

the gross presence of these bonds seems certain. A limit of $20 \pm 10^\circ$ for bending of the cyclopropane bonds seems reasonable. It might reasonably be argued that bending will not be equal in all bonds. The simplest case of equal bending is all that can be considered with the present data. Bending of less than 20° in one or two bonds would require greater bending in the remainder, to accord with the difference map.

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Thermal Expansion of the Alkali Metal Azides

BY R. B. PARSONS AND A. D. YOFFE

Physics and Chemistry of Solids, Cavendish Laboratory, Cambridge, England

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The lattice parameters of potassium and sodium azide have been determined as a function of temperature by X-ray diffraction. For potassium azide (tetragonal) the lattice constants at room temperature are significantly higher than those obtained by Hendricks & Pauling. The coefficients of thermal expansion are sensibly constant over the temperature range 20°C to 340°C . The expansion coefficient along the c axis is more than twice as large as the coefficient along the a axis. A sample of potassium azide (KN_3) heated at 360°C gave a diffraction pattern consistent with a cubic structure (lattice parameter 9.6 \AA) which is attributed to potassium nitride (K_3N).

The room temperature diffraction pattern of sodium azide is consistent with a monoclinic C -face-centred lattice, which can however be referred to a pseudo-rhombohedral unit cell close to that described by Hendricks & Pauling. Above room temperature (about 22°C) the structure is rhombohedral. In the temperature range – room temperature to 100°C – the coefficient of thermal expansion in the direction in which anions and cations alternate is 2.3 times the expansion coefficient in the direction in which they do not. This ratio is very close to that found for potassium azide.

POTASSIUM AZIDE

Introduction

Detailed information is now available on a number of the physical properties of the inorganic azides (Gray, 1963). It seems that the alkali metal azides, and to some extent the alkaline earth azides, are typical ionic solids, the atomic structure and the optical and electrical properties of both perfect and irradiated crystals being closely analogous to those of the alkali halides. The other azides are much less stable and show evidence of a large degree of covalent bonding.

The alkali metal azides thus provide a convenient example of an ionic structure in which one of the ions

is aspherical. Since the study of the lattice dynamics of simple ionic structures containing spherical ions is in a fairly advanced state, it would be interesting to see what differences the presence of a non-spherical ion would make. Apart from measurements of infrared absorption (Bryant, 1963, 1964) no detailed data on this aspect of the azides appear to have been published.

The present work was undertaken to try to throw light on this point through measurements of thermal expansion, as well as to clarify certain points concerning polymorphic transitions, and the effect of irradiation on the lattice constants. The results could also be of interest in connection with decomposition studies of the azides.

The structure of potassium azide

The crystal structure of potassium azide as determined by Hendricks & Pauling (1925) is shown in Fig. 1. The symmetry is tetragonal, the space group being $I4/m\ 2/c\ 2/m$. It will be seen that the anions and cations are arranged in alternate layers perpendicular to the tetrad (c) axis, and that the long axes of the azide ions are parallel to these layers.

It follows from the space group that the reflexions for which $h+k+l$ is odd are all absent, and further from the symmetry of the potassium atoms that they do not contribute to any reflexions for which l is odd. Since they have a much higher scattering factor than nitrogen atoms, it follows that these reflexions are relatively very weak.

The lattice parameters of potassium azide were given by Hendricks & Pauling as $a=6.094$, $c=7.056$ Å. Their measurements were made on a single crystal with $\text{Mo K}\alpha$ radiation, but the apparatus is not described in detail, and there is no estimate of the accuracy of their result.

Experimental

X-ray powder diffraction patterns were obtained with a Unicam 19 cm powder diffraction camera, and a 5–70 high-temperature powder camera. Copper and molybdenum radiations were available. The patterns were recorded on Ilford Industrial G X-ray film and measured with a travelling microscope. The indices of the lines were determined by comparison between the observed values of $\sin^2 \theta$ and calculated lists of values with the use of the observed structure of Hendricks & Pauling.

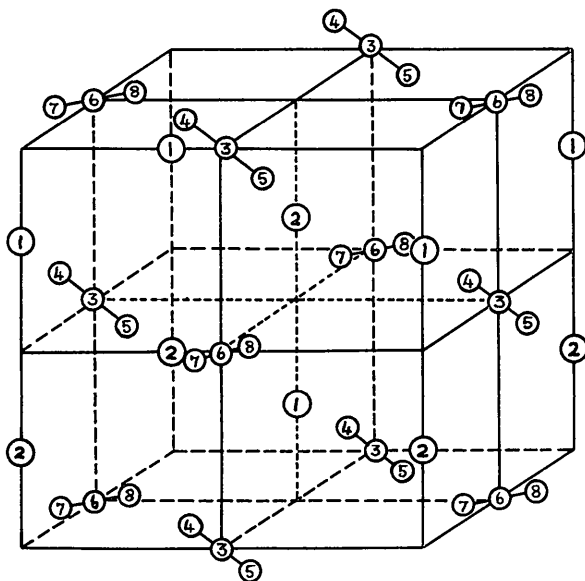


Fig. 1. The structure of potassium azide. K atoms at 1 and 2. N(1) atoms at 3 and 6. N(2) and N(3) atoms at 4, 5, 7 and 8. $[\text{N}_3]$ unit, N(2)N(1)N(3).

The temperature of the high-temperature camera was controlled by an Ether 'Transitrol' Type 992 Stepless Controller. The stability was checked by photographing the needle of the thermocouple galvanometer by time-lapse cinematography. The stability was found to be $\pm 1^\circ\text{C}$ over the range 100° to 350°C indicated temperature. The relation between the sample temperature and the temperature indicated by a fixed thermocouple inside the camera was found, as recommended by Brand & Goldschmidt (1956), by observing the lattice parameter of copper and calculating the corresponding temperatures by the formula for the thermal expansion of copper given by Esser & Eusterbrook (1941).

The potassium azide was used directly 'off the shelf' without any treatment except passing through a wire sieve. Measurements were made on samples from various sources, but the majority were on material supplied by Eastman Organic Chemicals Limited.

The diffraction patterns obtained with the ordinary diffraction camera showed a number of lines in the range $45^\circ > \theta > 70^\circ$ which could be measured and indexed. From these values of the lattice constants could be obtained by the method of Cohen (1935). That is, for each reflexion (hkl) an equation of condition can be written:

$$\frac{4}{\lambda^2} \sin^2 \theta = \frac{1}{a^2} (h^2 + k^2) + \frac{1}{c^2} l^2 + Df(\theta) \quad (1)$$

where $Df(\theta)$ is the so-called drift function, which allows for the various systematic errors due to absorption, sample eccentricity *etc.* which affect the measured values of θ . The form of the drifts function in the range $\theta > 45^\circ$ was taken to be (Nelson & Riley, 1945):

$$f(\theta) = \sin^2 2\theta (1 + \sin \theta/\theta).$$

The values of $1/a^2$, $1/c^2$ and D were then calculated for each film by the method of least squares.

The X-ray optics of the high temperature camera were relatively unfavourable and no lines could be measured for $\theta > 30^\circ$. Since the effect of the systematic errors is uncertain and irregular in this range (Nelson & Riley, 1945), no drift function was put into the equations of condition; *i.e.* D was assumed to be zero in equation (1). The accuracy obtainable from measurements of low angle lines is limited both by the failure to correct for the systematic errors, and also the width and diffuseness of the diffraction lines on the film.

Because of the large number of films obtained with the high-temperature camera, the least-squares calculations for low angle lines were performed on the EDSAC computer in Cambridge; the other calculations were all performed with a Diehl electric desk calculating machine.

There was no detectable difference in the behaviour of samples taken from different sources.

Results of measurements at room temperature

The values obtained using high-angle line results, allowing for systematic errors as described above, were:

$$a = 6.11404 \pm 0.00012 \text{ \AA}$$

$$c = 7.09910 \pm 0.00014$$

The low-angle line results are shown in Fig. 2. It will be seen that apart from one or two aberrant results attributable to bad films they lie between the results stated above, and those of Hendricks & Pauling. The mean values are:

$$\text{For Cu } K\alpha \text{ radiation: } a = 6.1103 \pm 0.0018 \text{ \AA}$$

$$c = 7.0803 \pm 0.0028$$

$$\text{For Mo } K\alpha \text{ radiation: } a = 6.1159 \pm 0.0020$$

$$c = 7.0826 \pm 0.0016$$

The differences between the mean values for the different radiations are not significant; neither is the difference between the mean value of a and that obtained by the high-angle line measurement. The difference between the values of c is, however, more than five times the standard deviation.

The values for the standard deviation of the parameters obtained in the course of the individual least-squares calculations are rather smaller than the observed scatter of the values about the mean would suggest (*i.e.* about 0.03% calculated against 0.1% observed). However, the values obtained by repeated measurements on the same sample usually agreed rather closely, much better than even the calculated standard deviation would imply.

An explanation of the discrepancy between the low- and high-angle line results is not easy to give. It is difficult to see why the systematic errors should affect the value of c much more than the value of a . A real variation in the value of the c parameter cannot be entirely excluded. It has been stated (Tompkins & Young, 1957) that azide crystals grown from aqueous solution contain a high concentration of lattice defects which anneal out on heating, and might be expected to produce an irreversible change in the lattice parameters. The high-angle line measurements were performed on an

unheated sample, whereas many of the low-angle line measurements were made on samples which had been heated. However the accuracy of the individual lattice parameter measurements is too low to enable anything conclusive to be said.

The thermal expansion coefficient

The values obtained for the lattice parameters as a function of temperature are shown in Fig. 3. The results can be fitted by straight lines, within the accuracy of the measurements, showing that the coefficients of expansion are constant. The values obtained are:

$$\alpha_{\parallel} = 1/c_0 (dc/dT) = 9.2 \times 10^{-5}$$

$$\alpha_{\perp} = 1/a_0 (da/dT) = 4.5 \times 10^{-5}$$

An approximate theory for the thermal expansion of a uniaxial crystal has been given by Riley (1945). It is roughly equivalent to the Grüneisen theory for an isotropic solid. It indicates that at temperatures above the Debye temperatures of the crystal the expansion coefficients should become constant. However, since the expressions for the two expansion coefficients contain four elastic constants and two Grüneisen γ parameters, none of which are known for potassium azide, a comparison between theory and experiment is hardly possible. However, it may be remarked that the coefficient of expansion in the direction in which ions of opposite charge alternate is 2.1 times the coefficient in the perpendicular direction, in which they do not. A similar result has been found for sodium azide (see below).

The measurements are not accurate enough to detect any contribution to the thermal expansion from the generation of vacancies at high temperatures.

The effect of irradiation on the lattice constants

According to Krause (1961) the lattice constants of several azides change steadily on exposure to X-rays.

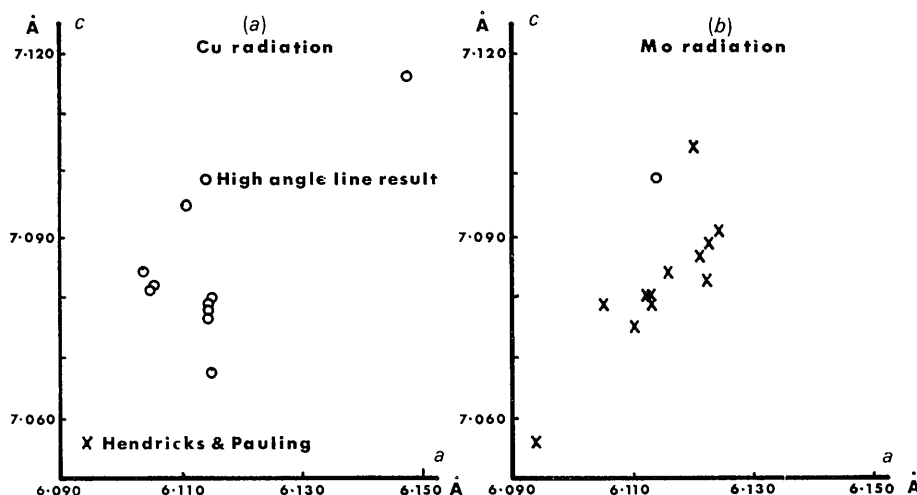
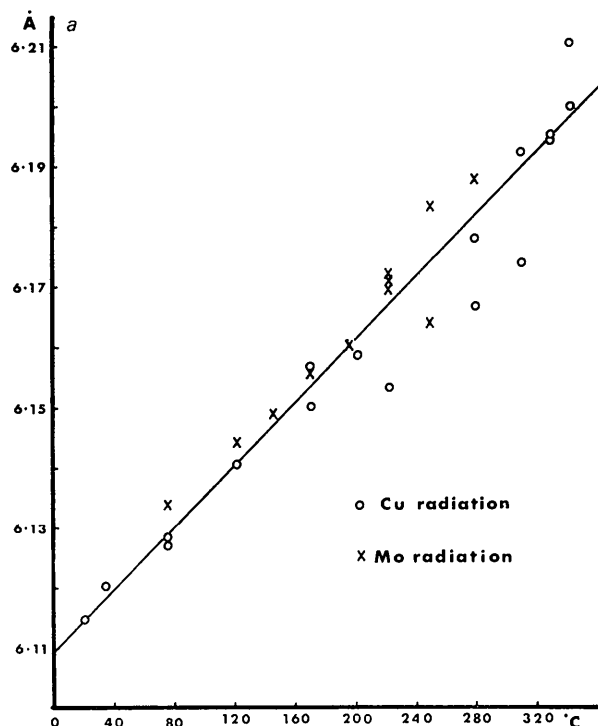
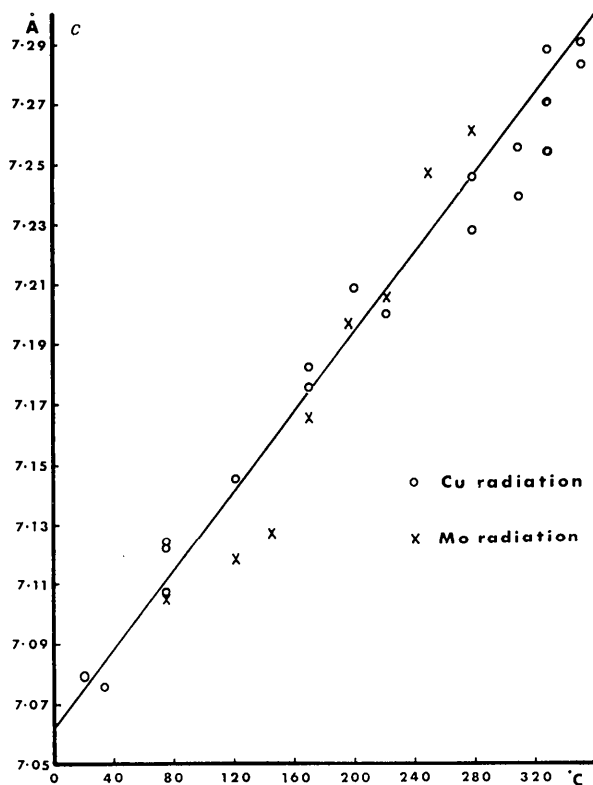


Fig. 2. Values obtained for the lattice constants of potassium azide at room temperature.



(a)



(b)

Fig. 3. (a) The lattice parameter a as a function of temperature. (b) The lattice parameter c as a function of temperature.

In potassium azide evidence was obtained of a very slight expansion along the c axis at room temperature. Since the mechanism is not known, it is not possible to say whether this effect should be larger or smaller at higher temperatures. Except at the highest temperatures, no consistent variation of the lattice constants with irradiation could be detected. On one sample, at 340°C, three successive exposures did show increases in the c parameter, but not the a parameter. The experiment was not successfully repeated because the samples were blown out of the tube. In the case of the alkali halides, irradiation with X-rays can cause expansion of the lattice at room temperature (Wiegand, 1962).

It should be observed that in Fig. 3 there is no divergence between successive observations made on the same sample and observations made on fresh samples at each temperature.

The diffraction pattern of potassium nitride

At the end of one series of measurements, when the sample was heated to 360°C it was found that the lines of the potassium azide pattern all disappeared and were replaced by a new pattern, which persisted when the sample was allowed to cool to room temperature. Several lines of the pattern were measurable, and have been indexed, assuming cubic symmetry and $\lambda^2/4a^2 = 0.0065$. Since Cu $K\alpha$ radiation was used this means that $a = 9.6$ Å. The details of the interpretation are shown in Table 1.

Table 1. Interpretation of the diffraction pattern attributed to potassium azide

hkl	$h^2 + k^2 + l^2$	$\sin^2 \theta_{\text{calc}}$	$\sin^2 \theta_{\text{obs}}$	Difference $\times 10^4$
300, 221	9	0.0585	0.0586	-1
222	12	0.0780	0.0780	0
320	13	0.0845	0.0840	5
330, 411	18	0.1170	0.1183	-13
430, 500	25	0.1625	0.1626	-1
600, 442	36	0.2340	0.2337	3
444	48	0.3120	0.3114	6

The mean value of the modulus of the difference is 4.2 whilst, if the fit were no better than random, the expected value would be $65/4$, *i.e.* 16.3.

When the camera was opened the sample tube was found to be partially filled with a white solid which appeared to have melted. Attempts to repeat the observations failed because the sample was blown out of the tube. It is believed that this pattern is due to potassium nitride, K_3N . No known substance which could conceivably have been present at 360°C can account for it. The formation of potassium nitride on gently heating potassium azide has been reported (Suhramann & Clusius, 1926; Wattenberg, 1930) but not by the latest investigators (Jacobs & Tompkins, 1952a). It is stated (Wattenberg, 1930) that the yield is enhanced by heating an intimate mixture of potassium azide and metallic potassium. In the present case, as a result of

the prolonged irradiation, the sample must have contained a good deal of colloidal potassium (Jacobs & Tompkins, 1952b).

It is of interest in connection with this work that Jacobs & Kureishy have evidence for the formation of sodium nitride during decomposition of sodium azide. This is due to a back reaction between sodium and nitrogen.

SODIUM AZIDE

Introduction

The structure of sodium azide as given by Hendricks & Pauling is shown in Fig. 4. The structure has rhombohedral symmetry, the space group being $R\bar{3}m$. It may therefore be referred to a primitive rhombohedral unit cell, or to a triply primitive hexagonal unit cell. The latter has the advantage of being more directly related to the underlying atomic structure, since the c axis is aligned along the long axes of the azide ions, and the a axis is perpendicular to them.

According to Hendricks & Pauling, the parameters of the rhombohedral unit cell are $a=5.48$, $\alpha=38^\circ 43'$, and those of the hexagonal unit cell are: $a=3.638$, $c=15.201$ Å.

This structure has until recently been generally accepted for sodium azide. For example, Bryant (1964) has interpreted the results of infrared absorption measurements at temperatures down to 77°K on the basis of trigonal symmetry, apparently quite successfully. However it has been shown recently by Miller & King (1963) on the basis of observations of nuclear magnetic resonance, electron spin resonance, optical interference figures and the profiles of a few X-ray diffraction lines that this structure holds only above 22°C. At lower temperatures the crystal must have a structure of lower symmetry. X-ray diffraction studies on sodium azide at low temperatures have also been reported by Pringle & Noakes (1963), from which they conclude there is a transition (probably a second order phase transition) which occurs at about 13°C.

The apparatus and experimental methods are identical with those used for potassium azide.

The interpretation of the room temperature powder pattern of sodium azide

In agreement with the observations of Miller & King it was found that the powder pattern obtained at room temperature was not compatible with trigonal symmetry, but that a trigonal pattern was obtained at higher temperatures. On cooling to room temperature, the room temperature pattern was immediately regained.

In Fig. 5 are shown the observed values of $\sin^2 \theta$, together with those calculated assuming a rhombohedral unit cell with the lattice parameters given by Hendricks & Pauling. It will be seen that the two patterns

are closely similar, except that many of the single lines in the rhombohedral pattern are replaced by pairs of lines in the low temperature pattern.

It is possible to associate nine of the rhombohedral lines unambiguously with thirteen of the lines in the low temperature pattern. By retaining the same indices, but referring the lines to a pseudorhombic cell in which one of the axes had a slightly different length from the other two, and one of the three interaxial angles was slightly different, the observed line splittings could be explained.

The indices assigned to the lines which it proved possible to index are tabulated in Table 2. In every case the observed line intensities are compatible with the different multiplicities of the components of the doublet as given in this table.

The equation for the Bragg angle thus had the form:

$$4/\lambda^2 \sin^2 \theta = a^{*2}(h^2 + k^2) + c^{*2}l^2 + 2a^{*2} \cos \gamma^* hk + 2a^*c^* \cos \alpha^* l(h+k).$$

The best values of the cell parameters, obtained by the method of least squares, were as follows:

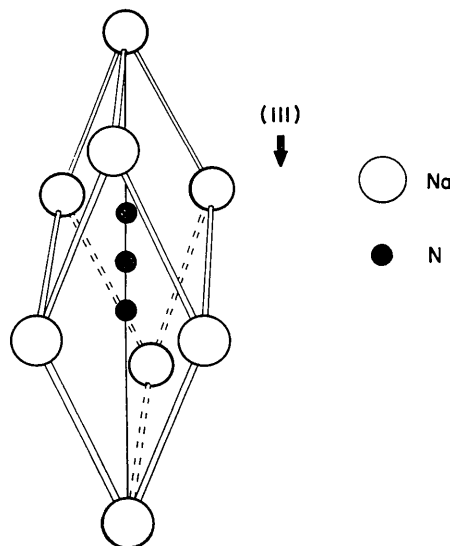


Fig. 4. Structure of sodium azide as given by Hendricks & Pauling.

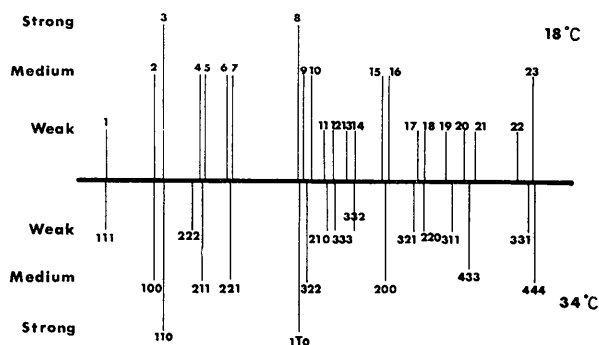


Fig. 5. Comparison between the observed values of $\sin^2 \theta$ for sodium azide at room temperature and those calculated assuming the structure of Hendricks & Pauling.

Direct lattice
 $a=b=5.526 \text{ \AA}$
 $c=5.454$
 $\beta=\alpha=38.760^\circ$
 $\gamma=38.655$

Reciprocal lattice
 $a^*=b^*=0.3221 \text{ \AA}^{-1}$
 $c^*=0.3256$
 $\beta^*=\alpha^*=115.904^\circ$
 $\gamma^*=116.168$

$A=5.454 \text{ \AA}$
 $B=3.657$
 $C=6.303$
 $\beta 111^\circ 20'$

Table 2. Assignment of indices to lines in the room temperature pattern of sodium azide

Line No.	$\sin^2 \theta$	hkl
1	0.0224	111
2	0.0620	100/010/001
3	0.0698	110/101/011
4	0.0992	121/211
5	0.1032	112
6	0.1208	221
7	0.1248	212/122
13	0.2184	332
14	0.2252	323/233
15	0.2465	200/020
16	0.2519	002
20	0.3126	433/343
21	0.3216	334
23	0.3683	444

The parameters given by Hendricks & Pauling are very close to the means of a and c , and α and γ , which makes it probable that they were observing the room temperature form of sodium azide but were not able to resolve the closely spaced pairs of lines.

By determining the reduced unit cell according to the procedure described by Azaroff & Buerger (1958) and comparing its Niggli matrix with the table of standard forms given by Buerger (1957), it was found that the lattice is a monoclinic C -face-centred lattice, and that the Bravais unit cell is related to the pseudorhombohedral one by the vector equations:

$$\begin{aligned} \mathbf{A} &= \mathbf{c} \\ \mathbf{B} &= \mathbf{a} - \mathbf{b} \\ \mathbf{C} &= \mathbf{a} + \mathbf{b} - 2\mathbf{c} \end{aligned}$$

The lattice parameters of the Bravais unit cell were found to be:

Because of the monoclinic symmetry, which made the powder pattern very complicated in the high angle region, the Cohen procedure could not be applied to determine the lattice parameters with high precision.

The thermal expansion of rhombohedral sodium azide

For reasons of time, observations on sodium azide were restricted to measurements on one sample in the range 30–100°C. The calculated values of the standard deviation were rather lower than those obtained for potassium azide and depended on which set of axes the reflexions were referred to. (0.02% for hexagonal axes, 0.005% for rhombohedral axes.) It is not known why this should be so, or whether the lattice constants are more accurately determined than are those of potassium azide.

The results obtained are shown in Fig. 6. The variation over the range appears to be linear, and the coefficients of expansion are found to be:

$$\alpha_{\parallel} = 1/c (dc/dT) = 5.01 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$$

$$\alpha_{\perp} = 1/a (da/dT) = 11.4 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$$

It will be seen that the coefficient of expansion in the direction perpendicular to the long axes of the azide ions is 2.3 times the coefficient parallel to them. The corresponding ratio in potassium azide is 2.1. (See the preceding section). As mentioned previously, the complexity of the theory precludes any detailed interpretation of these values.

The atomic structure of the low temperature form of sodium azide cannot be deduced without reflexion intensity measurements. However, the fact that the intensities are very similar to those of the rhombohedral form, and also the rapidity with which the transition occurs suggest that the atomic structure of the two forms must be closely similar. In fact Pringle &

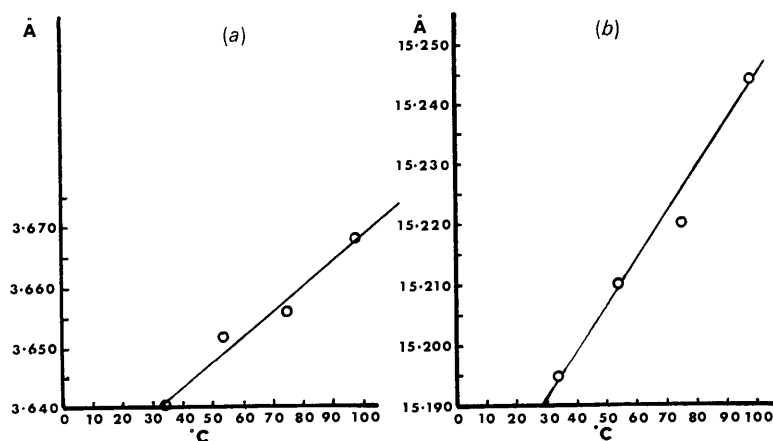


Fig. 6. Lattice parameters of trigonal sodium azide as a function of temperature: (a) a (hexagonal axes), (b) c .

Noakes (1963) consider that there may be a second-order phase transition to the low temperature form. A slight shift in the alignment of the azide ions is the most obvious difference which could occur.

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An X-ray Examination of the Chloroplatinate of an Alkaloid derived from *Senecio kirkii*

BY G. G. DODSON AND D. HALL

Chemistry Department, University of Auckland, New Zealand

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The chloroplatinate of an alkaloid believed to be senkirkine has been studied by three-dimensional X-ray methods, and its structure determined. The cation has the formula $[\text{C}_{18}\text{H}_{23}\text{NO}_6]^+$, and differs in the absence of a methylene group from that corresponding to the now known structure of senkirkine. The relationship of the two alkaloids is not known.

Introduction

The alkaloid senkirkine was first isolated from the shrub *Senecio kirkii* Hook. f. by Briggs, Mangan & Russell (1948), who ascribed to it the formula $\text{C}_{18}\text{H}_{25}\text{NO}_6$. Hydrolysis gave a lactone which was identified as that of senecic acid, $\text{C}_{10}\text{H}_{16}\text{O}_5$, but no definite information was obtained concerning the necine base. More recent investigations by Briggs, Cambie, Candy, O'Donovan, Russell & Seelye (1965) suggested a revised formula $\text{C}_{19}\text{H}_{27}\text{NO}_6$ and elucidated various features of the base, but difficulty in establishing both its structure and its mode of attachment to the necic acid led to an investigation of the crystal structure of a derivative of the alkaloid. Crystals were prepared which were thought to be the chloroplatinate of senkirkine, and the structure determination of these crystals is herein described.

In the interim the structure of senkirkine has been established by other means (Briggs *et al.*, 1965) and it appears that the compound studied is not the salt of senkirkine but that of a closely related alkaloid.

Experimental

Light-orange crystals were obtained by mixing aqueous solutions of chloroplatinic acid and what was considered to be a pure sample of senkirkine. The molecular weight from the crystal data was as expected, and no further precautions were taken to ensure the identity of the crystals.

Small equant crystals were used for X-ray photographs. Where necessary, larger crystals were cut to size with the use of the solvent saw technique described by Peterson, Steinrauf & Jensen (1960). Immediately following their preparation crystals could be obtained