Earlier results with alkali halides grown from solution suggested that for atomic mismatches of more than 12 % (Royer, 1928; Sloat & Menzies, 1931) orientation ceases. Results of this kind have significance only when the experimental conditions are considered.

A careful search was made for the possible effect of water vapor during growth from the vapor. Since most of the salts used are highly soluble, water vapor could lead to the formation of mixed crystals, but none was observed. LiCl and KF, which are very soluble as well as deliquescent, were selected as the most sensitive test materials. With a pressure below 10^{-5} mm. of Hg and a liquid-air trap near the substrate, even thin deposits were in all respects like deposits of relatively insoluble salts. They possessed the correct lattice constants and showed no alteration with time. Without the liquid-air trap, however, the diffraction patterns became obscured by background after about fifteen minutes. For deposits other than LiCl and KF there was no change with time, even without the liquid-air trap.

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The Crystal Structure of Sodium Nitrite

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The crystal structure of $NaNO_2$ has been re-examined by X-ray methods. The general features of the structure reported by Ziegler in 1931 are confirmed but significant changes in the shape of the nitrite ion are indicated. Fourier and least-squares refinement lead to these dimensions for the NO_2^- ion: N–O = 1·23 Å, ∠ O–N–O = 116°. The significance of the structure is discussed briefly.

Twenty years ago Ziegler (1931) published a determination of the crystal structure of sodium nitrite, $NaNO_2$. His determination led to values for the N–O bond length and O–N–O bond angle of 1·13 Å and 132°, respectively, within rather wide limits of error. This value for the bond length is less than the sum of pure *double*-bond radii (Pauling, 1945, p. 164) and the bond angle value is greater than simple considerations indicate. In view of these puzzling results, and of the desirability of knowing the structure of simple ions with some precision, a careful redetermination of parameters by modern techniques appeared desirable.

Unit cell and space group

Ziegler's determination of the unit cell and space group was verified in the present work, incidental to the preparation of photographs for estimation of intensities. For convenience his results are quoted here (with interchange of *b* and *c* axes to conform to *Internationale Tabellen* (1935) usage).

Body-centered orthorhombic lattice, space group C_{2v}^{20}–Imm

$$a = 3{\cdot}55, \quad b = 5{\cdot}38, \quad c = 5{\cdot}56\ \text{Å}$$

2 $NaNO_2$ per unit cell.

Relative structure factors

Photographs for intensity estimation were prepared with a rod-shaped crystal of approximately square cross-section, measuring 0·20 × 0·20 mm. The crystal was 0·84 mm. long in the direction of the *a* axis. It was grown by evaporation of an aqueous solution. Equatorial-, first- and second-layer equi-inclination Weissenberg photographs about the *a* axis were recorded with nickel-filtered Cu $K\alpha$ radiation. Since there were only three structure parameters to be evaluated, the 61 reflections recorded on these photographs were judged to be sufficient for a reasonably precise determination.

Intensities were estimated by the multiple-film technique (Robertson, 1943) with the help of a set of standard intensities prepared by making timed exposures of a strong reflection. The ratio of the intensity of a given spot on one film to the intensity on the next weaker film was determined to be 3·75 for Kodak No-Screen film. A correction for the change of this ratio with equi-inclination angle was estimated and applied; the corrected ratio was taken as

$$\exp [1{\cdot}322/\cos \psi],$$

where ψ is the angle between the diffracted X-ray beam and the film normal, here equal to the equi-inclination angle.

Relative structure factor magnitudes $|F|_o$ were obtained from the relative intensities by application of the usual Lorentz and polarization factors.

Scale and temperature factors

It is easy to show, on the basis of the usual assumptions, that the most general temperature factor for an orthorhombic crystal has the form

$$T_{hkl} = \exp(-\beta_h h^2 - \beta_k k^2 - \beta_l l^2),$$

where β_h, β_k and β_l are constants. To secure the best agreement between the observed structure factor magnitudes $|F|_o$ and the magnitudes $|F|_c$ calculated for a particular structure, it is necessary to find the values of the scale factor k and the temperature factor parameters β which most nearly satisfy

$$k|F|_o = |F|_c T$$

for all hkl. In the present case $|F|_o$ values for $h=0$, 1 and 2 were at hand, each on a different relative scale. Since the $\exp(-\beta_h h^2)$ factor is constant for a given layer, its reciprocal may be included in the k factor for that layer. The best solution for k_0, k_1, k_2, β_k and β_l were then calculated by standard least-squares treatment of the equations obtained by taking the logarithm of the previous equations. Each equation was given weight unity. This results in minimizing a function which is approximately

$$\sum_{hkl} \frac{(|F|_o - |F|_c)^2}{|F|_o^2}.$$

Since absorption or extinction errors were apparent in some reflections of high intensity, this appeared to be a reasonable function to minimize. However, the $|F|$ values for (002) and (110) were omitted from this calculation because the errors mentioned are very large. This calculation was repeated at intervals as the refinement progressed.

The scale and temperature factors based on the final structure are

$$k_0 = 0{\cdot}283, \quad k_1 = 0{\cdot}285, \quad k_2 = 0{\cdot}333,$$
$$\beta_k = 0{\cdot}0095, \quad \beta_l = 0{\cdot}0103.$$

Both the β values correspond to a root-mean-square displacement of an average atom of 0·12 Å, so the thermal motion in the plane of the b and c axes is isotropic within the limits of error. The trend in the scale factors arises primarily from the change in film factor with incidence angle since the k values apply to intensities on the scale of the middle film and since the exposures for the three photographs were the same as nearly as possible. Superimposed on this trend is the result of including the $\beta_h h^2$ term in $\ln k$; this is a small effect but it is not possible to make a more precise statement about the magnitude of β_h.

Refinement of the structure

Ziegler's parameters appeared to be nearly correct so they were taken as the starting point for further refinement. They are included in Table 1. The atoms in the unit cell (Imm) are: 2 Na in (a), 2 N in (a) and 4 O in (d) (*Internationale Tabellen*, 1935, p. 116). The z coordinate of the oxygen atoms was taken as zero by exercise of the arbitrary choice of origin along c.

The $0kl$ observed structure-factor magnitudes, with phases calculated from Ziegler's parameters, were used to synthesize an electron-density projection on (100). The calculation was performed with the aid of revised Beevers–Lipson strips (Anon., 1949). Atomic parameters were calculated from tabular values of the projected electron density by an analytic method (Carpenter & Donohue, 1950). Three successively improved versions of this projection were calculated and were followed by a synthesis using calculated structure factors to obtain the 'back-shift' correction as suggested by Booth (1946). Although the Fourier refinement had not yet converged, it was believed that further refinement might be speeded by use of all the intensity data.

Refinement was continued by a least-squares procedure (Hughes, 1941), appropriately modified for the non-centrosymmetric case. Each observational equation was weighted by $(|F|_c f_{\mathrm{Na}})^{-\frac{1}{2}}$, where the atomic scattering factor for sodium, f_{Na}, is taken as an average for this structure. This weighting causes the least-squares procedure to minimize the function

$$\sum_{hkl} \frac{(|F|_o - |F|_c)^2}{|F|_c f_{\mathrm{Na}}}.$$

For the present data this appears to be more reasonable than choosing weights to minimize the same function which is minimized by Fourier refinement (Cochran, 1948), namely,

$$\sum_{hkl} \frac{1}{f} (|F|_o - |F|_c)^2.$$

However, the reflections (002) and (110) were given weight zero in these calculations also.

The least-squares refinement was continued until no parameter changed by more than 0·0001 of a cell edge in the last step. The final results are shown in Table 1.

Table 1. *Final parameter values*

	Ziegler	hkl least squares
$z_{\rm Na}$	0·583	0·5870
$z_{\rm N}$	0·083	0·1180
$y_{\rm O}$	0·194	0·1941

As expected, the nitrogen position changed most from Ziegler's structure. However, it cannot be determined as precisely as the position of the other atoms because of the small contribution of the nitrogen atoms to the diffraction pattern as a whole. In fact, variations of 0·005 in $z_{\rm N}$ in both directions caused only a barely perceptible decrease in the agreement of calculated and observed structure-factor magnitudes. This corresponds to a range of 0·05 Å for the position of the nitrogen atoms.

The standard errors, σ, of the parameter values may be estimated from the differences $||F|_o-|F|_c|$ and the coefficients in the normal equations of the least-squares procedure (Whittaker & Robinson, 1940, chap. 9). The results are: $\sigma_{\rm Na}=0{\cdot}0011$, $\sigma_{\rm N}=0{\cdot}0023$, and $\sigma_{\rm O}=0{\cdot}0015$ in fractions of cell edges. These correspond to 0·006, 0·012 and 0·008 Å respectively. The (002) and (110) reflections were omitted from these calculations, as in the previous stages. This calculation does not take account of all possible sources of error but appears to give the major contribution (Shoemaker, Donohue, Schomaker & Corey, 1950).

The final value of the conventional discrepancy function

$$\Sigma\,||F|_o-|F|_c|\div\Sigma\,|F|_o$$

is 0·11 if the reflections (002) and (110) are omitted because the observed values are clearly affected by errors. If they are included, the discrepancy rises to 0·16. The observed structure-factor magnitudes and the corresponding magnitudes and phases calculated from the final structure are presented in Table 2. For each value of h the values are arranged in order of $\sin\theta$. Atomic scattering factors were taken from the tabulation of Viervoll & Ögrim (1949). No correction was made for ionization since the scattering factors do not change appreciably in the region of the observed reflections.

Description and discussion of the structure

The packing of ions in the crystal is illustrated in Fig. 1. The atoms are drawn with van der Waals or ionic radii (Pauling, 1945, pp. 189, 346). The centers of the heavily outlined atoms lie in a plane a distance $\frac{1}{2}a$ above the others. As usual, the ions are packed with impressive economy of space. The shortest non-bonded interatomic distances are Na$^+$–O, 2·47, 2·52; Na$^+$–N, 2·61; N–O, 3·22; and O–O, 3·35 Å. These are all larger than the corresponding sums of radii, Na$^+$–O, 2·35; Na$^+$–N, 2·45; N–O, 2·9; and O–O, 2·80 Å. But since van der Waals radii are not entirely appropriate for atoms in the nitrite ion, the distances nearest the radii sums must represent atoms in contact; these are the Na$^+$–O and Na$^+$–N distances.

The dimensions of the nitrite ion are

$$\text{N–O}=1{\cdot}233\pm0{\cdot}04\ \text{Å},$$

$$\angle\,\text{O–N–O}=115{\cdot}7\pm3^\circ.$$

The ranges are about 2·7 times the standard error in these directions produced by the standard errors in atom positions. Hence errors outside the indicated ranges are quite unlikely.

The number of molecules with which the nitrite ion

Table 2. *Comparison of observed and calculated structure factors*

$0kl$	$\|F\|_o$	$\|F\|_c$	α_c (°)	$1kl$	$\|F\|_o$	$\|F\|_c$	α_c (°)	$2kl$	$\|F\|_o$	$\|F\|_c$	α_c (°)
011	3·2	2·6	300	101	17·0	16·2	350	211	4·4	3·6	237
002	17·4	38·2	37	110	22·0	34·5	0	202	21·1	24·5	39
020	8·4	7·9	0	112	19·3	23·5	55	220	8·6	6·6	0
022	15·1	19·1	107	121	17·4	21·1	189	222	14·4	13·6	105
013	8·9	8·6	288	103	14·2	14·0	325	213	7·7	6·6	286
031	15·9	19·3	189	130	6·8	5·2	0	231	12·8	14·0	189
004	9·7	8·8	82	123	13·8	12·5	213	204	7·9	6·9	85
040	14·1	15·4	0	132	15·7	14·0	110	240	11·7	12·2	0
033	10·4	11·8	211	114	10·6	9·5	125	233	9·0	9·5	209
024	14·5	17·0	154	141	4·1	3·9	213	224	12·5	13·9	154
042	11·2	12·2	62	105	11·4	11·8	339	242	10·0	10·0	63
015	8·4	7·7	326	134	12·5	14·5	156	215	6·4	6·3	324
051	5·0	4·0	338	143	4·9	4·3	268	251	3·5	3·6	342
044	7·2	7·0	133	150	15·2	16·7	0	244	6·3	6·1	134
035	4·4	4·2	235	125	5·0	4·2	244	235	3·7	3·9	232
053	5·9	5·8	325	152	11·0	12·3	40	253	4·9	5·0	327
006	3·3	3·0	271	116	5·0	4·5	220	206	2·9	2·8	275
060	9·8	10·4	0	161	< 1·2	1·0	297	260	8·2	9·3	0
026	8·8	9·5	197	145	4·9	4·1	316	226	6·7	8·5	198
062	8·6	8·0	52	154	4·0	3·9	86				
017	5·1	5·2	6	136	7·7	8·8	197				
				163	2·8	2·6	302				

may be compared is very small.* The value of the bond angle in NO_2^- agrees with that found in ONCl (116°) and ONBr (117°) by electron diffraction (Ketelaar & Palmer, 1937). However, the unusually long nitrogen–halogen bonds in these molecules make it doubtful that the structures are closely comparable with that of the nitrite ion. The nitrite ion bond angle is also only a little less than the angle in SO_2 (119°) (Dailey, Golden & Wilson, 1947), which might exhibit some similarity.

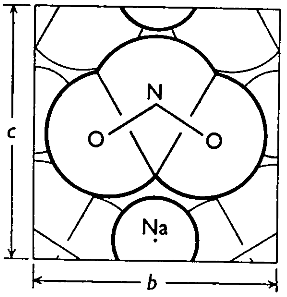
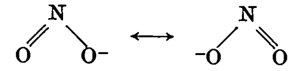


Fig. 1. The packing of ions in the sodium nitrite crystal.

The observed dimensions of NO_2^- from the present study are in accord with the picture given by the usual resonance treatment where the main contributing structures are



The N–O distance predicted on this basis by Pauling's method from his bond radii (Pauling, 1945, pp. 164, 175) is $1{\cdot}36-0{\cdot}21\times\frac{3}{4}=1{\cdot}20$ Å. Use of the Schomaker & Stevenson (1941) bond length for $N\text{–}O^-$, 1·46 Å, produces a value of 1·23 Å, in exact agreement with the X-ray structure.

A prediction of the O–N–O bond angle requires some consideration of the type of bond orbitals employed by the nitrogen atom. These orbitals may range from unhybridized orbitals (s, p_x, p_y, p_z) toward trigonal hybridization (tr_1, tr_2, tr_3, p_z) and beyond on the one hand, and toward tetrahedral hybridization (te_1, te_2, te_3, te_4) on the other. Orbitals intermediate between trigonal and tetrahedral, other than those on the range including the unhybridized set, are excluded by requiring the ion to possess a plane of symmetry through the three atoms. The range beyond equivalent trigonal orbitals toward digonal orbitals (di_1, di_2, p_y, p_z) is here included among the trigonal type possibilities. The reasonable alternatives are then a tetrahedral type and trigonal type bonding state. Since in both cases the angle between orbitals may be made more or less than the usual values (109·5 and 120°, respectively) by an unequal sharing of the s orbital among the hybridized orbitals, the experimental value of the bond angle cannot distinguish unequivocally between the alternatives. However, the experimental value 116° appears more reasonable if the bonding state is of the trigonal type. Then the unshared electron pair must occupy a trigonal type orbital with more than its equal share of s character, which appears reasonable (Pauling, 1945, p. 87). The repulsion of the oxygen atoms due to the formal negative charge distributed between them also contributes by increasing the O–N–O angle, so that the actual bonding state of the nitrogen atom in the absence of this charge might be somewhat nearer the unhybridized state.

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* *Note added in proof, 4 December* 1951: A preliminary account of a study of the same crystal by Truter (1951) has appeared since this paper was submitted. He reports, for the nitrite ion, the dimensions N–O = 1·13(9) Å and ∠O–N–O = 132° 148′. No explanation for the difference between his results and those reported here can yet be suggested.

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