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THE CRYSTAL STRUCTURE OF SODIUM NITRITE, $NaNO_2$*

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Abstract

The structure of $NaNO_2$ was determined in order to test W. H. Zachariasen's prediction (J. Am. Chem. Soc. **53,** 2123 (1931)) that the $(NO_2)^-$ group would be angular with 120° between the N–O bonds. Powdered crystal, rotating crystal, and Laue data were used. The lattice is body-centered, orthorhombic, space group C_{2v}^{20} (*Imm*), with a unit cell $a=3.55$A, $b=5.56$, $c=5.37$ containing two molecules. From visually estimated intensities the positions of the atoms in fractions of unit cell dimensions are:

Na	0	0.583	0	0.500	0.083	0.500
N	0	0.083	0	0.500	0.583	0.500
O	0	0	0.194	0	0	0.806
	0.500	0.500	0.694	0.500	0.500	0.306

Distances between atoms are: $N-O=1.13$A, $O-O$ same group $=2.09$, $O-O$ different groups >3.3, $Na-O$ two O's $=2.53$, $Na-O$ four O's $=2.46$, average $Na-O$ $=2.48$, $h=$displacement of N from $O-O$ line $=0.36$. The angle between the N–O bonds $=132°$. The observed data definitely disagree with a linear NO_2 group.

Introduction

SODIUM nitrite is one of the XO_2 group of crystals for which W. H. Zachariasen[1] predicted an angular cation-oxygen group with approximately 120° between the nitrogen to oxygen bonds. Accordingly the determination of its structure was made. In $NaNO_2$ each of the atoms present has an appreciable x-ray diffracting power with reference to the remaining atoms. This, together with the small number of atoms to be considered, made it possible to determine the structure entirely on the basis of the observed intensity of x-ray reflections. It was naturally necessary that in determining the structure no assumptions be made as to interatomic distances or the arrangement of the atoms, because any such assumptions would invalidate the determination as far as its being a test of the NO_2 group prediction.

Crystallographic Data

Crystal system, orthorhombic. (class not given)[2]
Axial ratio, $a:b:c=0.6399:1:0.9670$
Density, 2.157

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[1] W. H. Zachariasen, J. Am. Chem. Soc. **53,** 2123 (1931).

[2] P. Groth, Chemische Kristallographie **2,** 18 (1908).

OPTICAL PROPERTIES†

The indices of refraction are:

$\gamma = 1.648 \pm 0.003$ γ is parallel to c

$\beta = 1.460 \pm 0.010$ β is parallel to b

$\alpha = 1.354 \pm 0.010$ α is parallel to a

Positive birefringe $= 0.294 \pm 0.013$

The positive axial angle $2V = 75°$ approximately.

The crystals used in determining the structure were small platelets, 2 or 3 mm in the longest dimension, and were obtained by slow evaporation of a water solution of $NaNO_2$ at room temperature.

UNIT CELL SIZE AND TYPE OF LATTICE

An approximate unit cell size was determined from rotating single crystal photographs and verified by minimum wave-length calculations for Laue photographs. An accurate cell size was then determined from a powder photograph, which had been indexed with the aid of the rotating photograph cell size.*

$$a = 3.55\text{A} \quad b = 5.56\text{A} \quad c = 5.38\text{A}.$$

This unit cell size and the observed density leads to the determination that there are 2.011, i.e. 2 molecules in the unit cell. The calculated density is 2.144.

All reflections appearing on both the Laue and rotating crystal photographs were found to have $h+k+l$ even. This shows that the structure is built on a body-centered lattice. The Laue photographs were indexed by the usual gnomonic projection and the rotating crystal photographs by the graphical method of J. D. Bernal.[3]

DETERMINATION OF SPACE GROUP

Since the crystal class was not given by the crystallographic data it was necessary to investigate all space groups of the orthorhombic system and definitely to eliminate all but one. Space groups were eliminated as possibilities: (1) for not containing the two-fold, or one-fold, equivalent positions required for N and Na, (2) for not permitting the observed reflections, (3) for being equivalent to space groups of higher symmetry, (4) for not beng body-centered or permitting a body-centered lattice by special choice of the para-

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† I am indebted to Dr. T. Barth, Geophysical Laboratory, Carnegie Institution of Washington, for these measurements.

[3] J. D. Bernal, Proc. Roy. Soc. **A113**, 117 (1926).

* Since the choice of a, b and c for the axes in an orthorhombic crystal is arbitrary, the choice for this investigation was so made that they would be in agreement with the axes of the original crystallographic data as given by Groth. Mauguin's new space group notation, however, leads to another choice of axes, but it seems preferable to retain the original crystallographic axes. The data as given in this paper can be brought into agreement with Mauguin's notation very simply by interchanging b and c.

[4] R. W. G. Wyckoff, The Analytical Expression . . . of Space Groups, 2nd edition, 1930.

meters.[4] This procedure eliminated all space groups except $C_{2v}^{7}(Pmn)$,[5] $C_{2v}^{10}(Pnn)$, $C_{2v}^{20}(Imm)$, $V_3(P222)$, $V_8(I222)$, $Vh^{12}(nnm)$, and $Vh^{13}(mmn)$. A thorough consideration of these space groups with reference to the observed intensities served to eliminate as possibilities all space groups except $C_{2v}^{20}(Imm)$. Special care had to be exercised on account of the fact that the number of molecules in the unit cell is so small that for some space groups the atoms could be placed entirely in special positions.

Accordingly $C_{2v}^{20}(Imm)$ was assigned as the space group for $NaNO_2$.

DETERMINATION OF PARAMETERS

Powder crystal photograph data, verified by rotating crystal photograph data, were used in determining the values of the parameters, because reliable visual estimations of intensity can be easily made from a powder photograph.

Inspection of the intensities shows at once that reflections from faces $00l$ (002 *VW*, 004 *W*) and $0h0$ (020 *VS*, 040 *W*) do not have normal decline of intensity. Thus there must be parameters different from 0° and 180° in both the *c* and *b* directions of the crystal.

Rewriting the space group as given by Wyckoff so as to provide for this irregularity, and also choosing one of the parameters in the *b* direction as zero (pyramidal class), the following arrangements were found as possibilities:

1.	Na	$0u\frac{1}{2}$	N	$0v\frac{1}{2}$	*O*	$00w$	5.	Na	$\frac{1}{2}u0$	N	$\frac{1}{2}v0$	*O*	$00w$
2.		$0u\frac{1}{2}$		$0v0$		$00w$	6.		$0u0$		$\frac{1}{2}v0$		$00w$
3.		$0u0$		$0v\frac{1}{2}$		$00w$	7.		$0u0$		$0v0$		$00w$
4.		$\frac{1}{2}u0$		$0v0$		$00w$							

Eliminations were made as follows: 1 and 5, because they are equivalent to 7; 2, 3, and 4 because they do not account for the very strong 101 reflection 6 because it does not account for the absence of the 202 reflection. Thus all except 7 were eliminated.

The parameters *u*, *v*, and *w*, of 7 were somewhat limited by general considerations. Since 002 is very weak, *w* for oxygen must be in the neighborhood of 90° i.e. 45°–135°. Since 020 is very strong, while 022 is strong, the parameters in the *b* direction must be in the neighborhood of 0° or 180°. i.e. $-45° - +45°$ or 135°–225°. ($360° =$ length *a*, *b*, or *c* of unit cell.)

Intensities were calculated for successive values of the parameters within the ranges given above by means of the usual expression for intensity of powdered crystal reflections.

$$I = F^2 f \frac{1}{\sin^2\theta}\,\frac{1+\cos 2\theta}{2\cos\theta}$$

where: $I =$ intensity, $F =$ structure factor, $\theta =$ glancing angle, $f =$ number of faces contributing to reflection.

The atomic diffracting powers were obtained from "*F*" curves having the values given in Table I. The Na^+ curve is that derived from the values ob-

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[5] Ch. Mauguin, Zeits. f. Krist. **76**, 542 (1931).

tained for rock salt at room temperature.[6] The $O^=$ curve is virtually that obtained by J. West for KH_2PO_4.[7] The curve for N^{+3} is a reasonable extrapolation from Be and B "*F*" curves.

TABLE I. *"F" curve values* Mo*Kα*.

Sin θ	Na^+	$O^=$	N^{+3}
0.1	8.5	6.0	3.5
.15	7.2	4.3	2.8
.2	5.8	3.0	2.2
.25	4.6	2.3	1.6
.3	3.6	1.9	1.2
.35	2.9	1.6	0.9

The best agreement between the calculated and observed values of the intensity was obtained for the values:

$$u \text{ of Na} = 210°, \qquad v \text{ of N} = 30°, \qquad w \text{ of O} = 70°.$$

Table II lists the observed and calculated intensities for the powder photograph, while Table III lists the observed intensity and calculated structure factors for the rotating crystal photographs, which were used to check the

TABLE II. *$NaNO_2$. Powder crystal photograph data.*

Indices	Sin θ	Observed* intensity	Calculated intensity	Indices	Sin θ	Observed* intensity	Calculated intensity
011	0.091	1	2.9	202	0.239	nil	2.0
110	0.118		59.1	132	0.252		9.8
101	0.119	15	250.3	040	0.255	3	4.0
020	0.127	7	159.9	123	0.255		12.0
002	0.132	1	3.8	004	0.263	1	4.4
121	0.174	7	110.9	222	0.271	3	8.9
112	0.177	6	76.6	033	0.275	1	3.9
022	0.183	4	26.0	141	0.281	2	8.4
200	0.199	5	36.1	231	0.284	nil	2.8
031	0.202	1	6.2	042	0.287		9.2
013	0.208	4	22.5	213	0.288	5	11.6
130	0.216	3	13.4	114	0.289		1.3
211	0.219	nil	2.6	024	0.292	1	4.8
103	0.221	nil	2.0	310	0.306		0.5
220	0.236	4	25.8	301	0.306	2	5.4

* Intensity is given in arbitrary units.

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[6] W. H. Zachariasen, Zeits. f. Krist. **71,** 517 (1929).

[7] J. West, Zeits. f. Krist. **74,** 306 (1930).

powder data. Table IV gives the values of the parameters in degrees, fractions of the unit cell dimensions, and in angstrom units.

The possibility of a linear O—N—O group was carefully considered but the calculated intensities under all possible arrangements of the atoms failed to agree with the observed intensities. This complete lack of agreement is sufficient to show that a linear O—N—O group is impossible for $NaNO_2$.

TABLE III. *$NaNO_2$. Rotating crystal photograph data.*

Indices	Sin θ	Observed intensity	$\|F\|$	Indices	Sin θ	Observed intensity	$\|F\|$
110	0.118	S	14.5	103	0.221	W	5.2
101	0.119	VS	29.9	220	0.236	S	19.6
020	0.127	VS	36.2	202	0.239	W	5.6
002	0.132	W	5.8	132	0.252	M	9.3
112	0.177	S	17.7	040	0.255	M	11.9
022	0.183	S	15.0	123	0.255	M	10.4
200	0.199	VS	21.8	004	0.263	M+	13.1
031	0.202	W	8.2	222	0.271	M−	9.5
013	0.208	S	15.9	141	0.281	M	9.6
				231	0.284	W	5.6
				213	0.288	M	11.6

TABLE IV. *Values of the parameters.*

Na	0°	210°	0°	0	0.583	0	0A	3.24A	0A
	180	30	180	0.500	0.083	0.500	1.77	0.46	2.67
N	0	30	0	0	.083	0	0	0.46	0
	180	210	180	.500	.583	.500	1.77	3.24	1.77
O	0	0	70	0	0	.194	0	0	1.04
	0	0	290	0	0	.806	0	0	4.34
	180	180	250	.500	.500	.694	1.77	2.78	3.73
	180	180	110	.500	.500	.306	1.77	2.78	1.65

DISCUSSION OF STRUCTURE

The arrangement of the atoms as obtained with the parameters given in Table IV and the symmetry elements of the space group, C_{2v}^{20},(*Imm*) is shown in Fig. 1. A projection on the (*a*) face of the unit cell is shown in Fig. 2. The angular NO_2 group is easily seen in either figure. The angle between the N—O bonds is found to be 132°. It must be noted here that the diffracting power of nitrogen, although very favorable, is nevertheless small, relative to that of oxygen and sodium. This means that it is not possible to locate the nitrogen with great accuracy. It is found, however, that the parameter for nitrogen cannot vary by more than ten degrees from the value assigned without causing prohibitive disagreement between the observed and calculated intensities. This variation corresponds to a variation of the O—N—O angle from 146° for N parameter $= 40°$, to 118° for N parameter $= 20°$.

Thus it is conclusive that the NO_2 group is angular in the case of $NaNO_2$. Since the dimensions of the NO_2 group are small, which means that it is a tightly bound group, there is little reason to suspect that the group should vary much from crystal to crystal, for similar tightly bound groups, for ex-

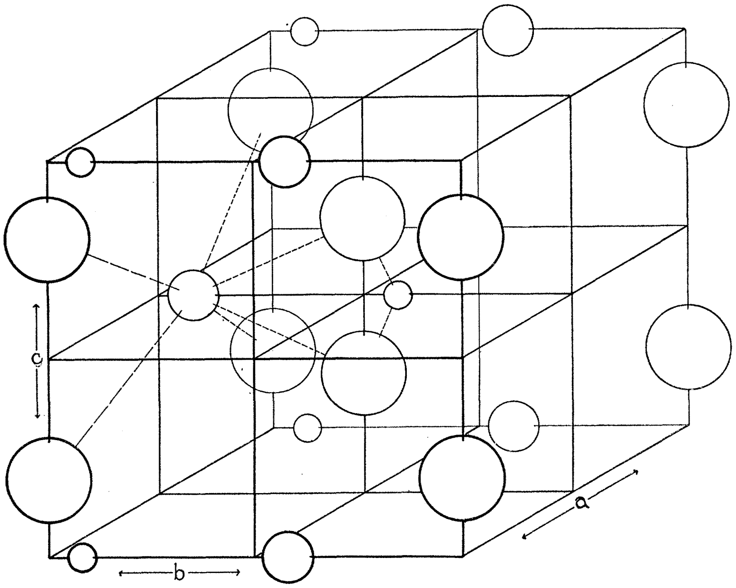

Fig. 1. $NaNO_2$. Parallel perspective drawing of structure. Large, medium, and small circles represent oxygen, sodium, and nitrogen, respectively.

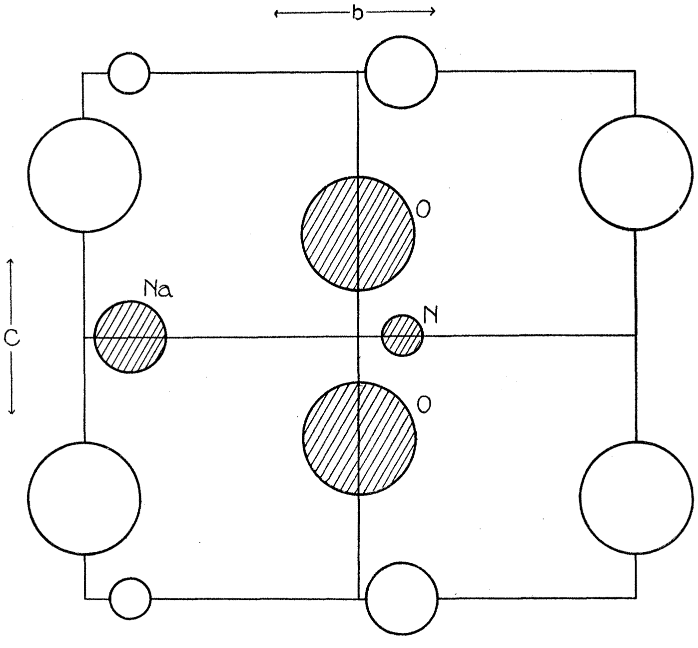

Fig. 2. $NaNO_2$. Projection on *a* face. Large, medium, and small circles represent oxygen, sodium, and nitrogen, respectively. Clear circles represent atoms placed at $a=0$ and shaded circles atoms at $a=\frac{1}{2}$.

ample the SO_4 group, maintain the same arrangement through a wide range of chemical compounds.

In addition to checking the angular group prediction, the structure of $NaNO_2$ is itself of special value and importance, due to the fact that it is a new type of structure. Since this NO_2 type of structure is new, its characteristics can be compared to those of known structures only to a limited extent. All of the interatomic distances found in the structure are very reasonable when compared to known empirical interatomic distances, and further the structure accounts for the very unusual birefringence.

The interatomic distances are of especial value because in deriving the structure no interatomic distance assumptions were used and further the small number of parameters adds to the certainty of the distances.

The interatomic distances are as follows:

$Na^{+}-O^{=}$ two O's	2.53A	$O^{=}-O^{=}$ different groups	>3.3A
$Na^{+}-O^{=}$ four O's	2.46	$N^{+3}-O^{=}$	1.13
$Na^{+}-O^{=}$ average	2.48	$O^{=}-O^{=}$ same group	2.09.

The value 2.48A for the average $N^{+}-O^{=}$ C. N. (coordination number) 6 distance agrees very well with the value of 2.46 as found[8] in $NaClO_3$. The minimum $O^{=}-O^{=}$ C. N. 6 distance different groups can be compared with the value obtained from W. H. Zachariasen's tables.[9] The value for closest approach from tables = 3.14A while the observed closest approach = 3.3A.

The $O^{=}-O^{=}$ distance NO_2 group and the $N^{+3}-O^{=}$ distance are distinctly new contributions to the available empirical interatomic distances. In comparing them with known distances all that can be said is that they are of the right order of magnitude. For example $N^{+5}-O^{=}$ C. N. 3 distance is given[10] as 1.22A in $LiNO_3$ while the new $N^{+3}-O^{=}$ C. N. 2 distance is 1.13A.

Following the method used by W. L. Bragg[11] in his consideration of the refractive indices of calcite and aragonite it is at once apparent from qualitative considerations that the unusually large birefringence is accounted for by the marked difference in the polarizibility of the NO_2 group in different directions. In a future paper quantitative calculations of the indices of refraction will be given, for such calculations should give information regarding the distribution of the outer electrons of oxygen.

For the electric vector perpendicular to the NO_2 group, the polarization is a minimum due to the fact that the induced electric moments oppose each other. This minimum polarization corresponds to the minimum index of refraction. Likewise for the electric vector parallel to the $O-O$ line of the NO_2 group the polarization is a maximum due to the fact that the induced electric moments aid each other. The optical data show that α, 1.354, has the direction of the *a* axis, which is the direction perpendicular to the NO_2 group,

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[8] W. H. Zachariasen, Zeits. f. Krist **71,** 529 (1929).

[9] W. H. Zachariasen, Zeits. f. Krist. in press.

[10] R. W. G. Wyckoff, Phys. Rev. **16,** 149 (1920).

[11] W. L. Bragg, Proc. Roy. Soc. **A105,** 370 (1924); Proc. Roy. Soc. **A106,** 346 (1924).

while γ, 1.648 has the direction of the *c* axis, which is the direction of the O – O line of the NO_2 group.

Thus the structure as given is in complete agreement with available x-ray and optical data.

I wish to express my best thanks to Dr. W. H. Zachariasen for his interest and advice throughout the course of this investigation.