

$$J(\sin \theta) = \int_0^{\infty} i \left( \frac{2 \sin \theta}{\lambda} \right) \varphi(\lambda) d\lambda \quad (8)$$

(Guinier & Fournet, 1955, p. 85). Dans cette équation  $J(\sin \theta)$  et  $\varphi(\lambda)$  sont connus: on cherche à calculer  $i(s)$ .

L'équation (8) peut se mettre sous la forme:

$$f(x) = \int_0^{\infty} k(xy)g(y)dy \quad (2)$$

identique à celle discutée ci-dessus. On peut donc la résoudre de la même manière.

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## The Crystal Structure of Nitramide, $\text{NH}_2\text{NO}_2$

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The structure of the unstable crystals of nitramide,  $\text{NH}_2\text{NO}_2$ , has been investigated. The monoclinic unit cell has dimensions  $a = 6.65$ ,  $b = 4.79$ ,  $c = 7.86$  Å,  $\beta = 112^\circ 24'$ , and the space group is  $A2/a$ . Good agreement ( $R = 16\frac{1}{2}\%$ ) is obtained for all reflexions with one index zero and for all the planes with  $k = 1$ . The parameters chosen are  $\text{N}_I$  at (0.250, 0.575, 0),  $\text{N}_{II}$  at (0.250, 0.866, 0), O at (0.367, 0.466, 0.137), whilst the probable hydrogen positions are (0.42, 0, 0.08). The hydrogen atoms did not show up in the  $b$ -axis difference maps (although these showed evidence of anisotropic movements of the nitrogen and oxygen atoms) but there were indications of the hydrogen positions in the other two difference maps.

### Introduction

The high melting point and low volatility of nitramide indicate a high degree of hydrogen bonding in the crystal. Because the compound contains a high proportion of hydrogen atoms to heavier atoms, it appeared that a study of the crystal structure might have provided interesting information on the N-H-O hydrogen bond. Furthermore, it was hoped that the study would throw light on the disputed question of the structure of the compound.

The chemical and physical properties of nitramide indicate (Bell & Trotman-Dickenson, 1949) that in solution it is predominantly in the form of  $\text{NH}_2\text{NO}_2$  molecules, the structure originally suggested by Thiele & Lachmann (1895). However, a small proportion of the dissolved molecules probably have the tautomeric structure  $\text{NH}\cdot\text{NOOH}$  suggested by Pedersen (1934).

The present work indicates that the structure of the crystals is that shown in Fig. 1, and suggests that the formula  $\text{NH}_2\text{NO}_2$  is to be preferred although it proved difficult to locate the hydrogen atoms precisely. All the presumed hydrogen bond distances are rather long, each amide nitrogen having six N-O distances of 3.1 Å.

### Experimental details and unit cell

The nitramide was synthesized by the method of Marlies, LaMer & Greenspan (1939) (we are indebted to Mr J. S. Slater for this preparation). The nitramide was dissolved in anisole at about  $25^\circ\text{C}$ . to form a saturated solution. This was stored in a refrigerator ( $6^\circ\text{C}$ .) at which temperature the crystals precipitated out. They were kept under these conditions for several months. When mounted on a goniometer head in the X-ray camera the crystals completely disappeared in 24 hours.

The crystals have the shape of laths of a few millimetres length and of width about 0.4 mm. and thickness 0.2 mm. Many were striated parallel to the long dimension. They show a parallel extinction. It was not easy to find good single crystals, but, when found, X-ray photographs showed them to be monoclinic, with the unique ( $b$ ) axis parallel to the length. The dominant form was  $\{10\bar{1}\}$  referred to the axes given below. The axial lengths were calculated from the position on the films of moderately high order spots. The cell found was:

$$a = 6.65 \pm 0.03, \quad b = 4.79 \pm 0.03, \quad c = 7.86 \pm 0.03 \text{ Å}, \\ \beta = 112^\circ 24'.$$

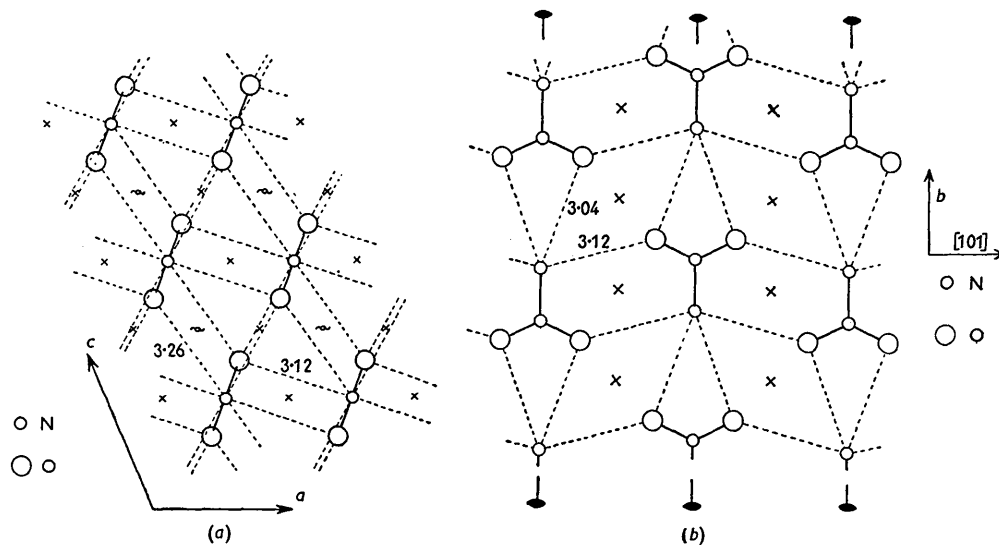


Fig. 1. (a) Projection of the structure down the  $b$  axis. The two nitrogen atoms are superimposed in the positions of the twofold axes. The broken lines show distances between the atoms of the different molecules. (b) One of the approximately flat sheets of molecules parallel to the  $(10\bar{1})$  plane, the broken lines showing the bonding between molecules in the plane.

This cell contains 4 molecules of  $\text{NH}_2\text{NO}_2$ , the observed density being  $1.783 \text{ g.cm.}^{-3}$ . The calculated density agrees with this to 1 part in 4000.

Photographs were obtained about the three principal axes. The  $b$ -axis films included Weissenberg photographs of zero and first layer lines, one being a multiple-film exposure of the zero layer line. The  $a$ -axis photographs were a number of oscillation photographs for adjustment purposes and a zero-layer-line Weissenberg exposure. About the  $c$  axis a set of oscillation photographs were obtained. Spots were visible on the photographs up to the limit of  $\text{Cu } K\alpha$  radiation. The specimens used were chopped to a roughly cylindrical shape about the three axes, using a razor blade.

#### Space group and method of analysis

The  $a$ -axis zero-layer-line Weissenberg photograph showed that the  $(0kl)$  spots are present only when  $(k+l)$  is even. The  $b$ -axis photographs show that the  $(h0l)$  spots are present only when  $h$  and  $l$  are both even, and that the  $(h1l)$  spots are present only when  $l$  is odd. These absences are explained by the rules that  $(hkl)$  is present only when  $k+l$  is even, and  $(h0l)$  is present only when  $h$  is even. These rules suggest as space group either  $A/a$  or  $A2/a$ . The more symmetrical space group was chosen as it possesses the necessary number of general positions (eight) for the oxygen and hydrogen atoms and puts the nitrogens on to special positions. This situation provides a very simple problem, and as a satisfactory structure was reached on this assumption a detailed consideration of structures based on  $A/a$  was considered unnecessary.

The space group  $A2/a$  contains centres of symmetry, rotation axes, screw axes and two kinds of glide plane

perpendicular to the  $b$  axis. The general equivalent points are

$$(0, 0, 0) \text{ and } (0, \frac{1}{2}, \frac{1}{2}), \pm(x, y, z), (\frac{1}{2}+x, \bar{y}, z).$$

The nitrogen atoms cannot be situated on the centres of symmetry, so that they must be placed on the rotation axes. Neglecting the hydrogen atoms for the time being, we are left with only one oxygen to find in the  $b$ -axis projection. This was done by means of the Patterson projection using the  $(h0l)$  planes. This projection showed one  $2\text{N-O}$  peak which gives the  $(x, z)$  coordinates of the oxygen with respect to the nitrogens. Assuming an  $\text{N-O}$  distance of  $1.2 \text{ \AA}$  we then obtained the  $y$  parameter difference between  $\text{N}$  and  $\text{O}$ , and assuming an  $\text{N-N}$  distance of  $1.45 \text{ \AA}$  we could also get the  $y$  parameter difference between the nitrogens. Then, from the  $(0k0)$  intensities, we deduced the absolute values of the  $y$  coordinates of all the atoms. These were used to calculate the  $(hk0)$  and  $(0kl)$  intensities, and gave excellent agreement. Refinement was carried out by Fourier difference maps down all three axes.

On the  $b$ -axis difference map there were typical 'clover-leaf' patterns, suggesting some anisotropy of the heat motion of the two nitrogen atoms and also of the oxygen atom. This heat motion is a maximum in a direction roughly perpendicular to the plane of the molecule, i.e. perpendicular to  $(10\bar{1})$ . The hydrogen atom did not show up clearly on the  $b$ -axis projection, possibly owing to the heat-motion effects and to its being quite near the oxygen position, but the parameters given for the hydrogen atom are reasonable from the other two projections.

Table I shows calculated and observed  $F$  values for the  $(h0l)$ ,  $(0kl)$  and  $(hk0)$  planes. The accuracy is

Table 1. *Observed and calculated  $F$  values of nitramide*

$h$	$l$	$F_o$	$F_c$	$h$	$l$	$F_o$	$F_c$	$k$	$l$	$F_o$	$F_c$
0	2	35	33	$\frac{4}{2}$	19	-29		4	0	0	-2.0
	4	8.5	-5.6	$\frac{2}{2}$	0	0.8		2	2	17	-14
	6	29	28	0	11	-10		4	4	22	-22
	8	29	26	2	29	-29		6	6	6.0	-4.4
2	$\frac{10}{8}$	24	-21	4	12	-12		5	1	0	-4.2
	$\frac{8}{6}$	22	-26	8	$\frac{6}{4}$	14	23	3	3	8.4	7.7
	$\frac{6}{4}$	1.7	0.8	$\frac{4}{2}$	$\frac{4}{2}$	4.8	2.4	5	0	0	3.4
	$\frac{4}{2}$	18	-13	$\frac{2}{2}$	$\frac{2}{2}$	5.2	4.8	6	0	0	-0.5
	0	45	-41					2	0	0	-5.0
	2	11	7	$k$	$l$	$F_o$	$F_c$	$h$	$k$	$F_o$	$F_c$
	4	30	-25	1	1	39	-38	1	2	21	15
	6	34	-31	3	3	30	29	4	4	0	1
	8	6.4	-6.4	5	5	5.2	7.2	6	6	0	2
4	$\frac{10}{8}$	21	22	7	7	19	-19	2	2	6.5	-10
	$\frac{8}{6}$	4.7	3.2	9	9	0	-0.6	4	4	12	10
	$\frac{6}{4}$	7.7	4.8	2	0	55	45	3	2	7	5
	$\frac{4}{2}$	37	45	4	2	0	2.0	4	4	14	17
	0	7.0	-5.6	6	6	8	12	4	2	21	-17
	2	20	18	8	8	12	14	5	4	20	-20
	4	38	33	3	1	22	-25	6	2	7	-5
	6	9	10	3	3	7.8	9.1	4	4	15	-18
6	$\frac{8}{8}$	4.8	-2.4	5	5	0	-1.8	6	2	0	1
	$\frac{6}{6}$	27	-27	7	7	17	-18				

highest for the ( $h0l$ ) planes since the crystal habit is difficult for the other two projections. The ( $hk0$ ) intensities are the least accurate of all, being derived only from oscillation photographs. The reliability index  $R$  is  $16\frac{1}{2}\%$  for all these planes. Intensity values were also calculated for the  $k = 1$  planes and showed good agreement.

### Description of the structure

The parameters finally chosen are:

	$x$	$y$	$z$
$\text{N}_I$	0.250	0.575	0
$\text{N}_{II}$	0.250	0.866	0
O	0.367	0.466	0.137

with a probable hydrogen position of (0.42, 0, 0.08). Fig. 1(a) shows a projection of the structure down the  $b$  axis, and gives the position of the nitrogen and oxygen atoms. The planar molecules are inclined at  $6^\circ$  to  $(10\bar{1})$  and thus form almost flat layers parallel to this plane. One of these layers is shown in Fig. 1(b), and the remarkable number of  $\text{N}_{II}$ -O bonds is shown in this figure: each  $\text{N}_{II}$  is bonded to four oxygen atoms in the sheet, and each oxygen to two  $\text{N}_{II}$  atoms. Between different sheets the  $\text{N}_{II}$ -O distances are 3.28 and 3.5 Å, but there is one  $\text{N}_I$ -O distance of 3.12 Å. Probably this involves a van der Waals repulsion which is responsible for the departure of the molecules from the exact  $(10\bar{1})$  plane.

The interatomic distances and angles found within the molecule are:

$$\begin{aligned} \text{N}_I\text{-N}_{II} &= 1.40, \quad \text{N}_I\text{-O} = 1.18, \quad \text{O-O} = 2.13 \text{ \AA}, \\ \text{O-N}_I\text{-O} &= 129^\circ. \end{aligned}$$

These agree well with the dimensions of the nitro group obtained from other determinations, and the  $\text{N}_I\text{-N}_{II}$  distance suggests that this bond is single.

Other interatomic distances are:

within one sheet, between molecules separated by  $b$ :

$$\text{O-N}_{II} = 3.04 \text{ \AA};$$

between molecules side by side:

$$\text{O-N}_{II} = 3.12 \text{ \AA}.$$

The hydrogen atoms lie roughly between these two bonds. Between separate sheets are the following interatomic distances:

$$\text{O-N}_{II} = 3.26, \quad \text{O-N}_{II} = 3.50, \quad \text{O-N}_I = 3.12 \text{ \AA}.$$

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