

Disodium Ethane-bis-Nitraminate

By NORMAN ALLENTOFF AND GEORGE F WRIGHT

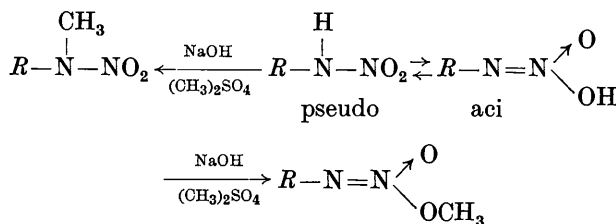
Department of Chemistry, University of Toronto, Canada

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The crystal and molecular structures of disodium ethane-bis-nitramine, $\text{Na}^+(\text{NO}_2-\text{N}^--\text{CH}_2-\text{CH}_2-\text{N}^--\text{NO}_2)\text{Na}^+$, have been determined as zigzag layers of nearly-planar anions interposed with sodium cations in a monoclinic cell $5.039 \times 18.39 \times 3.625 \text{ \AA}$ with $\beta = 93^\circ$. The interatomic distances indicate degeneracy in the anion. This degeneracy favors the nitro-oxygen atoms rather than the amino nitrogen as the anionic focus.

Interest in the nitramino linkage has been renewed in recent years. In addition to considerable organic chemical research on the linkage, the structure of a secondary nitramine (dimethylnitramine) has been solved partially (Costain & Cox, 1947) by X-ray diffraction methods. By the same method the structure of a primary nitramine, bis-nitraminoethane, has been solved by Llewellyn & Whitmore (1948) completely except, of course, in respect of the hydrogen positions. In the present research we have extended the latter study by examination of the alkali metal salts of bis-nitraminoethane.

Primary nitramines are acidic (K_A ca. 10^{-5}) in aqueous solution. By analogy with the 'pseudo' and 'aci' forms of nitroalkanes, Hantzsch & Dollfuss (1902) attributed this acidity to a tautomeric change from the 'pseudo' or 'true nitramine' to the 'aci' or 'isonitramine' form, although this supposed tautomerism is too rapid for measurement.



Others have considered both forms to be acidic, and recent Raman spectral studies (Kohlrausch & Witteck, 1948) of salts such as potassium methylnitraminate and ethylnitraminate suggest that the metal is more closely associated with the amino nitrogen than with the nitro group in these compounds. Actually the real reason for postulation of the two forms is the isolation of two compounds upon alkylation of a primary nitramine. One of these is known to be the N-alkyl analogue of the pseudo form and the other is presumed to be the O-alkyl analogue of the aci form.

Of course it is a presumption that the two alkyl derivatives arise out of two preexistent forms of the primary nitramine. Therefore it seemed worthwhile to examine the structures of disodium and/or dipotassium ethane-bis-nitraminate in their crystals and to

compare such structures with that of the parent compound, bis-nitraminoethane. It was hoped that the study would be facilitated by comparison of several salts, but the dipotassium salt formed a hydrate which was not isostructural with the anhydrous disodium salt. Likewise, neither mono salt could be obtained in recognizable crystal form. In consequence, single-crystal studies were confined to the disodium ethane-bis-nitraminate.

Space-group symmetry and structure-factor expression

The experimental section describes the designation for disodium ethane-bis-nitraminate of the monoclinic space group $P2_1/n$, in which the primitive cell contains four general positions.

The expression for F_c for hkl planes in this space group is:

$$\begin{array}{l}
 h+k+l = 2n \\
 F = 4\sum f_n \cos(2\pi hx + 2\pi lz) \cos 2\pi ky, \\
 h+k+l = 2n+1 \\
 F = -4\sum f_n \sin(2\pi hx + 2\pi lz) \sin 2\pi ky.
 \end{array}$$

In the case of $(hk0)$ planes (Broomhead & Nicol, 1948) this reduces to:

$$\begin{array}{ll}
 h+k = 2n & F = 4\sum f_n \cos 2\pi hx \cos 2\pi ky, \\
 h+k = 2n+1 & F = -4\sum f_n \sin 2\pi hx \sin 2\pi ky.
 \end{array}$$

The $(0kl)$ planes are analogously formulated. In the case of the $h0l$ reflexions,

$$h+l = 2n \qquad F = 4\sum f_n \cos(2\pi hx + 2\pi lz).$$

The scattering power, f_n , for each atom and for the scattering angle θ of each plane has been taken from *International Tables* (1935, vol. 2, p. 571) and corrected for temperature effect by application of the Debye-Waller factor according to the expression,

$$F = F_0 \exp[-B(\sin \theta/\lambda)^2]$$

with choice of $1.8 \times 10^{-16} \text{ cm}^2$ for B , which terminates the high θ values satisfactorily.

Preliminary discussion of the structure determination

Since there are only two molecules in a unit cell possessing four general positions the asymmetric unit must consist of the six atoms ($-\text{C}-\text{N}_1-\text{N}_2\text{O}_1\text{O}_2$)Na so that only eighteen parameters require evaluation. It may be postulated tentatively that the molecules are themselves centrosymmetric (as Llewellyn & Whitmore found for the free nitramine) and thus that the C-C bond will be centered at the origin and at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. This postulate is supported by the prevalence in the crystal of (110) faces, which are expected from a cell with molecules at its center and corners (Bunn, 1946, chap. 8).

The shape of the crystals, needles elongated along [001], indicates a layer structure with planes roughly perpendicular to the needle axis. The high indices of refraction in this plane, as contrasted with the low value in the direction tilted by 20° from [001], add further support to this conclusion. Consideration of the shape of the unit cell and of the molecules which it contains indicates that the direction of the chains in the a b plane will tend to be parallel to the b axis.

Determination of atomic parameters in ($hk0$) projection

Using the Llewellyn & Whitmore model of the 1,2-dinitraminoethane molecule, distances of 2.5 Å for Na-O and 2.0 Å for Na-N₁ and the restrictions imposed by the preliminary considerations above, the atomic positions eventually found for the c projection (Fig. 3, one half molecule being the asymmetric unit) were ascertained approximately by comparison of a few calculated axial structure factors with the observed numerical data. Using these tentative coordinates for calculation of more structure factors representing the strongest planes, the signs were adjusted by several successive Huggins photographic Fourier summations. These structure factors, adjusted to an absolute calculated scale by use of the factor $\sum |F_c| \div \sum |F_o|$, were found to give a correlation factor ($R = \frac{\sum [|F_o| - |F_c|]}{\sum |F_o|}$) of 22%. Inclusion of

the remaining planes (94 total) increased R to 43%.

Beevers-Lipson evaluations of electron density were made at intervals of 1/60 along the a axis and 1/120 along the b axis. Three successive two-dimensional Fourier summations with appropriate intermediary changes in sign gave improving coordinates, as shown in Table 1. The dimensions of the ($hk0$) projection of the molecule are shown in Fig. 1.

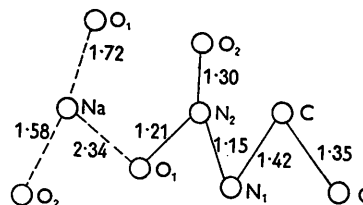


Fig. 1. Projected ($hk0$) bond distances in Ångström units.

Determination of atomic parameters in ($0kl$) projection

A set of trial parameters on ($0kl$) was derived from the y parameters and projected bond distances for ($hk0$), assuming the bond lengths to approximate those found for 1,2-dinitraminoethane. In this derivation the z parameters of Na and O₂ were separated by the greatest possible amount ($\frac{1}{2}c$ or 1.82 Å) since the O₂-Na distance projected on ($hk0$) was so short that otherwise a reasonable value of about 2.4 Å could not have been obtained. The calculated structure factors from these tentative parameters were in fair agreement ($R = 26\%$) with those observed.

The b axis was divided into 120 parts and the c axis into 30 parts in the subsequent summations with Beevers-Lipson strips. The first summation showed good peaks for all atoms with exception of N₂ and O₂, which combined into one large peak because of their proximity in the projection. Subsequent summations with adjustment of sign utilized the z value of this combined peak. The coordinates resulting from these successive summations (Table 2) finally gave structure factors in good agreement with those observed.

Table 1. x, y Coordinates from Beevers-Lipson summation

Set	C		N ₁		N ₂		O ₁		O ₂		Na		R (%)
	x	y	x	y	x	y	x	y	x	y	x	y	
1	0.439	0.4724	0.076	0.0914	0.451	0.3551	0.065	0.2010	0.204	0.3519	0.429	0.1834	25
2	0.417	0.4720	0.081	0.0916	0.459	0.3560	0.086	0.2000	0.201	0.3543	0.420	0.1838	17
3	0.415	0.4717	0.078	0.0906	0.456	0.3568	0.081	0.1998	0.198	0.3543	0.419	0.1832	15

Table 2. z, y Coordinates from Beevers-Lipson summation

Set	C		N ₁		N ₂		O ₁		O ₂		Na		R (%)
	z	y	z	y	z	y	z	y	z	y	z	y	
1	0.409	0.4699	0.353	0.4091	0.152	0.3571	0.078	0.2987	0.152	0.3543	0.115	0.1820	22
2	0.425	0.4696	0.332	0.4096	0.137	0.3571	0.071	0.2995	0.137	0.3545	0.101	0.1827	13
3	0.430	0.4709	0.328	0.4095	0.131	0.3568	0.069	0.3000	0.131	0.3543	0.101	0.1830	12

Determination of z parameters of N_2 and O_2

Since the x and y parameters of these two atoms were closely defined by the $(hk0)$ projection, and the combined peak in the $0kl$ summations was almost circular, the difference in z could not be great. Little useful information concerning these z parameters could be derived from a summation for the $(h0l)$ projection because six atoms would be included in a space of $2.52 \times 1.82 \text{ \AA}$ with correspondingly few reflexions. In order to avoid a three-dimensional Fourier section we elected to ascertain the separation of N_2 and O_2 by trial and error.

The two atoms had only a small difference in y parameters and were to be moved in opposite directions from the combined peak, but it could not be shown by change of correlation factor which atom moved in the positive z direction and which in the negative. However, if O_2 were to be moved positively, the O_2 -Na value would fall rapidly to an impossibly low value. A change in the opposite direction would, within limits, maintain a distance of about 2.4 \AA .

Thus the value of R was calculated for successive movement of N_2 8 units up from, and O_2 7 units down from the z coordinate of their combined peaks. The curve of error as indicated by plot of correlation factor, R , versus the separation of the two atoms (Fig. 2) showed a regular fall to a low of 11.3% at the value 0.24 \AA . The z coordinates corresponding to this separation were (0.166) for N_2 and (0.101) for O_2 . When these values were included in calculation of the $(h0l)$ structure factors the correlation with F_o was 13.4%.

The coordinates were refined further by the method of steepest descents (Booth, 1947) according to the formula given by Qurashi (1949):

$$\varepsilon_i = \frac{\sum_{hkl} (F_o - F_c) \frac{\delta F_c}{\delta X_i}}{\sum_{hkl} \left(\frac{\delta F_c}{\delta X_i} \right)^2},$$

where ε_i is the correction of coordinate i (x , y or z) of a certain atom. Evaluating this equation in terms of the structure-factor expressions for space group $P2_1/n$, this equation may be evaluated, for example, in correction of the X coordinate of a carbon atom, all structure factors being given equal weight

$$\varepsilon_{x_c} = - \frac{\sum_{h \neq 0} (F_o - F_c) (hf_c \cos 2ky_c \sin 2hx_c) + \sum_{hk0} (F_o - F_c) (hf_c \sin 2ky_c \cos 2hx_c)}{8\pi \left[\sum_{hk0} (hf_c \cos 2ky_c \sin 2hx_c)^2 + \sum_{hk0} (hf_c \sin 2ky_c \cos 2hx_c)^2 \right]},$$

where the first summations in numerator and denominator apply for $h+k=2n$ and the latter summations for $h+k=2n+1$. Similarly the z coordinates were corrected by use of the $(0kl)$ planes and the y coordinates with both $(h0l)$ and $(0kl)$. Terms derived from the axial structure factors were halved before summation, as was done in the case of the Fourier

synthesis. Although the few $(h0l)$ planes were again not used, their structure factors were finally recalculated with the revised values of the coordinates. Repeated application of the steepest-descent refinement to the $(hk0)$ projection changed the x and y

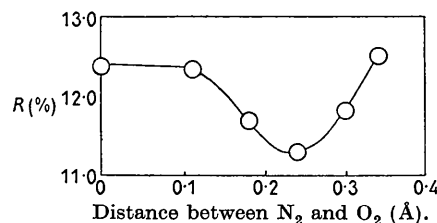


Fig. 2. Change of correlation factor with movement of N_2 and O_2 .

coordinates by -0.068 \AA and -0.026 \AA for carbon, -0.015 \AA and $+0.003 \text{ \AA}$ for N_1 , -0.0325 \AA and $+0.007 \text{ \AA}$ for N_2 , $+0.010 \text{ \AA}$ and -0.005 \AA for O_1 , -0.005 \AA and $+0.013 \text{ \AA}$ for O_2 ; finally -0.025 and -0.008 \AA for Na. The second application produced such small changes that further refinement seemed unnecessary. The revised $(hk0)$ x and y coordinates in fractions of unit cell axes are: C (0.4018, 0.47029; N_1 (0.0751, 0.09077); N_2 (0.4494, 0.35718); O_1 (0.0830, 0.19950); O_2 (0.1970, 0.35500); Na (0.4139, 0.18278). Comparison of structure factors calculated from these coordinates with those observed showed a decrease in correlation factor R from 15.4% to 13.3%.

The first refinement on $(0kl)$ improved R from 11.3% to 10.5%, but when the corrections to N_2 and O_2 were recalculated they were found to be large. In consequence a second refinement for all coordinates was carried out to give revisions shown in Table 3.

Table 3. z , y Coordinates after second steepest-descent refinement

Atom	Fraction of cell axes		Corrections (Å)	
	x	y	x	y
C	0.4262	0.47040	-0.003	-0.0008
N_1	0.3239	0.41018	-0.001	+0.006
N_2	0.1674	0.35726	-0.043	+0.016
O_1	0.0708	0.30142	+0.004	-0.004
O_2	0.1085	0.35490	-0.024	+0.013
Na	0.1007	0.18211	+0.0001	-0.0009

When these coordinates were used for structure-factor calculation R fell to 10.1%. It was apparent that only

the z coordinates of N_2 and O_2 needed further refinement. Two successive calculations were applied to these two atoms. The z -axis fractions for the four refinements of these atom positions are listed as follows:

N_2	0.179	0.167	0.174	0.168
O_2	0.115	0.109	0.115	0.112

The alternation in these values indicated that a 'rest point' would be reached at fractional axis lengths of 0.171 for N_2 and 0.113 for O_2 , both ± 0.001 (or 0.004 Å). When R was recalculated including these values it was found to be 9.8%.

From a comparison of the y values on $(hk0)$ and $(0kl)$ the positional differences for the several atoms are 0.002 Å for C, 0.018 Å for N_1 , 0.0015 Å for N_2 , 0.017 Å for O_1 , 0.002 Å for O_2 and 0.012 Å for Na. The superior resolution offered by the 'steepest descents' refinement is obvious in the close agreement of the N_2 and O_2 $(0kl)$ y values with those of the $(hk0)$ refinement; the $(0kl)$ Fourier projection showed only a single peak for these two atoms from which separate y coordinates were not obtainable. Since the differences for the other atoms involved a mean of better than ± 0.01 Å, the changes shown in Table 4 in the coordinates obtained by Fourier synthesis were accepted. Use of these values in recalculation of structure factors for the $(h0l)$ projection decreased R from 13.4 to 9.5%.

Table 4. *Changes in coordinates*

	Δx (Å)	Δy (Å)	Δz (Å)
C	-0.066	-0.010	-0.014
N_1	-0.015	+0.004	-0.015
N_2	-0.033	+0.007	+0.018
O_1	+0.010	+0.018	+0.007
O_2	-0.005	+0.012	+0.044
Na	-0.025	-0.010	-0.001

Two values in Table 6 may be questioned. The C-C bond is abnormally long and the C-C-N angle is smaller than the expected 109.5° . These discrepancies may be attributed to neglect of the hydrogen atoms in the structure determination. The effect of these hydrogen atoms may indeed be accentuated by the positions they must assume in a planar disposal of carbon, nitrogen and oxygen atoms. The total of bond angles around N_2 is 360° , and this planarity extends within 0.01 Å over each half of the molecule ($C-N_1-N_2O_2O_1$) although the planes of each half are separated by 0.08 Å.

The disposition of the molecules is shown in the Fourier projections reproduced in Fig. 3. One half of the cell shows the contour lines drawn at arbitrary equal levels, except about the sodium and combined N_2-O_2 peaks where the interval is twice as great as about the others. The other half of the cell, related to the contoured area by the centre of symmetry at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, shows schematically the arrangement of atoms as interpreted from the electron-density contours. The circles have the approximate covalent or ionic radii of the atoms or ions which they represent. The atoms of the molecules centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and their closest sodium ions are outlined more heavily than those about the origin.

It may be seen from Fig. 3 that the glide planes, perpendicular to b at $\frac{1}{2}b$, are crossed only by a few of the bonds (Na-O). Cleavage should thus be expected in this plane. Actually crystals crushed between glass slides under the microscope do show a good cleavage parallel to the needle axis.

Inspection of Fig. 3 shows that all atoms of the molecule are included in a plane which lies at an angle of about 10° with the a axis and 80° with the c axis. These angles are rather less than would be expected in respect of the refractive indices in the ac plane, owing, no doubt, to the influence of the sodium atoms. Because of the operation of the glide planes the traces on bc of the atom-rich planes are tilted 24° on either side of the b axis, the net result being in conformity with a high index of refraction parallel to the b axis.

The bond lengths and angles for the molecule are shown as a schematic c projection in Fig. 4, with the values reported by Llewellyn & Whitmore for bis-nitraminoethane in brackets. There is some similarity. Thus the planarity of the nitramino group in the disodium and dihydrogen ethane-bis-nitraminates is almost identical, and in both cases the N-O bonds are equivalent. Both molecular species are biplanar, although the separation of planes is much less in the disodium salt (0.08 *v.* 1.26 Å) than in the free nitramine.

In other respects the distortion caused by the sodium

Table 5. *Final coordinates, disodium bis-nitraminate*

	$(x, y$ and z values are ± 0.01 Å)					
	x/a	y/b	z/c	x (Å)	y (Å)	z (Å)
C	0.4018	0.4704	0.4262	2.025	8.650	1.545
N_1	0.5751	0.4097	0.3239	2.898	7.535	1.174
N_2	0.4494	0.3572	0.171	2.265	6.569	0.620
O_1	0.5830	0.3010	0.0708	2.938	5.535	0.257
O_2	0.1970	0.3550	0.113	0.993	6.528	0.410
Na	0.4139	0.1825	0.1007	2.086	3.355	0.365

Table 6. *Bond lengths and angles, disodium bis-nitraminate*

(Bond lengths are ± 0.02 Å; bond angles $\pm 0.5^\circ$)							
C-C	1.57 Å	O_1-Na_1	2.34 Å	O_2-Na_2	2.44 Å	C-C- N_1	103.9°
C- N_1	1.46	O_1-Na_1'	4.22	O_2-Na_1	3.36	C- N_1-N_2	113.3
N_1-N_2	1.28	O_1-Na_2	2.40	O_2-Na_1'	4.91	$N_1-N_2-O_1$	117.8
N_2-O_1	1.29	O_1-Na_2'	2.56	N_1-Na	2.61	$N_1-N_2-O_2$	125.7
N_2-O_2	1.29	O_2-Na_2	2.37	Na-Na'	3.63	$O_1-N_2-O_2$	116.4

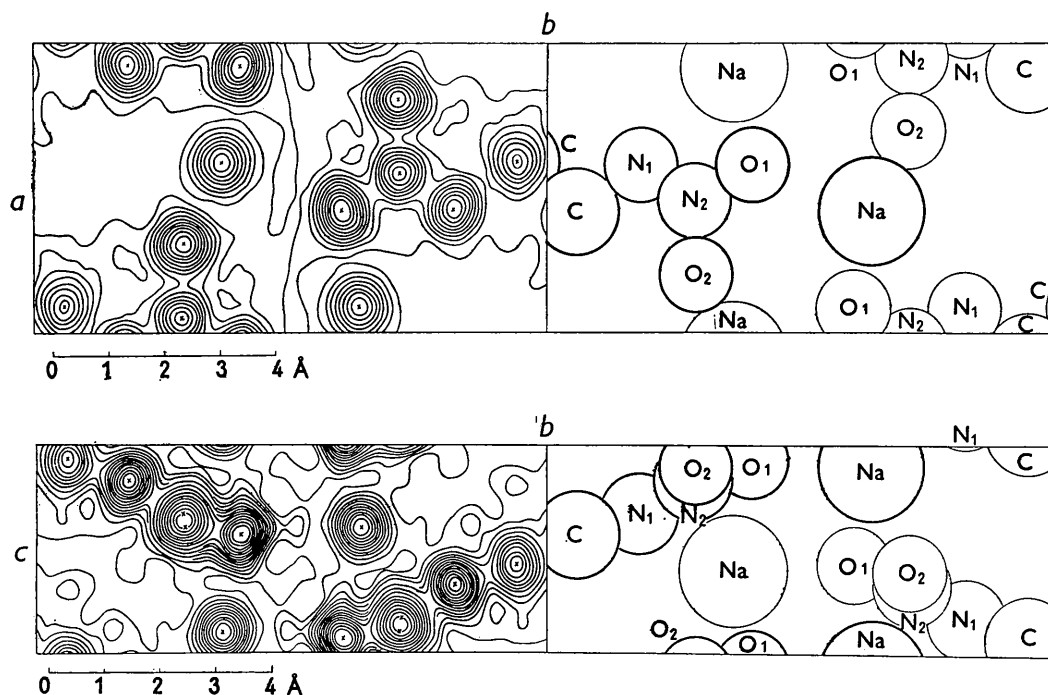


Fig. 3. Fourier projections on (001) and (100).

ions is apparent. Thus the oxygen atoms are closer to each other and more removed from the nitro-nitrogen than they are in the free nitramine. The N-N bond in the disodium salt is shortened by 0.05 Å and the entire length of the molecule is decreased by the change in the bond angles N_2-N_1-C and N_1-C-C . The dimensional compensation in the bond lengths N_1-C and $C-C$ may be significant as part of an overall degeneracy in passing from the free nitramine to its anion.

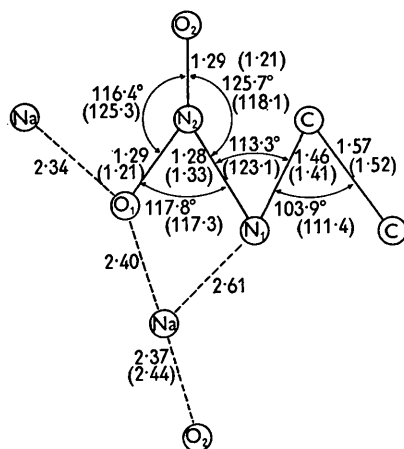


Fig. 4. Bond lengths and angles. Llewellyn & Whitmore's values are given in brackets.

It would be inadvisable to attribute the type of structure found in the present instance to nitramine

salts of alkali metals in general, since the ethane-bis-nitraminate ion may be exceptional because of its unique symmetry.

The sodium ions seem definitely to be associated with oxygen rather than with amino-nitrogen in the crystal. The average Na-O distances are in reasonable agreement with those calculated by Pauling (2.35 Å) and recorded by Zachariassen (1940) (2.35, 2.45, 2.50 Å). However, the oxygen atoms do not appear exactly equivalent in relation to the sodium ions. Whereas O₂ is separated by 2.37 and 2.44 Å from two sodium ions, the corresponding distances from O₁ are 2.34 and 2.40 Å. These relatively small differences may be due to experimental error.

The symmetrical disposition of the oxygen atoms might lead one to the expectation that methylation of disodium ethane-bis-nitraminate would lead predominantly to the O-dimethyl derivative. Expectations of this kind are based on the concept that the ions of the disodium salt react with methyl cations and methosulfate anions. However, careful isolation of the products of methylation shows that three times as much N-dimethyl derivative is formed as in O-dimethyl derivative. The structure which we have determined for the ethane-bis-nitraminate ion is therefore probably not significant to the actual methylation process. It is more likely that this reaction proceeds through a nitraminate ion which is deformed by coordination with methyl sulphate. In other words, the methylation may be thought to proceed in spite of the symmetry of the ethane-bis-nitraminate ion rather than because of this symmetry.

DISODIUM ETHANE-BIS-NITRAMINATE

Table 7. Observed and calculated structure factors

Plane	F_o	F_c	Plane	F_o	F_c	Plane	F_o	F_c
200	36.7	34.4	350	4.7	-4.2	011	10.1	7.4
400	13.7	-15.5	360	15.0	-14.6	021	44.6	40.9
020	27.2	-34.4	370	12.4	11.9	031	29.7	25.8
040	38.1	-42.0	380	15.7	14.9	041	12.4	12.0
060	53.4	51.8	390	2.4	-3.4	051	4.4	6.5
080	28.1	-25.7	3,10,0	24.9	23.6	061	20.9	-20.0
0,10,0	9.7	9.1	3,11,0	6.8	-6.4	071	13.5	-13.7
0,12,0	0	-1.2	3,12,0	17.4	-16.7	081	2.8	2.4
0,14,0	2.6	-2.8	3,13,0	6.4	7.0	091	10.1	-9.4
0,16,0	3.1	-0.9	3,14,0	5.1	6.5	0,10,1	16.8	15.4
0,18,0	23.0	-24.2	3,15,0	3.5	4.4	0,11,1	25.2	24.6
0,20,0	4.6	4.4	3,16,0	0	-0.1	0,12,1	13.9	-15.3
002	10.2	10.1	3,17,0	4.7	-5.0	0,13,1	12.2	-11.6
004	13.5	-15.6	3,18,0	1.2	-3.3	0,14,1	8.6	7.5
110	39.4	32.8	410	15.0	13.7	0,15,1	19.1	-18.4
120	5.5	4.0	420	3.5	3.3	0,16,1	17.1	17.4
130	11.9	9.8	430	1.7	2.1	0,17,1	10.4	11.4
140	19.2	14.6	440	4.0	-5.5	0,18,1	13.6	-14.0
150	14.5	-15.4	450	19.1	-18.6	0,19,1	9.6	-11.0
160	28.1	-28.2	460	3.8	-5.2	012	47.4	-43.4
170	7.8	-6.2	470	14.6	14.9	022	10.2	-9.2
180	36.0	28.6	480	9.9	11.5	032	15.6	14.9
190	21.7	19.6	490	15.0	15.9	042	11.2	12.0
1,10,0	26.9	22.9	4,10,0	8.0	-8.9	052	41.7	38.8
1,11,0	12.9	-13.7	4,11,0	5.6	-6.6	062	13.2	13.3
1,12,0	27.2	-24.7	4,12,0	0	0.7	072	25.3	-25.3
1,13,0	4.0	5.1	4,13,0	0	-0.6	082	12.5	-11.8
1,14,0	6.7	7.3	4,14,0	6.3	8.7	092	2.8	4.0
1,15,0	2.2	2.4	4,15,0	0	-1.7	0,10,2	4.8	5.7
1,16,0	6.1	7.3	510	6.1	-8.4	0,11,2	4.6	4.3
1,17,0	24.4	-22.6	520	2.5	-3.8	0,12,2	6.7	-6.4
1,18,0	5.4	-6.6	530	1.7	-3.0	0,13,2	8.7	8.5
1,19,0	3.5	3.8	540	2.5	2.8	0,14,2	6.3	-6.8
1,20,0	1.2	0.6	550	4.6	4.3	0,15,2	4.8	6.8
210	0	1.7	560	4.0	-6.8	0,16,2	4.7	4.1
220	10.8	-8.9	570	2.4	-2.1	0,17,2	8.9	-10.4
230	5.0	-5.7	580	5.9	6.4	013	0	-0.3
240	0	-0.3	590	3.7	-4.9	023	0	1.4
250	3.0	-5.9	5,10,0	5.4	6.2	033	0	-2.0
260	3.4	4.9	103	8.0	-10.3	043	5.5	5.7
270	31.2	27.3	101	47.2	-45.8	053	0	-1.3
280	17.8	-17.2	10 $\bar{1}$	5.4	-5.8	063	0	0.3
290	10.4	7.4	10 $\bar{3}$	14.3	13.7	073	13.6	15.0
2,10,0	15.9	15.6	204	7.0	-10.4	083	3.1	3.6
2,11,0	0	-0.4	202	7.0	6.7	093	2.3	-2.1
2,12,0	0	0.7	20 $\bar{2}$	8.4	-8.4	0,10,3	14.0	14.4
2,13,0	11.2	12.4	20 $\bar{4}$	4.4	6.3	0,11,3	13.2	-14.8
2,14,0	6.8	-8.1	303	2.3	-2.0	0,12,3	4.7	-5.8
2,15,0	12.4	-13.8	301	14.8	-14.3	0,13,3	4.6	4.6
2,16,0	0	2.8	30 $\bar{1}$	6.8	-5.6	0,14,3	0	0.1
2,17,0	2.5	4.0	30 $\bar{3}$	11.4	10.2	014	6.2	-7.9
2,18,0	5.9	-6.3	402	9.7	10.0	024	3.6	5.0
2,19,0	6.5	7.1	40 $\bar{2}$	25.4	-22.8			
310	10.3	10.0	501	6.9	7.8			
320	32.9	-28.8	50 $\bar{1}$	13.9	12.8			
330	20.0	-17.7						
340	31.6	29.7						

Experimental*Preparation of crystals*

Disodium 1,2-ethane-bis-nitramide was prepared by solution of 1,2-dinitraminoethane in an excess of 10% alkali, followed by addition of ethanol to induce

precipitation. Slow spontaneous evaporation of aqueous solutions of the salt gave radial clusters of long, thin, monoclinic, colorless needles showing only the faces of the $\{kh0\}$ zone, parallel to the needle axis [001]. Segments with maximum width of 0.3 mm. were obtained by rough cleavage in a direction approxi-

mately perpendicular to the needle axis. These were used in the X-ray goniometry.

The refractive indices were determined by the immersion method (Bunn, 1946, p. 149 ff.) as $\alpha=1.71$ along [010]; $\beta = 1.71$ in the (101) plane about 20° from [100] and $\gamma = 1.48$ in the same plane, about 20° from [100].

Powder diffraction

The spacing (A) and relative intensities [I/I_0] of the disodium and anhydrous dipotassium (prepared as described above and dehydrated at $93^\circ\text{C}/10\text{ mm.}$) powdered salts were determined with nickel-filtered $\text{Cu } K\alpha$ radiation. The dipotassium salt dihydrate is also included. The dipotassium salt was studied at 22°C . while the sodium salt was examined at 22°C .

and 72°C . in a 32 cm. heated camera. The patterns seemed identical at these two temperatures.

Unit cell and space group

Weissenberg ($\text{Cu } K\alpha$, Ni filtered) and precession ($\text{Mo } K\alpha$, Zr filtered) photographs of the disodium salt showed that the needle axis was a principal one in a monoclinic cell. This c axis and the b axis perpendicular to it were thus determined easily by optical goniometer orientation. The a axis was then determined by trial and error. No general extinctions were found in any layer line of the rotation photographs, thus excluding any halving of the axes. The zero layers of the three axes gave the cell dimensions shown in Table 9.

Reasonable agreement was obtained between the

Table 8. Powder diffraction data

(a) Dipotassium 1,2-ethane-bis-nitraminate dihydrate

Arc	Relative intensity I/I_1	Spacing d/n (Å)	Arc	Relative intensity I/I_1	Spacing d/n (Å)	Arc	Relative intensity I/I_1	Spacing d/n (Å)
1	1.0	5.12	13	0.3	3.74	25	0.2	2.10
2	0.9	3.17	14	0.3	3.34	26	0.2	2.01
3	0.9	3.02	15	0.3	2.85	27	0.2	1.37
4	0.5	1.94	16	0.3	2.64	28	0.15	1.97
5	0.45	2.30	17	0.3	2.18	29	0.15	1.59
6	0.4	2.76	18	0.3	1.89	30	0.1	3.43
7	0.4	2.34	19	0.3	1.51	31	0.1	2.92
8	0.4	2.14	20	0.25	3.64	32	0.1	2.38
9	0.4	1.82	21	0.25	1.34	33	0.1	2.06
10	0.35	1.70	22	0.2	7.77	34	0.1	1.45
11	0.3	5.87	23	0.2	3.27	35	0.05	4.79
12	0.3	4.16	24	0.2	2.23	36	0.05	2.55

(b) Disodium 1,2-ethane-bis-nitraminate

Arc	Relative intensity I/I_1	Spacing d/n (Å)	Arc	Relative intensity I/I_1	Spacing d/n (Å)	Arc	Relative intensity I/I_1	Spacing d/n (Å)
1	1.0	9.24	10	0.3	3.06	18	0.1	2.84
2	0.9	4.90	11	0.3	2.88	19	0.1	2.52
3	0.6	4.60	12	0.2	5.10	20	0.1	2.01
4	0.5	3.38	13	0.2	3.13	21	0.1	1.98
5	0.5	2.98	14	0.2	2.34	22	0.1	1.81
6	0.35	10.20	15	0.15	2.62	23	0.05	3.91
7	0.35	2.75	16	0.15	1.93	24	0.05	1.83
8	0.35	2.10	17	0.15	1.63	25	0.05	1.66
9	0.3	5.41						

Dipotassium 1,2-ethane-bis-nitraminate (anhydrous)

Arc	Relative intensity I/I_1	Spacing d/n (Å)	Arc	Relative intensity I/I_1	Spacing d/n (Å)	Arc	Relative intensity I/I_1	Spacing d/n (Å)
1	1.0	2.79	12	0.4	6.94	23	0.2	1.94
2	1.0	3.31	13	0.4	5.66	24	0.2	1.81
3	0.9	4.79	14	0.4	2.62	25	0.2	1.69
4	0.9	3.46	15	0.4	2.32	26	0.2	1.65
5	0.8	2.96	16	0.4	2.27	27	0.2	1.58
6	0.8	2.19	17	0.4	1.98	28	0.2	1.42
7	0.7	2.87	18	0.3	2.72	29	0.2	1.37
8	0.6	4.13	19	0.3	2.05	30	0.2	1.34
9	0.6	2.55	20	0.3	1.73	31	0.1	1.30
10	0.5	2.01	21	0.3	1.47	32	0.1	3.77
11	0.5	1.88	22	0.2	3.14			

Table 9. Cell dimensions of disodium 1,2-ethane-bis-nitraminate

Method	a (Å)	b (Å)	c (Å)	β (°)
Precession	5.037 ± 0.01	18.42 ± 0.05	3.624 ± 0.01	93.2
Weissenberg	5.041 ± 0.02	18.36 ± 0.05	3.623 ± 0.01	92.6
Mean	5.039 ± 0.02	18.39 ± 0.03	3.626 ± 0.01	93

observed density (1.95 g.cm.⁻³ by flotation in tetra-bromoethane-benzene mixture) and that calculated as 1.917 g.cm.⁻³ from the unit-cell data assuming two molecules per unit cell. The space group $P2_1/n-C_{2h}^5$ derived from zero-, first- and second-layer photographs on all axes was indicated since (hkl) were all present but ($0k0$) were present only with k even, and ($h0l$) present only with $h+l$ even. (*International Tables*, 1935, vol. 1, p. 381). The centro-symmetry was checked by pyroelectric test in liquid air.

Structure-factor determinations

Crystal segments were cut to 0.1–0.3 mm. in each dimension to give small regular reflexions. Intensity scales were prepared for each crystal by recording on a single film a gradation of 1–20 5° oscillations about a chosen strong reflexion (Cox & Shaw, 1930). The zero-layer reflexions required for intensity measurements were recorded for all three axes on a pack of six films separated by opaque paper (Robertson, 1943). All measurements in the same film pack were brought to the same relative basis by applying an empirical factor of 2.10 in relating one film to the next in the pack. This factor was calculated from 120 observations of 30 different reflexions.

Two complete sets of such measurements, differing fourfold in exposure time, were made and interrelated to a common exposure time by another factor. Likewise a third empirical factor related reflexions on the three axes among themselves. The data of Buerger (1941) were used to correct for Lorentz and polarization factors.

The final intensity values were multiplied by three in order to give a range for $[F_o]^2$ of 1–1600, thus providing a range of structure factors $[F_o]$ from 1–40 needed for reasonably complete termination of Fourier Series. The final listing showed, other than the systematic extinctions, a total of 164 structure factors.

Alkylation of disodium ethane-bis-nitraminate

The alkylation resembled that used by Backer (1912) on dipotassium ethane-bis-nitraminate. To a stirred suspension of sodium bicarbonate in water were added separately and proportionately equivalent amounts of dimethyl sulphate and an aqueous solution of disodium ethane-bis-nitraminate over two hours. The alkali insoluble product was separated by fractional cry-

stallization into a 44 mole percent yield of bis-methylnitraminoethane, m.p. 134.5–135.6° C. and 15 mole percent of an oil from which 2% of the first product was separated by chromatographic adsorption with 'Doucil' from a petroleum ether solution. The remaining oil was evidently isomeric with the solid product. It was distilled, b.p. 120–130° C. (0.001 mm.) with some decomposition. The distillate was washed with water and analyzed by slow combustion (with added dichromate) in order to obtain a result for carbon that was not too high.

Analysis: Calculated for $C_4H_{10}N_4O_4$: C, 26.9; H, 5.66; N, 31.4. Found: C, 27.4; H, 5.52; N, 31.3.

The aqueous phase of the reaction mixture was carefully acidified to precipitate 21 mole percent of N-methyl-1,2-dinitraminoethane, m.p. 123–125° C. Evaporation of the filtrate yielded 10 mole percent as unchanged bis-nitraminoethane. About 90% of the reactant is thus accounted for.

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