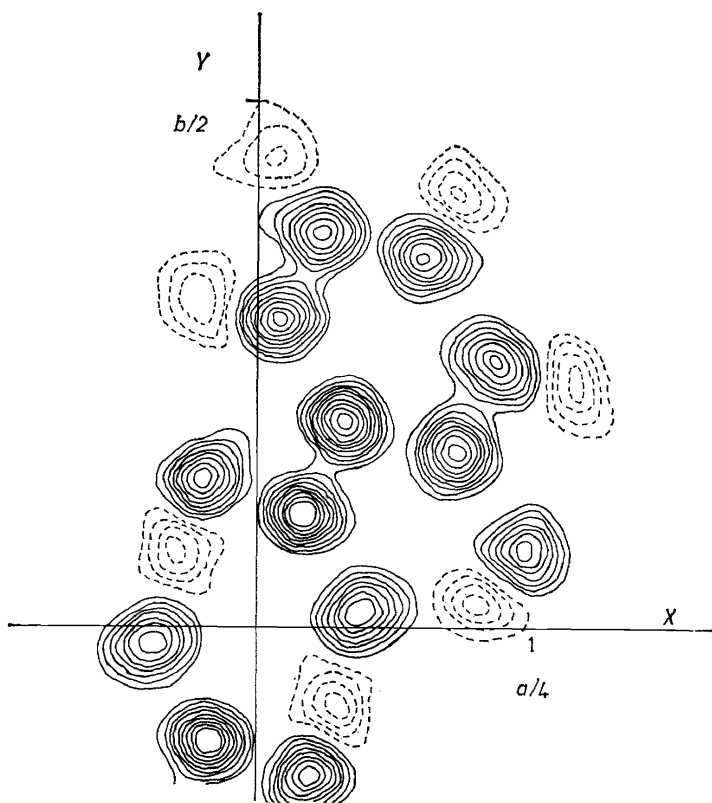
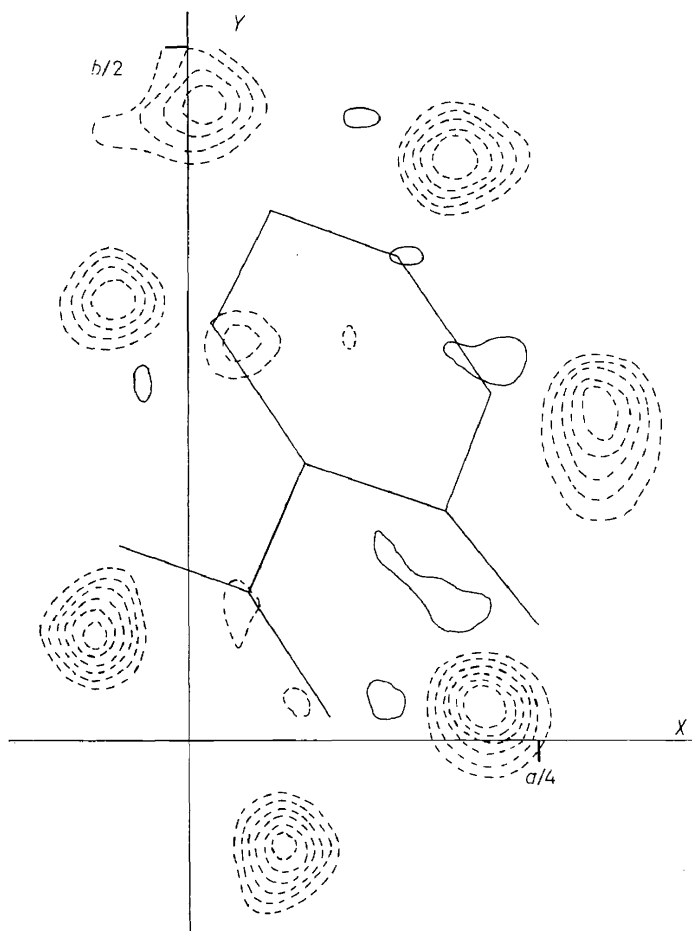


Figure 10. A Fourier projection<sup>10</sup> of the neutron scattering density of salicylic acid on the 001 planes, constructed from intensity measurements of  $hk0$  reflections

001 plane. We have utilized in turn (a) the observed factors  $F_0$  (b) the observed factors reduced by the calculated contributions from the oxygen and carbon atoms as arrived at by the rigid body analysis, i.e.  $F_0 -$

$F_{(C,O)_R}$  which displays only the hydrogen atoms. A third version which uses the observed factors reduced by the calculated contributions from oxygen, carbon as arrived at by conventional deduction of the motions of individual atoms is being prepared. Projections (a), (b) in their present preliminary form, are illustrated in *Figures 10 and 11*. *Table 1* compares the lengths of the C—H bonds as given in the different studies. The new values



*Figure 11.* A Fourier projection<sup>10</sup> on the 001 plane of the hydrogen atoms in salicylic acid constructed from  $F_{obs} - F_{C,O}$ .  $F_{C,O}$  is the computed contribution from the carbon and oxygen atoms, as evaluated from a 3 dimensional analysis in which the molecule is assumed to move as a rigid body about an arbitrary centre

are much more compatible with expectations for the C—H bond length. They, like the other values given above, have not yet been corrected for the shortening arising from thermal motion. They are in acceptable agreement with the uncorrected value of 1.07 Å for benzene<sup>13</sup> at  $-55^{\circ}\text{C}$  and with the value of 1.081 Å in the gas phase<sup>14</sup>, as determined by electron diffraction. The continued shortness of the bond from  $C_5$  is a noticeable feature, particularly

Table 1. A comparison of the lengths of different bonds in Å

Bond length	Cochran	S and J	Neutron
C <sub>3</sub> —H <sub>3</sub>	0.90	0.986	1.06
C <sub>4</sub> —H <sub>4</sub>	0.92	1.025	1.07
C <sub>5</sub> —H <sub>5</sub>	0.78	0.904	1.01
C <sub>6</sub> —H <sub>6</sub>	0.94	0.983	1.09
Mean value	0.88	0.97	1.06

in view of the reduced standard deviation of 0.017 Å which we estimate for our hydrogen atom positions.

The comparable accuracies of x-ray and neutron diffraction in fixing the carbon atom positions can be seen from the comparison of the C—C bond lengths and the angles of the benzene hexagon given in Table 2.

Table 2. A comparison of the C—C bond lengths and the angles of the benzene hexagon

Bond length	Cochran	S and J	Neutron
C <sub>1</sub> —C <sub>2</sub>	1.393	1.404	1.403 Å
C <sub>2</sub> —C <sub>3</sub>	1.411	1.381	1.392
C <sub>3</sub> —C <sub>4</sub>	1.369	1.379	1.396
C <sub>4</sub> —C <sub>5</sub>	1.374	1.384	1.419
C <sub>5</sub> —C <sub>6</sub>	1.371	1.365	1.378
C <sub>6</sub> —C <sub>1</sub>	1.414	1.394	1.396
<i>Hexagon angle</i>			
At C <sub>1</sub>	118.6	118.5	118.8°
C <sub>2</sub>	119.5	119.6	120.7
C <sub>3</sub>	120.1	120.5	119.5
C <sub>4</sub>	120.9	120.5	120.5
C <sub>5</sub>	120.2	119.4	118.5
C <sub>6</sub>	120.7	121.5	121.9

## SUMMARY

The value of neutron diffraction in chemistry arises primarily from its ability to locate hydrogen atoms accurately, thereby not only increasing the precision of determining bond-lengths but also contributing substantially to the assessment of the thermal motion of the molecules. Present day techniques of 3-dimensional analysis, although still requiring larger crystals than for x-ray methods, do now give, for all atoms, comparable accuracies. At the same time, because of the large incoherent scattering of hydrogen, a study of the inelastic scattering is of value in identifying those molecular vibrations which are dominated by hydrogen atoms. An account is given of some recent analyses, with particular reference to thermal motion and to the value of complex scattering amplitudes in assisting with the problem of phase determination.

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