

Refinement of a Non-Centrosymmetrical Structure: Sodium Nitrite*

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In a re-determination of the structure of sodium nitrite it was found necessary to use the 'modified Fourier method' for accurate refinement and for calculation of the standard deviation. The factors limiting the accuracy possible in the determination of this type of structure were examined, particularly the effect of variations in the scattering factors on the atomic parameters and the agreement index. The accuracy attainable was lower than that expected for a structure with few parameters and indicated the importance of investigating all the assumptions made in the refinement of a crystal-structure determination.

The dimensions obtained for the nitrite ion were: N-O bond length $1.24(7) \pm 0.035$ Å and O-N-O angle $114.2 \pm 4^\circ$, the limits being the standard deviations.

1. Introduction

An approximate determination of the structure of sodium nitrite was made by Ziegler (1931) but the methods at his disposal did not yield results sufficiently accurate for bond length determination. An accurate determination of this structure was started some years ago as part of a programme to determine the bond lengths and angles of N-O bonds in some simple molecules and ions (Cox, Jeffrey & Truter, 1948; Truter, 1951).

The structure contains two molecules per unit cell in the space group $Im(2)m$. An original choice of origin at the sodium ion, using the equations in the form given in the *International Tables*, proved unfortunate; this was because the parameters, found by Ziegler and confirmed by Patterson synthesis, were N at 0, 0.500, 0 and O at 0, 0.583, 0.194 so that the $|F| \sin \alpha$ terms in the three-dimensional Fourier syntheses used for refinement were very small compared with the $|F| \cos \alpha$ terms, and no indication of movement of y_N from the centrosymmetrical position $0, \frac{1}{2}, 0$ was obtained. However, differential syntheses using structure amplitudes which were not rounded-off showed a small net (i.e. corrected for termination-of-series errors) change in y_{Na} and a larger one in y_N . Since the sodium and nitrogen were not separated by exactly $\frac{1}{2}b$, the origin was re-chosen so that the oxygen atoms lay on the c axis (at 0, 0, $\pm z_O$) and the nitrogen and sodium on the b axis (at 0, y_N , 0 and 0, y_{Na} , 0). Subsequent differential syntheses always showed a net shift of the oxygen in the y direction, and in the calculation of new co-ordinates this was subtracted from those of nitrogen and sodium so that they referred to $y_O = 0.000$.

Three successive changes of parameter were made

as a result of differential syntheses. The final co-ordinates were determined by the 'modified Fourier method' from parameters (E) for which the agreement index, $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$, was 0.154. These give values of $1.24(7)$ Å for the N-O bond length and 114.2° for the bond angle.

Recently Carpenter (1952) has independently re-determined the structure, using the method of least squares with the weighting factor $w = 1/|F_c| \times f_{Na}$. He obtained values of $1.23(3)$ Å for the bond length and 115.7° for the bond angle. The two determinations agree within the limits of experimental error.

The object of the present paper is to examine some of the limitations of the accuracy possible in the determination of a structure of this type. During the refinement it was found that the usual practice of neglecting the effect of a small change in one of the parameters on the others is unjustifiable in this case, and probably also in that of other non-centrosymmetrical structures in which some of the atoms are in special positions. In § 2 the methods and results of refinements, one neglecting and one allowing for these effects, are described; the magnitude of the effects was surprisingly large.

In this structure the agreement index, R , is relatively insensitive to changes in the co-ordinates of the nitrogen atom, but it is considerably affected by variations in the scattering factors; the determination of the uncertainty in the bond length and angle arising from uncertainty in the scattering factors is described in § 3.

Finally in § 4 other causes of error are discussed and their magnitudes estimated. The standard deviation calculated by Carpenter (0.017 Å)* differs considerably from that of the present writer (0.035 Å); possible reasons for this are discussed in § 4.

* Part of a thesis accepted by the University of London for the award of the Ph.D. degree.

* Revised value (private communication).

2. Methods of refinement

Differential syntheses in non-centrosymmetrical structures

Two assumptions are made in using differential Fourier syntheses: the first is that the shifts in parameters are small and the second that the position of one atom is not affected by any movement of any other atom. For an orthorhombic space group it is also convenient to assume that one parameter of an atom is not affected by changes in co-ordinates at right angles to it.

If these three assumptions are made, Booth (1946) has shown that in a centrosymmetrical structure, ϵ , the small shift in the co-ordinate required to bring the atom to the position of maximum electron density, is given by:—

$$\epsilon_x = -(\partial\rho/\partial x)/(\partial^2\rho/\partial x^2), \quad (1)$$

with two similar equations for ϵ_y and ϵ_z .

For completely non-centrosymmetrical structures, the shifts given above must be doubled to allow for changes in the phase angles. If, however, the structure contains a centrosymmetric projection, the double shift is too large and some allowance must be made for centring. Donohue, Shoemaker, Schomaker & Corey (1950) have suggested an 'n' shift rule, where 'n' is 1 for centrosymmetrical space groups and 2 for non-centrosymmetrical space groups. The value of 'n' is found empirically from two refinements to the same parameters and is an average for all parameters. The method devised here gives an individual value of 'n' for each parameter; this is reasonable since a shift in one parameter may have a large effect on the phase angles while an identical shift (in Å) in another has a small effect. The new method is based on the 'double-shift' rule; the second differential term in equation (1) is modified to give twice as much weight to the centrosymmetrical planes. The second differential term for a centrosymmetrical space group is

$$-\frac{4\pi^2}{Va_i^2} \sum_3 |F| h_i^2 \cos(\theta_r - \alpha), \quad (2)$$

where $i = 1, 2, 3$; $\theta_r = 2\pi(hx + ky + lz)$ and x, y, z are the fractional co-ordinates of atom r ; the summation is over all (hkl) . The modified expression for a non-centrosymmetrical space group is

$$-\frac{1}{2} \cdot \frac{4\pi^2}{Va_i^2} \sum_3 m |F| h_i^2 \cos(\theta - \alpha), \quad (3)$$

where the factor, m , is 2 for centric planes and 1 for acentric planes.

Expression (3) is similar to

$$-\frac{1}{2} \cdot \frac{4\pi^2}{Va_i^2} \sum_3 m h_i^2 f \quad (4)$$

obtained by Cruickshank (1952) from the full equations of the 'modified Fourier method' when the three

simplifying assumptions given above are made, and an average is taken over all atoms. The two expressions should be equal if the assumptions are justified; both were computed for ϵ_{z_0} and the values were 11.8 from (3) and 10.0 from (4). Exact agreement cannot be expected unless the assumptions are justified; for sodium nitrite, as shown below, this is not the case.

In sodium nitrite only the $h0l$ projection is centrosymmetric, so that there are no centric planes contributing to $\partial^2\rho/\partial y^2$, the value of m is 1 for all planes and the 'n' shift is 2. This projection does contribute to $\partial^2\rho/\partial z^2$ and comparison of the values of the second differential terms obtained from (2) and from (3) gave a value of 'n' of 1.60 from the observed and 1.59 from the calculated structure amplitudes.

The value of ϵ_y for oxygen was -0.0064 Å (ideally it should be zero); this indicates considerable interaction from the other atoms, and possibly from z_0 , so that one of the assumptions on which the differential method is based is not justified.

'Modified Fourier method'

The only assumption made is that the shifts are small (< 0.05 Å), which is certainly true in this case.

Cruickshank (1952) has shown that the corrections $\epsilon_{s,j}$ for a non-centrosymmetrical structure are given by

$$\left(\frac{\partial\rho_o}{\partial x_i}\right)_r = \left(\frac{\partial\rho_c}{\partial x_i}\right)_r - \sum_{s,j} \epsilon_{s,j} \frac{1}{V} \sum_3 h_i \frac{\partial|F_c|}{\partial x_{s,j}} \sin(\theta_r - \alpha); \quad (5)$$

x_i is a particular co-ordinate direction and $(\partial\rho/\partial x_i)$ is evaluated at the position of a particular atom, r , while $x_{s,j}$ is a parameter of any atom, s , and those related to it by symmetry. The first differential terms are the same as those used in the previous method. The use of this equation automatically allows for termination-of-series errors and double or 'n' shifts. It is necessary for F_o and F_c to be on the same scale, and for $\partial^2\rho_o/\partial x^2 = \partial^2\rho_c/\partial x^2$, which is the case at this stage of refinement. There are as many of these simultaneous equations as there are parameters.

In sodium nitrite there are three parameters; $\epsilon_{y_{Na}}$, ϵ_{y_N} and ϵ_{z_0} are required, ϵ_{y_O} is not because allowance for interactions is already made. The three appropriate equations are of the form

$$C_{Na, N\epsilon_{Na}} + C_{N, N\epsilon_N} + C_{O, N\epsilon_O} \\ = -(\partial\rho_o/\partial y - \partial\rho_c/\partial y)_N = \partial\rho(N),$$

where $\partial\rho(N)$ is adopted as a convenient notation.

The coefficients $C_{O, Na}$ and $C_{Na, O}$ are not the same, and this gives rise to the result observed that the relative effect of varying the oxygen or sodium parameters on the other atom is different. The equations giving $C_{O, Na}$ and $C_{Na, O}$ are

$$C_{O,Na} = \frac{1}{V} \cdot \frac{2\pi}{b} k \{ -(8\pi/c) l \cdot f_O \sin 2\pi l z_O \cos \alpha \} \\ \times \{ \sin 2\pi k y_{Na} \cos \alpha - \cos 2\pi k y_{Na} \sin \alpha \}$$

$$C_{Na,O} = \frac{1}{V} \cdot \frac{2\pi}{c} l \{ -(4\pi/b) k \cdot f_{Na} (\sin 2\pi k y_{Na} \cos \alpha \\ - \cos 2\pi k y_{Na} \sin \alpha) \} \{ \sin 2\pi l z_O \cos \alpha - \cos 2\pi l z_O \sin \alpha \}.$$

The equations for the other coefficients are analogous. The values obtained were

$$C_{Na,Na} = 18.32, C_{N,Na} = 5.42, C_{O,Na} = 0.03, \\ C_{Na,N} = 20.43, C_{N,N} = 20.69, C_{O,N} = 0.82, \\ C_{Na,O} = 13.44, C_{N,O} = 0.89, C_{O,O} = 16.93.$$

The results rearranged to correspond to equation (5) in the form

$$\epsilon_{i,r} = \sum_{s,j} a_{s,j,i,r} \frac{\partial(\rho_o - \rho_c)}{\partial x_{s,j}} \quad (6)$$

were

$$\epsilon_{y_{Na}} = -0.000,8096 \partial \rho(Na) - 0.000,2123 \partial \rho(N) \\ + 0.000,009 \partial \rho(O) = +0.0068 \text{ \AA}, \\ \epsilon_{y_N} = -0.000,776 \partial \rho(Na) - 0.000,7176 \partial \rho(N) \\ + 0.000,032 \partial \rho(O) = +0.00948 \text{ \AA}, \\ \epsilon_{z_O} = -0.000,602 \partial \rho(Na) - 0.000,131 \partial \rho(N) \\ - 0.000,642 \partial \rho(O) = +0.0071 \text{ \AA}.$$

These give the bond length N-O, 1.247 Å and bond angle 114° 14'.

For comparison the results of the last differential synthesis corrected by the back-shift method, are set out in the same form:

$$\epsilon_{y_{Na}} = -0.000,333 \partial \rho(Na) \\ = +0.00228 + 0.00640 \text{ (from } \epsilon_{y_O}) = +0.00868 \text{ \AA}, \\ \epsilon_{y_N} = -0.001,211 \partial \rho(N) \\ = +0.00755 + 0.00640 \text{ (from } \epsilon_{y_O}) = +0.01395 \text{ \AA}, \\ \epsilon_{z_O} = -0.000,650 \partial \rho(O) \\ = +0.00221 \text{ \AA}.$$

These give a bond length and angle of 1.243 Å and 113° 40'. The striking feature of these results is the relative importance in the refinement of the sodium ion, so that even the z co-ordinate of the oxygen atom is as much affected by changes in y_{Na} as by those in z_O . This is due to the large influence of the sodium ion on the phase angles.

3. Scattering factors

The only large improvement (0.076) in the agreement index was obtained by changing the scattering factors; very small improvements (0.015) were obtained from considerable alterations in the parameters affecting the bond length by 0.1 Å. All scattering factors were obtained from the *International Tables*; the range of $\sin \theta/\lambda$ did not necessitate the use of the values given by Ögrim & Viervoll.

The f -curves used originally were for Na⁺, N⁻ and O with no temperature factor because these gave the best agreement with the observed intensities of the (200) and (400) reflexions. A large value of R showed that new scattering factors were required and comparison of the observed and calculated peak electron densities for the atoms indicated a larger thermal motion for O and N than for Na⁺. Set III, accordingly was chosen as those for Na⁺, N and O multiplied by a temperature factor $\exp[-B(\sin \theta/\lambda)^2]$, where $B=0, 2$ and 2 \AA^2 respectively. The values of B were chosen by inspection from the agreement for a few structure factors. For refinement, the structure factors were always calculated using set III.

It was not possible to determine the best scattering factors either by drawing empirical f -curves or from difference syntheses; the three-dimensional $\rho_o - \rho_c$ map for set III, parameters E , was inconclusive, relatively large regions in the neighbourhood of the atoms being at the same level, 0.1 e.Å⁻³. Therefore, an investigation of the effect of uncertainty in the f -curves on the bond length and agreement index was made.

Table 1

	I	II	III	IV	V	
R	0.190	0.1765	0.154	0.169	0.199	
N-O (Å)	1.277	1.273	1.243	1.248	1.218	Mean: 1.252 ± 0.022
O-N-O	109° 14'	109° 32'	113° 40'	111° 03'	120° 21'	Mean: 112° 46' ± 4° 6'
$\epsilon_{y_{Na}}$	{ obs. +0.000,831	+0.000,831	+0.000,584	+0.000,083	+0.000,187	
	{ calc. +0.000,158	-0.000,054	+0.000,175	+0.000,283	+0.000,006	
ρ_c/ρ_o	0.983	1.019	1.017	1.000	1.047	
ϵ_{y_N}	{ obs. +0.002,945	+0.002,945	-0.002,87	-0.000,085	-0.009,49	
	{ calc. -0.007,11	-0.006,73	-0.004,23	-0.005,56	+0.002,06	
ρ_c/ρ_o	1.129	1.132	0.983	1.058	0.778	
ϵ_{y_O}	{ obs. +0.000,738	+0.000,738	+0.001,78	+0.001,865	+0.001,770	
	{ calc. +0.003,595	+0.003,200	+0.002,93	+0.003,44	+0.002,780	
ϵ_{z_O}	{ obs. -0.009,09	-0.009,09	-0.008,72	-0.008,315	-0.006,830	
	{ calc. -0.009,33	-0.009,15	-0.009,13	-0.006,41	-0.009,59	
ρ_c/ρ_o	1.140	1.129	1.041	1.089	1.060	

Table 1 shows a comparison of the interatomic distances, agreement factors and peak electron densities for five sets of scattering factors. These were all based on those for Na⁺, N and O, only the temperature factors being varied; where necessary the scaling factor was altered. The shifts were calculated from the final parameters (E) by differential syntheses. The temperature factors applied were:

- I. No temperature factor.
- II. The factor obtained from the slope of the graph $\log |F_c| \div |F_o|$ versus $\sin^2 \theta$. The calculated structure factors were those of case I. The value of B so obtained was 0.46 \AA^2 and the corresponding temperature factor was applied to the scattering-factor curves of all the atoms.
- III. The factors with $B = 0$ for Na and $B = 2 \text{ \AA}^2$ for N and O, which have already been discussed.
- IV. Factors with $B = 2 \text{ \AA}^2$ for Na and $B = 4 \text{ \AA}^2$ for O and N, to give the same difference as in III but with an overall temperature factor in addition.
- V. Factors with $B = 0$ for Na and $B = 4 \text{ \AA}^2$ for O and N, to give a greater difference than III.

The mean deviation in the bond lengths, $\pm 0.02 \text{ \AA}$, is a measure of the error arising from uncertainty in the calculated structure factors. The scattering factors II come nearest to being 'observed' scattering factors, but the agreement definitely indicates that III are the best.

4. Errors

Termination-of-series and the much smaller errors due to overlapping of the electron densities of different atoms as a result of thermal vibration, are largely removed by either of the methods of calculation described above. Other possible sources of uncertainty in the bond length include errors in the determination of the unit-cell dimensions, systematic and random errors in observation of intensities and errors in the calculated structure factors.

Errors in the unit-cell dimensions may affect the bond length by $\pm 0.001 \text{ \AA}$.

Extinction appeared to affect only the planes (020) and (200) for which $|F_c| > |F_o|$; omitting these from the calculation of R reduced its value from 0.192 to 0.169 and they are omitted in the final value quoted, 0.154. $F_{(200)}$ does not affect the parameters and the refinements were carried out giving $F_{(020)}$ zero weight by using F_c in the observed syntheses; if $F_{(020)}$ were given its full weight the bond length would differ by $+0.004 \text{ \AA}$ and the angle by $-0^\circ 15'$.

For a spherical specimen the absorption correction is very nearly equivalent to the use of an artificial temperature factor. In the experimental conditions used for sodium nitrite the equivalent temperature factor would be $\exp[-0.4(\sin \theta/\lambda)^2]$; by analogy with the effect of other temperature factors on the bond

length, the uncertainty introduced would not be more than $\pm 0.005 \text{ \AA}$.

The agreement between the structure amplitudes observed by Carpenter and those of the author for the same planes is $R = 0.10$. When the two sets of observations are used in identical calculations (differential syntheses) the bond lengths obtained differ by $\pm 0.01 \text{ \AA}$; this may be taken as a measure of the effect of random error in the observed structure amplitudes, while it has been shown above that the effect of uncertainty in the calculated structure factors is $\pm 0.02 \text{ \AA}$.

Instead of endeavouring to compute these effects separately, it is usual to assume that the errors in both the observed and calculated structure amplitudes are random and that a measure of both is given by $|\Delta F| = |(F_o - F_c)|$. Using this criterion, the standard deviation was calculated by a method, suggested by Cruickshank & Robertson (1953), in which allowance is made for the interaction of the parameters; hence it corresponds to the 'modified Fourier method'.

If equation (6) is written in terms of ΔF we have

$$\varepsilon_{i,r} = \sum_3 b_{hkl} \Delta F_{hkl},$$

and in this case

$$b_{hkl} = \{a_{\text{Na},r} (\sin 2\pi ky_{\text{Na}} \cos \alpha - \cos 2\pi ky_{\text{Na}} \sin \alpha) \\ + a_{\text{N},r} (\sin 2\pi ky_{\text{N}} \cos \alpha - \cos 2\pi ky_{\text{N}} \sin \alpha) \\ + a_{\text{O},r} \sin 2\pi lz_{\text{O}} \cos \alpha\}.$$

The coefficients $a_{s,i,r}$ are those determined previously. The standard deviation in ε is

$$\sigma_\varepsilon^2 = \sum b_{hkl}^2 \cdot \sigma_{(F_{hkl})}^2 \quad \text{and} \quad \sigma_{(F_{hkl})} = \Delta F_{hkl}.$$

Calculated by this method, $\sigma_{\text{Na}} = 0.01 \text{ \AA}$, $\sigma_{\text{N}} = 0.03 \text{ \AA}$, $\sigma_{\text{O}} = 0.018 \text{ \AA}$, the standard deviation in the bond length is 0.035 \AA and in the angle 4° . The magnitude of the deviation is disappointing but is consistent with the small effect on R of a comparatively large movement of the nitrogen atom and also with the separate assessment from random errors in the observed and calculated structure amplitudes.

This method also gives an estimate of the rounding-off errors; the trigonometrical terms in the expression for b_{hkl} are the same as those used to calculate the first differential, $\partial \rho / \partial x_i$, in determining the shifts, so that $\Sigma (\sin 2\pi ky_{\text{N}} \cos \alpha - \cos 2\pi ky_{\text{N}} \sin \alpha) \Delta F$ should be equal to $\partial \rho_o / \partial y_{\text{N}} - \partial \rho_c / \partial y_{\text{N}}$, and similarly for the other two atoms. A small discrepancy between the two values, giving a difference of 0.001 \AA in the bond length, was found; checking showed that it was entirely due to rounding-off in computation.

The value obtained for the standard deviation depends on the method of calculation. Using the approximate method (i.e. that based on the same assumptions as differential syntheses) a value of 0.025 \AA instead of 0.035 \AA is obtained, although the accuracy with which the co-ordinates are determined

is less and not greater when unjustified assumptions are made.

The difference between the standard deviation 0.035 Å and that obtained by Carpenter, 0.017 Å, must be attributed mainly to the different method of calculation used. The accuracy of the determinations is approximately equal; in the present work more structure amplitudes (87 compared with 62) were used and more independent values for each observation were obtained; on the other hand the value of R is larger, being 0.142 compared with Carpenter's 0.110 for the same planes. Choice of weighting factor can provide only a partial explanation for the discrepancy; the ratio between the standard deviation obtained by the approximate Fourier method and by the method of least squares with Carpenter's weighting factor is 1:0.92. It seems likely that the larger value of the standard deviation gives a true picture of the accuracy obtainable in this structure analysis; this view is confirmed by Carpenter's statement that movement of the

nitrogen atom by 0.05 Å produced a barely perceptible change in the agreement index.

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The Crystal Structure of TiB

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The structure of titanium monoboride has been determined by single-crystal and powder methods to be of the FeB-type. The dimensions of the orthorhombic unit cell are $a_0 = 6.12$, $b_0 = 3.06$ and $c_0 = 4.56$ Å. As in other borides of composition MB , the boron atoms form zigzag chains through the lattice. Short interatomic distances indicate a higher-than-normal valence for the titanium atoms, when calculated by application of the Pauling equation, $D(n) = D(1) - 0.6 \log n$.

Introduction

Two borides of titanium have been reported by Ehrlich (1949) as a result of his examination of the titanium-boron system: TiB_2 , a hexagonal phase with the AlB_2 structure, and TiB , a cubic phase of the zincblende type. The latter structure appears unlikely, as pointed out by Andersson & Kiessling (1950), who have suggested instead a NaCl-type structure. A more reasonable explanation (Brewer, Sawyer, Templeton & Dauben, 1951) of the cubic pattern obtained by Ehrlich is that it represents TiN . Consequently, there exists doubt as to the existence of the compound TiB . In any event, it has been concluded (Kiessling, 1950) that titanium does not form a boride wherein there occur chains of boron atoms, such as is characteristic of other transition metal borides of formula MB .

We have found that a boride of composition TiB exists and that, furthermore, it is of the FeB type (Bjurström, 1933) containing boron chains.

Experimental

The material used in this investigation was obtained from Dr F. H. Horn of the Physics Division of this laboratory, who prepared it by arc-melting a mixture of powdered boron and titanium of high purity. An excess of titanium was used (77 atomic %) and the TiB formed by reaction occurred as needles embedded in the excess titanium. Preferential solution of the titanium by hot sulfuric acid allowed the needles to be collected and examined. Many of the needles were found to be single crystals.

The empirical formula from chemical analysis was $TiB_{1.1}$. No reliable experimental density could be obtained from the small amount of material available.

The X-ray data were obtained with $Cu K\alpha$ (nickel filtered) radiation both from a single crystal (approximately 0.1 mm. in diameter and 1 mm. in length) and from powdered specimens. Weissenberg photographs were obtained for the equator and first layer