

## The Crystal Structures of Lithium, Sodium and Strontium Azides

By G. E. PRINGLE AND D. E. NOAKES\*

School of Chemistry, University of Leeds, Leeds 2, England

(Received 18 April 1967)

$\text{LiN}_3$  has been found to be isostructural with a low-temperature phase of  $\text{NaN}_3$  designated  $\alpha\text{-NaN}_3$ . Both of these have been studied by powder methods. The phase-transition of the sodium salt is found to be predominantly of second order. The higher form ( $\beta\text{-NaN}_3$ ) has been reinvestigated by single-crystal methods. The structure of  $\text{Sr}(\text{N}_3)_2$  has been refined from already published data. It is found that many of the interatomic distances can be rationalized on the assumption that the end nitrogen atoms of the azide ion are apparently earth-shaped. This is in agreement with the anisotropy of the thermal motions which points to a considerable libration of these ions.

### Introduction

The most obvious evidence of covalency between the azide and other groups is a disparity of about 0.1 Å of the N–N bond lengths as shown in the typically covalent azides  $\text{HN}_3$ ,  $\text{CH}_3\text{N}_3$  and cyanuric triazide. The smaller disparity of 0.06 Å found by Palenik (1964) in the coordinated azide group of azidopentamminecobalt(III) azide may be typical for a coordinate bond. In situations of higher symmetry the azide group would not be expected to show similar disparities (although Bassière (1943) claimed that it does so); but other evidences of deficient ionicity might be sought in the possible variability of mean bond-length.

Stereochemical evidence is also important in the event that a cation exhibits more than one interionic distance to its coordinated nitrogen atoms (e.g. in  $\text{AgN}_3$ ). There were in this field some outstanding difficulties in that the 1.12 Å N–N bond in  $\text{Sr}(\text{N}_3)_2$  found by Llewellyn & Whitmore (1947) appeared measurably shorter than that in ionic azides generally (about 1.16 Å). The coordination of N atoms round the cation in an (approximate) square antiprism though qualitatively like that in  $\text{KN}_3$ , differs from the latter in that there are two unequal distances involved. Should we conclude that there is some covalency, and that covalency can even shorten the mean N–N distance?

Equally puzzling is the coordination of nitrogen atoms round Na in  $\beta\text{-NaN}_3$  in a trigonal antiprism rather than in a regular octahedron, and at reduced temperature in a figure of still lower symmetry (*vide infra*). The present investigation has helped to clarify these issues by studying interatomic distances collectively, and by offering an alternative explanation unconnected with covalency for these minor stereochemical features.

### Problems studied

Attention was given to the following points:

- (i) Study of the phase transition of  $\text{NaN}_3$  by optical and X-ray powder methods.

- (ii) Single-crystal X-ray structure analysis of the ordinary form of  $\text{NaN}_3$  (designated  $\beta\text{-NaN}_3$ ).
- (iii) Computational refinement of the  $\text{Sr}(\text{N}_3)_2$  structure from the already published data.
- (iv) Determination of the structure of  $\alpha\text{-NaN}_3$ .

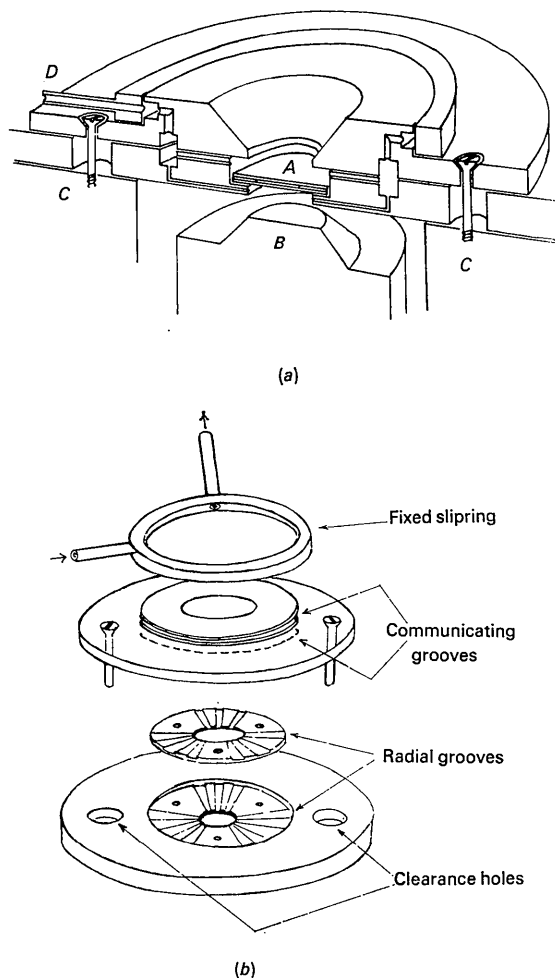


Fig. 1. (a) Low temperature microscope stage. A Specimen, B Condenser, C Rotating stage, D Cold gas inlet port. (b) Construction of the cold stage.

\* Present address: Mid-Essex Technical College, Chelmsford, England.

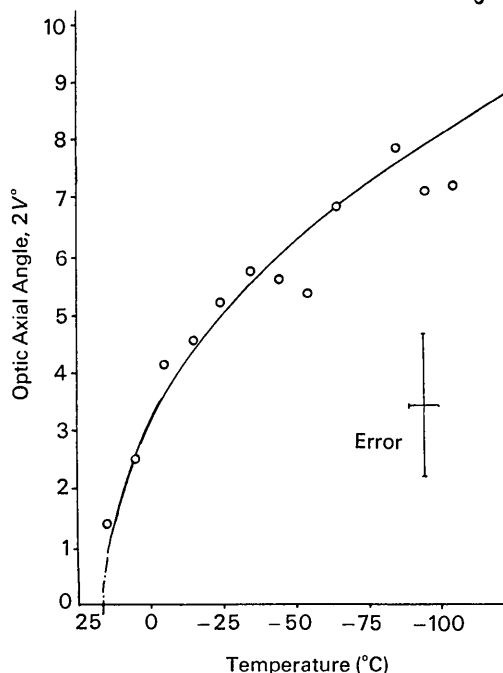


Fig. 2. Variation of optic axial angle of sodium azide with temperature.

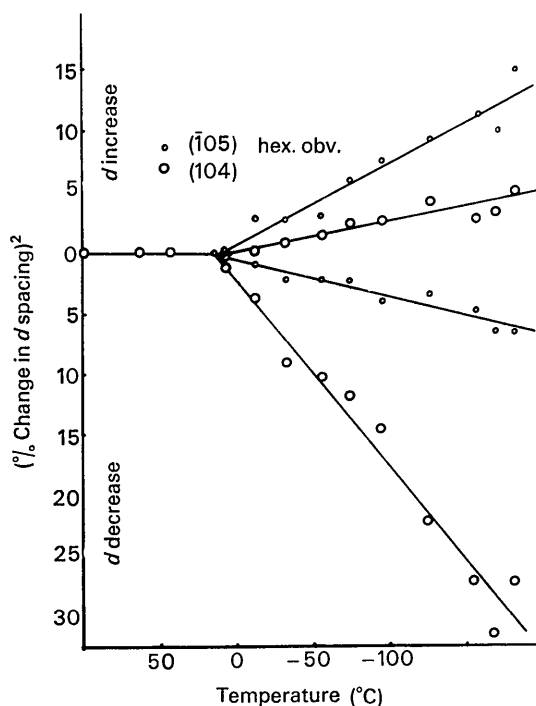


Fig. 3. Variation in  $d$  spacing with temperature for sodium azide.

(v) Determination of the structure of  $\text{LiN}_3$ .

An investigation by Bradley, Grace & Munro (1964) in the Leeds high pressure laboratory is related to topic (i).

**The transition point of  $\text{NaN}_3$**

Observations with the polarizing microscope on sufficiently large monocrystalline plates can be made by means of a cold stage constructed mostly of Perspex and depicted in Fig. 1; the coolant is a stream of dry evaporated nitrogen, and impinges above and below a sandwich of thin circular cover slides holding the specimen. In this way it was noticed that sodium azide becomes biaxial at reduced temperature; the variation of interaxial angle  $2V$  with temperature is shown in Fig. 2. Because of the low accuracy with which  $2V$  can be measured, it was still not certain whether the change of crystal structure implied by this result was a first or second order transition: the transition point appeared to be at room temperature. In either event, the major part of the change took place progressively towards lower temperatures and was far from complete even at  $-100^\circ\text{C}$ . The occurrence of a phase change was also reported independently by Miller & King (1963) by electron spin resonance (e.s.r.) studies. As will be seen, their assignment of orthorhombic symmetry to  $\alpha\text{-NaN}_3$  is probably incorrect.

A series of X-ray powder photographs at different temperatures shows clearly the character of the transition. These were taken on a Weissenberg goniometer with the carriage stationary, but translated between exposures. Because of the low resolution, the exact onset of splitting of certain lines due to a lowering of the lattice symmetry can be determined only approximately. The splitting follows fairly closely the quadratic law (Fig. 3):

$$\frac{d_1 - d_2}{d} \propto \sqrt{T_c - T} \quad T < T_c,$$

where  $d_1$  and  $d_2$  are spacings of the components of a doublet originally of spacing  $d$ ,  $T$  is the temperature and  $T_c$  the transition point. The transition point so determined by ourselves (Pringle & Noakes, 1963) was about  $13^\circ\text{C}$ , markedly lower than that ( $\sim 22^\circ\text{C}$ ) recently given by Parsons & Yoffe (1966). Whether this is due to their higher resolution, or to differences in the specimens, has not been determined. Miller & King quote DTA results of Petz (1957) from which the transition was determined as  $18^\circ\text{C}$  and their own e.s.r. result was  $19^\circ\text{C}$ . We have observed a qualitative change in appearance of a single crystal, probably a result of cleavage flaking, which occurred at about  $18^\circ\text{C}$  and like that in Miller & King's experiments was 'sharp, reversible and reproducible'. This therefore seems the most typical transition temperature, and  $13^\circ\text{C}$  probably too low.

For obvious reasons it seems unsuitable to label either form as a 'room temperature' modification: we propose  $\alpha$  for the lower,  $\beta$  for the higher form.

## X-ray data

Table 1 summarizes the experimental data for the structures discussed.  $\text{LiN}_3$  is so deliquescent that no single crystals were grown, and instead we used powder data obtained by means of a diffractometer. The sample was protected from atmospheric moisture by loading the thick layer of powder into a hollow slide in a dry box and sealing this with a thin film of cellulose acetate. The radiation shield was itself made nearly airtight with another plastic film and dried with silica gel. It was already clear from photographs lent by Professor P. Gray which powder lines were those of the anhydrous substance; one sample approximated very closely to that pattern and was used to obtain the chart record with  $\text{Cu } K\alpha$  radiation. The integrated intensities were measured by quadrature on the chart. Unresolved lines were measured as total intensities and then artificially split, by calculation, in the ratios of the calculated intensities. This procedure would give a falsely optimistic accuracy to the structure refinement, and accordingly some allowance has been made for this in the quoted s.d. of coordinates.

The corresponding experiment on  $\alpha\text{-NaN}_3$  was done with the use of a thermally insulated radiation shield, cooled by a stream of liquid-bearing cold nitrogen generated by vigorously boiling the liquid. The temperature was assessed by using a thermocouple attached to the powder holder, and also by interpolation in the results of Fig. 3. The value attained was in the range  $-90^\circ\text{C}$  to  $-100^\circ\text{C}$ , but was not maintained exactly, only by hand control.

The single-crystal data for  $\beta\text{-NaN}_3$  were obtained by Weissenberg photography with  $\text{Cu } K\alpha$  and  $\text{Mo } K\alpha$  radiation for rotation axes  $[10.0]$  and  $[24.1]$ . Lattice parameters were redetermined from single-crystal and

powder photographs in cameras calibrated with lines of copper and silver in the high range of  $2\theta$ .

## Space groups

The structure of  $\beta\text{-NaN}_3$  is already known from the work of Hendricks & Pauling (1925). It is rhombohedral,  $R\bar{3}m$ , with one molecule per unit cell, or 3 molecules in the hexagonal cell (Fig. 4). Evidence brought by Bassière to support the space group  $R3m$  was not conclusive as it depended on a rather dubious correction for extinction, and used only  $00.l$  reflexions. Though the  $\text{N}_3$  group may not necessarily have the same symmetry even in different ionic compounds, crystallographic evidence mostly favours the linear symmetric form. The uncoordinated ion in  $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{N}_3(\text{N}_3)_2$  shows in the published structure no significant asymmetry although it is in a general position in the unit cell. On a site with a twofold axis in  $\text{Sr}(\text{N}_3)_2$  the anion in our refinement as in the original version appears substantially linear. In both forms of  $\text{NaN}_3$  and in  $\text{LiN}_3$  the middle nitrogen atom occupies a centre of symmetry; an attempt to refine  $\beta\text{-NaN}_3$  coordinates in the space group  $R3m$  with the anion linear but acentric was inconclusive. From the rhombohedral structure of  $\beta\text{-NaN}_3$  we can deduce the  $\alpha$  structure on observing that (i) the  $00.l$  reflexions remain almost unaffected by temperature, (ii) the general reflexions become doublets below the transition point, one component having approximately double the intensity of the other, (iii) the structural change must be displacive in character. This led us to conclude that the new cell is monoclinic, space group  $C2/m$ , with two molecules per unit cell. The permitted reflexions having  $h+k=2n$ , the powder diagram was satisfactorily indexed for both  $\alpha\text{-NaN}_3$  and the isostructural  $\text{LiN}_3$ .

Table 1. Crystal data and refinement procedures

Substance	Crystal		Temp- erature	Cycles refinement (Space group)	Weighting scheme	Final <i>R</i> index	Lattice parameters			<i>F</i> table	
	Axis	Radius					<i>a</i>	<i>b</i>	<i>c</i>		$\beta$
$\beta\text{-NaN}_3$	$[10.0]$	0.013 ( $\text{Cu } K\alpha$ )	Room	8 in $R\bar{3}m$	1 $\frac{1}{A+BF+CF^2}$	12½%	3.646 $\pm 0.002$	—	15.213* $\pm 0.005$	—	Table 3
	$[24.1]$	( $\text{Cu } K\alpha$ )		4 in $R\bar{3}m$							
	$[10.0]$	0.015 cm ( $\text{Mo } K\alpha$ )		4 in $R\bar{3}m$							
	$[24.1]$	0.035 cm ( $\text{Mo } K\alpha$ )		3 in $R\bar{3}m$							
$\alpha\text{-NaN}_3$	Powder (ground but not sieved)		$-90^\circ\text{C}$ to $-100^\circ\text{C}$	8 in $C2/m$	1 $\frac{1}{1+F/6}$	8%	6.211	3.658	5.323	108.43	Table 4
$\text{LiN}_3$	Powder (ground but not sieved)		Room	7 in $C2/m$	1 $\frac{1}{1+F/6}$	12%	5.627	3.319	4.979	107.4	Table 5
$\text{Sr}(\text{N}_3)_2$	Llewellyn & Whitmore's (1947)		Room	15 in $Fddd$	1 $\frac{1}{A+BF+CF^2}$	9½%	11.82	11.47	6.08		As pub- lished $\times 1.05$

\* Values about 2% higher than those given recently by Parsons & Yoffé (1966) (extrapolated down to  $23^\circ\text{C}$ ).

## Structure refinement

The refinement procedures and crystal data are summarized in Table 1, with atomic parameters in Table 2 and structure factors in Tables 3-5.

The atomic scattering data used in calculating structure factors were those of *International Tables for X-ray Crystallography* (1962). Charges of 0.8 electron (nega-

tive) and 0.6 electron (positive) were assigned to end and middle nitrogen atoms respectively, approximately those calculated by Bonnemay & Daudel (1950). The curve for  $\text{Sr}^{2+}$  was interpolated between those for Sr and Kr. The final  $R$  value for  $\text{Sr}(\text{N}_3)_2$  is considerably lower (0.095) than that attained by isotropic refinement by the original authors of the data (0.27) and there was also some improvement in the final difference electron density map of the azide ion. In the refinement process for  $\beta\text{-NaN}_3$ , various sets of data were handled separately, but the final results were not significantly at variance, and only one set is given in detail.

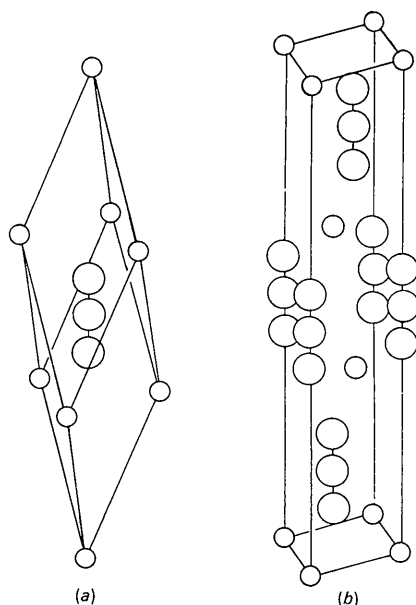


Fig. 4. Unit cells of  $\beta\text{-NaN}_3$ . (a) Rhombohedral,  $Z=1$ ,  $a=5.49$  Å,  $\alpha=38.7^\circ$ . (b) Hexagonal,  $Z=3$ ,  $a=3.65$  Å,  $c=15.2$  Å. Small circles Na, large circles N.

## Isostructural Li and Na salts

Both forms of sodium azide are layer structures (Figs. 4 and 5). In the rhombohedral form, end nitrogen atoms are in close-packed arrangement at a spacing of  $3.64_7$  Å, the next layer being a similar arrangement of sodium ions at a N-Na distance of  $2.50_7$  Å. On going to the low temperature structure the principal change is a shear of the layers, but the equilateral contact triangle becomes isosceles with base  $3.65_8$  Å (the monoclinic  $b$  axis) and sides  $3.60_4$  Å. The spacing between layers of sodium ions becomes  $5.05_1$  Å instead of  $5.07_1$  Å. These changes can partly be accounted for as ordinary thermal contraction, except for the shear movement of  $0.4$  Å which is much too large to be so explained. The anion tilts from its original position along the hexagonal  $c$  axis through an angle of  $12.3^\circ$  at  $-100^\circ\text{C}$ , much more than the shear angle of  $4.8^\circ$ . In consequence the end nitrogen atom N(1) comes closer to one Na ( $2.44_4$  Å) than to two others ( $2.54_1$  Å),

Table 2. Atomic parameters

Atom	$U_{\text{iso}}$	Axes $a, b, c^*$			Fractional coordinates			s.d.		
		$U_{11}$ $U_{23}$	$U_{22}$ $U_{31}$	$U_{33}$ $U_{12}$	$x$	$y$	$z$	$\sigma_x$	$\sigma_y$	$\sigma_z$
$\beta$	Na	0.040			0	0	0	0	0	0
	N(1)	0.043			0	0	0.5771	0	0	0.0008
	N(2)	0.030			0	0	0.5	0	0	0
$\alpha$	Na	0.0117	0.0096	0.0140	0	0	0	0	0	0
	N(1)	0.0236	0.0180	0.0222	0.1016	0.5	0.7258	0.0021	0	0.0024
	N(2)	0.0147	0.0092	0.0204	0	0.5	0.5	0	0	0
Li	0.0529	0.0413	0.0851	0	0	0	0	0	0	
N(1)	0.0268	0.0289	0.0253	0.1048	0.5	0.7397	0.0018	0	0.0020	
N(2)	0.0146	0.0221	0.0246	0	0.5	0.5	0	0	0	
Sr	0.008	0.005	0.006	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	0	0	0	
N(1)	0.005	0.005	0.005	0.00220	0.05937	0.7715	0.0020	0.0017	0.0039	
N(2)	0.008	0.022	0.008	-0.00389	$\frac{1}{8}$	$\frac{5}{8}$	0.0028	0	0	
N(3)	0.005	0.005	0.005	0.00220	0.19063	0.4785	0.0020	0.0017	0.0039	

Table 3. Structure factors for  $\beta$ -NaN<sub>3</sub>, [100]

$F(0,0,0)=96$ . Hexagonal unit cell.

$h$	$k$	$l$	$F_o$	$F_c$	$h$	$k$	$l$	$F_o$	$F_c$
0	0	3	8.34	4.94	2	0	5	15.08	15.91
0	0	6	11.83	12.02	2	0	2	26.60	31.84
0	0	9	19.12	14.34	2	0	$\bar{1}$	5.31	-4.70
0	0	12	28.63	27.14	2	0	$\bar{4}$	18.26	17.74
0	0	15	1.83	-0.43	2	0	$\bar{7}$	16.64	16.01
0	0	18	4.14	5.17	2	0	$\bar{10}$	15.42	15.18
0	0	21	2.84	2.77	2	0	$\bar{13}$	1.93	-3.04
0	0	24	5.10	5.21	2	0	$\bar{16}$	9.50	8.41
1	0	19	6.97	4.45	2	0	$\bar{19}$	5.50	3.19
1	0	16	12.81	10.78	3	0	12	11.39	11.35
1	0	13	1.74	-3.38	3	0	9	2.44	4.03
1	0	10	23.36	21.70	3	0	6	5.94	5.51
1	0	7	25.53	25.65	3	0	3	1.81	2.79
1	0	4	24.03	27.11	3	0	0	18.68	20.51
1	0	1	17.58	-16.57	3	0	$\bar{3}$	1.81	2.79
1	0	$\bar{5}$	25.90	26.11	3	0	$\bar{6}$	7.75	5.51
1	0	$\bar{8}$	16.58	13.93	3	0	$\bar{9}$	3.45	4.03
1	0	$\bar{11}$	1.58	0.33	3	0	$\bar{12}$	12.25	11.35
1	0	$\bar{14}$	22.73	18.88	3	0	$\bar{15}$	3.99	-1.42
1	0	$\bar{17}$	6.30	3.35	4	0	4	3.82	5.62
2	0	14	14.81	14.29	4	0	1	2.18	-2.46
2	0	11	1.79	-0.15	4	0	$\bar{2}$	8.02	9.36
2	0	8	11.55	9.98					

Table 4. Structure factors of  $\alpha$ -NaN<sub>3</sub> $F(0,0,0)=64$ . Bracketed planes were unresolved.

$h$	$k$	$l$	$F_o$	$F_c$	$h$	$k$	$l$	$F_o$	$F_c$
0	0	1	5.51	3.55	-1	1	4	4.39	3.40
1	1	0	7.81	-8.48	0	2	3	9.09	8.81
-2	0	1	10.81	-11.78	2	2	2	9.65	9.35
2	0	0	35.56	31.89	1	3	0	0.51	0.97
-1	1	1	42.86	40.04	-3	1	4	8.59	11.19
0	0	2	8.08	7.88	-4	2	1	3.47	3.66
1	-1	1	16.39	16.42	-1	3	1	17.45	16.65
-2	0	2	20.13	23.74	-5	1	1	10.96	10.11
2	0	1	20.57	21.90	-5	1	2	0.02	0.48
-1	1	2	16.96	16.24	-4	2	2	17.15	17.21
0	2	0	31.67	32.74	-4	0	4	4.86	4.71
1	1	2	18.46	18.94	4	2	0	5.56	6.10
-3	1	1	35.91	30.17	1	3	1	7.71	8.45
3	1	0	11.08	11.35	4	0	2	13.09	14.52
0	2	1	5.12	5.50	5	1	0	10.01	11.79
-2	0	3	17.45	18.19	-1	3	2	8.41	9.34
0	0	3	11.00	11.95	1	1	4	0.20	-0.29
2	0	2	11.51	12.36	-5	1	3	11.84	13.04
-3	1	2	0.53	0.34	-4	2	3	5.90	6.04
-1	1	3	7.86	8.20	-2	2	4	7.78	8.07
-2	2	1	3.58	-3.12	3	1	3	14.53	15.50
2	2	0	21.20	20.38	-2	0	5	0.18	0.11
-4	0	1	2.63	2.93	4	2	1	8.30	8.99
3	1	1	6.83	7.49	2	2	3	1.21	1.14
-4	0	2	24.46	25.57	1	3	2	11.60	10.43
0	2	2	6.95	7.56	-3	3	1	15.57	14.91
4	0	0	7.98	8.63	2	0	4	14.94	13.93
-2	2	2	17.14	16.34	3	3	0	7.48	6.87
-3	1	3	7.67	9.61	-6	0	2	12.58	12.29
2	2	1	10.84	14.38	5	1	1	9.99	9.53
1	1	3	15.56	16.66	0	2	4	14.65	14.13
-4	0	3	5.83	6.76	-6	0	1	9.53	8.58
-2	0	4	10.04	11.47	-3	3	2	0.99	1.44
4	0	1	11.56	10.90	-1	1	5	14.82	14.45
2	0	3	0.53	0.33	0	0	5	0.71	0.48
3	1	2	4.25	5.42	-1	3	3	5.25	5.38
0	0	4	19.24	19.08	-3	1	5	12.07	11.42
-2	2	3	12.27	12.42	-5	1	4	8.04	7.74
					-6	0	3	0.53	-0.44

but the weighted mean distance (2.50<sub>9</sub> Å) is still close to the corresponding value of 2.50<sub>7</sub> Å in the β-NaN<sub>3</sub> structure.

The structure of LiN<sub>3</sub> is closely analogous to that of α-NaN<sub>3</sub>. The layers are again nearly in a close packed arrangement of spheres with adjacent N-N distances of 3.31<sub>9</sub> Å (=b) and 3.26<sub>7</sub> Å, both shorter than in the sodium salt. The ion is tilted at an angle of 11.5° to c\*.

### Anion-anion contacts

It is only when we examine the N-N distances between adjacent azide ions that a consistent plan emerges. If we take the N-N-N line as polar axis, the various crystallographically non-equivalent end nitrogen distances of Table 6 can be presented on a polar diagram as in Fig. 6. The points lie on an ellipse with semi-axes 1.5 and 1.67 Å in the case of LiN<sub>3</sub> and Sr(N<sub>3</sub>)<sub>2</sub>, or on a larger ellipse with similar axis difference for the two forms of NaN<sub>3</sub>. Spherical cations of radii 0.65, 1.10 and 0.9 Å touch the smaller ellipsoid very satisfactorily. It is natural to conclude that anion-anion contact distances in the ionic azides are such as would result if the end nitrogen atoms were earth-shaped, but that closeness of contact is also affected, as it is in the tetragonal alkali azides, partly by cation size.

Possible explanations of the effect just described could be (i) that the bonding within the anion distorts

Table 6. *End-nitrogen contacts in azides*

(1) = dependent only on lattice parameters.

	N(1) radius	e.s.d.	Latitude
LiN <sub>3</sub>	1.550	0.009	56.9°
	1.576	0.012	40.1
	1.633	(1)	9.9
	1.659	(1)	0
α-NaN <sub>3</sub>	1.722	0.013	57.4°
	1.764	0.016	39.3
	1.802	(1)	10.7
	1.829	(1)	0
β-NaN <sub>3</sub>	1.720	0.009	52.2
	1.823	(1)	0
CuN <sub>3</sub> (Wilsdorf, 1948)	1.355 (mean)		1.6, 18.6°
Sr(N <sub>3</sub> ) <sub>2</sub>	1.548	0.022	75.2°
	1.623	(1)	± 11.6
	1.630	0.024	13.9
	1.635	0.022	-14.0
AgN <sub>3</sub> (West, 1936; Marr & Stanford, 1962)	1.56 (mean)		-20.9, 32.5°
	1.58		78.7, -22.9
	1.67		-16.3
	1.75		-23.8

Table 5. *Structure factors for LiN<sub>3</sub>*

F(0,0,0)=48. Bracketed planes were unresolved.

h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>
0	0	1	8.98	-9.32	0	0	4	12.48	9.60
1	1	0	21.23	-20.55	3	1	2	2.83	-3.87
2	0	1	28.50	-23.97	-1	1	4	4.95	-6.21
2	0	0	16.03	16.30	-2	2	3	3.66	2.78
-1	1	1	22.84	23.26	0	2	3	1.01	-1.28
0	0	2	6.02	-5.64	2	2	2	1.01	1.95
1	1	1	1.31	1.72	-3	1	4	1.01	0.17
-2	0	2	6.73	8.09	1	3	0	5.60	-5.69
2	0	1	8.68	8.81	4	2	1	1.01	0.38
-1	1	2	4.46	4.47	-1	3	1	9.85	7.16
1	1	2	4.41	5.61	-5	1	1	3.27	2.94
0	2	0	17.69	18.06	-4	0	4	1.01	-0.74
-3	1	1	18.48	16.60	-5	1	2	8.35	-7.37
-2	0	3	6.20	5.44	-4	2	2	9.64	8.30
0	0	3	1.39	-1.84	4	2	0	1.01	-0.36
3	1	0	1.01	0.42	1	3	1	1.01	1.13
0	2	1	3.60	-3.70	4	0	2	7.86	7.15
2	0	2	2.81	2.87	1	1	4	6.87	-6.51
-3	1	2	6.81	-8.59	5	1	0	1.01	2.28
-1	1	3	1.01	-0.61	-1	3	2	1.01	1.14
-2	2	1	10.54	-10.74	-5	1	3	5.77	5.22
2	2	0	7.24	8.21	-2	0	5	7.37	-6.83
-4	0	1	6.02	-6.83	3	1	3	8.47	7.10
3	1	1	1.01	-1.63	-2	2	4	3.40	3.05
0	2	2	2.13	-1.80	2	0	4	4.18	4.74
-4	0	2	12.33	12.90	-4	2	3	0.83	-1.32
4	0	0	1.01	-0.77	2	2	3	5.19	-5.60
-2	2	2	4.40	4.64	4	2	1	1.01	0.38
-3	1	3	0.75	-0.25	0	2	4	5.91	6.62
2	2	1	3.99	4.07	1	3	2	1.07	1.73
1	1	3	8.88	7.74	-3	3	1	6.64	6.64
-2	0	4	3.83	4.42	0	0	5	3.24	-3.39
-4	0	3	1.01	-1.71	-1	1	5	6.91	5.89
2	0	3	8.06	-8.03	5	1	1	4.00	3.29
4	0	1	1.01	0.81					

the electron density in such a way as to cause longitudinal compression of end atoms, (ii) that the libration of the ion is responsible. The first explanation does not appear to be supported by the molecular orbital calculations of Clementi (1961). The second may be acceptable, if we make the reasonable assumption that the motion is highly anharmonic, in accordance with known data on van der Waals contact. The semi-axis difference (0.17 Å) is of the same order as the amplitude of 'measured' libration but should on this theory be dependent on the temperature, the Debye temperature, and the site symmetry. If we accept that a geoid of contact is consistently valid in the ionic azides, the non-regular antiprisms of N atoms round Sr and Na are at once explained, without recourse to any other theory of bond inequality.

We also note the much smaller equatorial radius (1.35 Å) of end nitrogen in Wilsdorf's (1948) structure of  $\text{CuN}_3$ . If accurate, this may be peculiar to covalent bonding which, because of its strength and directionality is presumably able to suppress much of the librational mode.

#### Azide ion bond length

It does not now seem that there is any significant difference between the different N-N bond lengths for various ionic azides. Table 7 shows the more recent results, together with the libration correction as proposed by Cruickshank (1961).

Table 7. Lengths of N-N bonds in azides

	Bond length	Suggested libration addendum	Corrected bond length
$\text{Co}(\text{NH}_3)_5\text{N}_3(\text{N}_3)_2$	$1.165 \pm 0.005$	0.012*	1.177
$\beta\text{-NaN}_3$	$1.173 \pm 0.012$	0.005	1.178
$\alpha\text{-NaN}_3$	$1.167 \pm 0.013$	0.007	1.174
$\text{LiN}_3$	$1.162 \pm 0.014$	0.007	1.169
$\text{Sr}(\text{N}_3)_2$	$1.163 \pm 0.024$	0.007†	1.170
		Weighted mean	1.176

\* Our estimate based on the published thermal motion of atoms N(8) and N(9), since that of N(10) appears to be anomalous.

† Estimate based on the previous entries, as our refinement fails to indicate libration for this structure, the  $U_{ij}$  values being anomalous.

The mean corrected bond length nearly lies on an empirical curve of bond lengths drawn through those for hydrazine, azomethane and nitrogen. The earlier agreement of the crystallographic value 1.15 Å (Fréval, 1936) with Bernstein's (1947) relation occurred because the latter is systematically low, when compared as in Fig. 7 with the more recent N-N bond lengths of various orders.

#### The nature of the phase change of $\text{NaN}_3$

Following up the discovery of the phase transition of  $\text{NaN}_3$  Bradley, Munro & Grace (1964) compressed that substance at room temperature and were able to demonstrate that high pressure also caused transition.

The distortion described above as mainly one of shear also includes a general contraction of the lattice along the monoclinic  $a$  axis and other small changes such that the unit-cell volume per molecule decreases by nearly 2% between room temperature and  $-100^\circ\text{C}$ . It is therefore natural that pressure favours the transition  $\beta \rightarrow \alpha$ . Roughly one can equate the effect of a drop of  $1^\circ\text{C}$  in temperature to a rise of 35 bars in pressure. The behaviour of  $\text{NaN}_3$  strikingly resembles that of  $\text{KSCN}$  as described by Yamada & Watanabe (1963). If we reject the idea of an asymmetric  $\text{N}_3^-$  ion, it is likely that the thermodynamic functions are dependent in a significant way on the monoclinic  $\beta$  angle. A contributory physical cause is probably the proximity of end (-) N atoms to middle (+) atoms when the ion is in its tilted position: in fact their separation changes by 0.25 Å between room temperature and  $-100^\circ\text{C}$ . It would be reasonable to regard this change as an increase of 2 in coordination number of the end nitrogen atom, the arrangement becoming approximately square

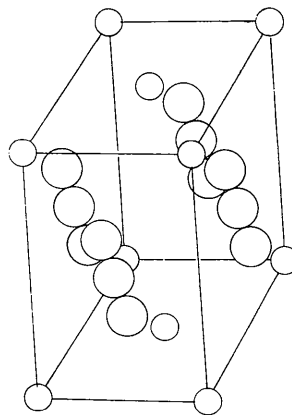


Fig. 5. Unit cell of  $\alpha\text{-NaN}_3$  or  $\text{LiN}_3$ , monoclinic,  $Z=2$ .  $\alpha\text{-NaN}_3$  has  $a=6.21$ ,  $b=3.66$ ,  $c=5.32$  Å,  $\beta=108.4^\circ$ .  $\text{LiN}_3$  has  $a=5.63$ ,  $b=3.32$ ,  $c=4.98$  Å,  $\beta=107.4^\circ$ . Small circles Na or Li, large circles N.

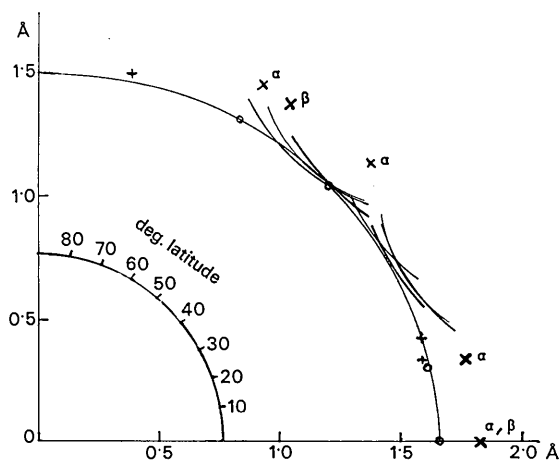


Fig. 6. Polar diagram of N-N contacts in  $\circ \text{LiN}_3$   $\times \text{NaN}_3$   $+ \text{Sr}(\text{N}_3)_2$ . Arcs show contact with cations ( $\text{Li}=0.65$ ,  $\text{Na}=0.90$ ,  $\text{Sr}=1.10$  Å radius).

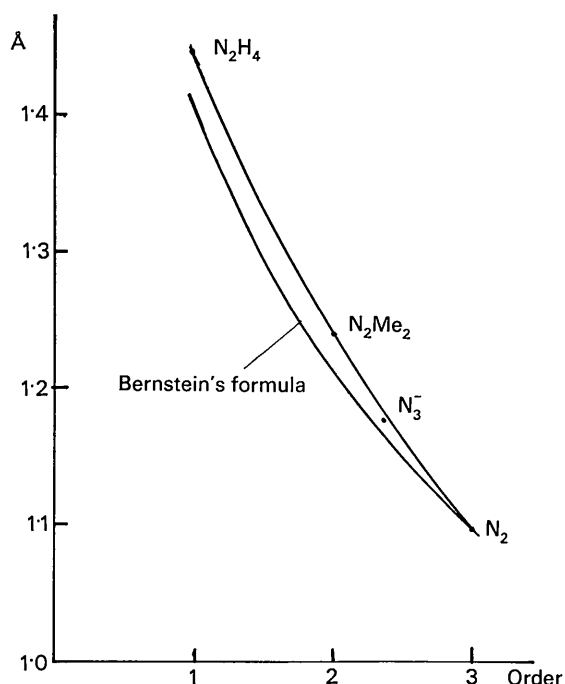


Fig. 7. Order and length of N-N bonds.

pyramidal (octahedral if we include nitrogen of the same ion); similarly in alkali halides, the higher of two coordination numbers is promoted by low temperatures or high pressure. The equivalence ratio of pressure and temperature is in reasonable accord with a thermodynamic estimate based on the postulate of an order-disorder mechanism.

*Acta Cryst.* (1968). B24, 269

### The Crystal Structure of $K_3Cu(CN)_4$ \*

By R. B. ROOF, JR., ALLEN C. LARSON AND DON T. CROMER

*University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, U.S.A.*

(Received 7 June 1967)

The crystal structure of  $K_3Cu(CN)_4$  and the absolute configuration for the particular crystal used have been determined. The space group is  $R3c$ , rather than the previously reported space group of  $R32$ . The rhombohedral cell with two formula units has dimensions  $a=8.039$  Å and  $\alpha=73^\circ 54'$ ; the hexagonal cell has  $a=9.665$  and  $c=17.361$  Å. Anomalous dispersion for copper and potassium was included in the calculations, and anisotropic least-squares refinement leads to a conventional  $R$  index of 0.0249 for the correct absolute orientation and 0.0431 for the incorrect, inverse structure. There are discrete  $Cu(CN)_4^{3-}$  tetrahedra with three Cu-C distances of  $1.992 \pm 0.007$  Å and one Cu-C distance of  $2.014 \pm 0.011$  Å. These distances are about 0.1 Å longer than the Cu-C distances in trigonally bonded copper(I).

#### Introduction

As a continuation of our studies of complexes of  $CuCN$  (*e.g.* see Cromer & Larson, 1962; Cromer, Larson &

We are indebted to Mr G. W. C. Taylor for preparing samples of  $LiN_3$ , and Dr M. R. Truter and the staff of the Leeds Computing Department for generous help with computation.

Acknowledgment is also made to the Ministry of Aviation, who supported this work.

#### References

- BASSIÈRE, M. (1943). *Mem. des. serv. chim. de l'Etat*, **30**, 33.  
 BERNSTEIN, H. J. (1947). *J. Chem. Phys.* **15**, 284.  
 BONNEMAY, A. & DAUDEL, R. (1950). *C.r. Acad. Sci. Paris*, **230**, 2300.  
 BRADLEY, R. S., GRACE, J. D. & MUNRO, D. C. (1964). *Z. Kristallogr.* **120**, 349.  
 CLEMENTI, E. (1961). *J. Chem. Phys.* **34**, 1468.  
 CRUICKSHANK, D. W. J. (1961). *Acta Cryst.* **14**, 896.  
 FRÉVEL, L. K. (1936). *Z. Kristallogr.* **94**, 197.  
 HENDRICKS, S. B. & PAULING, L. (1925). *J. Amer. Chem. Soc.* **47**, 2904.  
*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.  
 LLEWELLYN, F. S. & WHITMORE, F. E. (1947). *J. Chem. Soc.* p. 881.  
 MARR, H. E. & STANFORD, R. H. (1962). *Acta Cryst.* **15**, 1313.  
 MILLER, B. S. & KING, G. J. (1963). *J. Chem. Phys.* **39**, 2779.  
 PALENIK, G. J. (1964). *Acta Cryst.* **17**, 360.  
 PARSONS, R. B. & YOFFÉ, A. D. (1966). *Acta Cryst.* **20**, 36.  
 PETZ, J. (1957). Univ. of Arkansas (unpublished).  
 PRINGLE, G. E. & NOAKES, D. E. (1963). *Acta Cryst.* **16**, A192.  
 WEST, C. D. (1936). *Z. Kristallogr.* **95**, 421.  
 WILSDORF, H. (1948). *Acta Cryst.* **1**, 115.  
 YAMADA, Y. & WATANABE, T. (1963). *Bull. Chem. Soc. Japan*, **36**, 1032.

\* Work performed under the auspices of the U.S. Atomic Energy Commission.

Roof, 1966) we have determined the structure of  $K_3Cu(CN)_4$ . This compound was first studied by Cox, Wardlaw & Webster (1936) who reported a unit cell and space group but did no further work other than to deduce that the  $Cu(CN)_4^{3-}$  ion must be tetrahedral. They also noted a strong pyroelectric effect. Staritzky & Ellinger (1956) reported morphological, optical and