Therefore it appears that purely 'mechanical' forces do not appreciably affect bond length, whereas bond angles are not as rigorous in their demands for constancy.

I should like to conclude by thanking Dr C. A. Beevers for much helpful discussion and advice, and also to express my gratitude to the University of Edinburgh for an award of a Post-Graduate Studentship.

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The Crystallographic, Elastic, and Piezoelectric Properties of Ammonium Pentaborate and Potassium Pentaborate

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The crystallographic descriptions of potassium and ammonium pentaborate are given, including a review of previous conflicting data. The full set of elastic, piezoelectric, and dielectric coefficients of potassium pentaborate were obtained, as well as piezoelectric and dielectric data for ammonium pentaborate.

Potassium pentaborate ($KB_5O_8.4\,H_2O$) and its isomorphous compounds form well defined orthorhombic crystals. The early crystallographic literature (Groth, 1908) indicated central symmetry, but a structure determination by Zachariasen (1937) led to the polar space group C_{2v}^{17}–*Aba*. At the suggestion of Prof. Zachariasen (1941), we studied the piezoelectric effect in this crystal group, and we found the effect at a substantial level as well as a somewhat unusual elastic behavior. These studies were given in a government report (Jaffe, 1948). The purpose of the present note is to make these results generally available as well as to clarify discrepancies in the crystallographic descriptions of this crystal type. These discrepancies were brought to our attention especially by correspondence with Prof. A. N. Winchell.

Potassium pentaborate is orthorhombic, class C_{2v},

$$a = 11{\cdot}065{\pm}0{\cdot}002,\quad b = 11{\cdot}171{\pm}0{\cdot}001,$$
$$c\ \text{(polar axis)} = 9{\cdot}054{\pm}0{\cdot}0006\ \text{Å}\,,$$
$$\text{axial ratio } 0{\cdot}9905:1:0{\cdot}8105\,.$$

Zachariasen (1937) found the space group to be C_{2v}^{17}–*Aba* and dimensions close to those here reported; our choice of axes agrees with his. The crystal is biaxial positive, optic plane 010,

$$N_\alpha = 1{\cdot}422,\quad N_\beta = 1{\cdot}436,\quad N_\gamma = 1{\cdot}480\,,$$
$$c = X(\alpha),\quad b = Y(\beta),\quad a = Z(\gamma)\,.$$

Predominant crystal forms are {111}, {100}, and $\{00\overset{+}{1}\}$, with perfect 010 and distinct 100 cleavage; generally twinned on $01\bar{1}$ and occasionally on $00\bar{1}$. The density is 1·740 g.cm.$^{-3}$, and the hardness is $2\frac{1}{2}$ on Mohs scale.

Ammonium pentaborate is orthorhombic, class C_{2v},

$$a = 11{\cdot}324{\pm}0{\cdot}002,\quad b = 11{\cdot}029{\pm}0{\cdot}001,$$
$$c = 9{\cdot}235{\pm}0{\cdot}004\ \text{Å}\,,$$
$$\text{axial ratio } 0{\cdot}9740:1:0{\cdot}8155\,.$$

The crystal is biaxial positive, optic plane 010,

$$N_\alpha = 1{\cdot}427,\quad N_\beta = 1{\cdot}431,\quad N_\gamma = 1{\cdot}486,$$
$$c = X(\alpha),\quad b = Y(\beta),\quad a = Z(\gamma)\,.$$

Predominant crystal forms are {100}, {111}, $\{00\overset{+}{1}\}$, with distinct 100 and 010 cleavage; generally twinned on $01\bar{1}$ and occasionally on $00\bar{1}$. The density is 1·57 g.cm.$^{-3}$, and the hardness is $2\frac{1}{2}$ on Mohs scale.

The source of confusion in the early literature is easily seen. In both crystals the *a* and *b* axes are nearly equal, with *a* larger in the ammonium compound and *b* larger in the potassium compound. Conventionally, $b > a > c$, but, since the crystals are isostructural, we have chosen to describe both crystals in terms of the potassium pentaborate axes, its crystal structure having been determined more precisely. These orientations are related to those described in the literature as follows:

Ammonium pentaborate: Rammelsberg (1855) has the *a* and *b* axes the same as above.

Potassium pentaborate: Rammelsberg (1855) listed the forms $\{111\}$, $\{100\}$, $\{010\}$, so the orientation of his axes is unknown. The *a* and *b* axes of Lang (1862) are reversed from above. He noted the 011 twinning. Zachariasen (1937) determined the crystal structure and used the same axes as above. The older references are summarized in Groth (1908).

Further isomorphs: Rollet & Andres (1930) reported the cesium pentaborate and Rosenheim & Leyser (1921) the rubidium pentaborate. We have prepared deuterated potassium pentaborate. Thallium pentaborate was also obtained, but decomposed within a few hours.

A complete set of elastic constants of potassium pentaborate has been obtained by a combination of resonance measurements (Jaffe, 1948) on piezoelectrically excited bars and plates with ultrasonic pulse data on a block (Huntington & Rose, 1948) with edges about 2 cm. long parallel to the *a*, *b*, and *c* axes. The pulse measurements give the stiffness coefficients c_{11} to c_{66}. Three of these were confirmed by piezoelectric thickness resonances of plates. Longitudinal resonances of bars parallel to the *b* and *c* axes and of bars with length at 45° to each pair of axes give combinations of compliance coefficients which permit completion of the set, including two cross-checks.

Table 1 gives the adjusted results calculated by Prof. Huntington. The superscripts *D* and *E* indicate constant electric displacement and field respectively. The compliance s_{44} is the only one materially affected by piezoelectric coupling.

Table 1. *Elastic compliances and stiffness coefficients of* $KB_5O_8.4\,H_2O$

Values of s in m.^{2}/newton; values of c in newton/m.^{2}

s_{11}	$23{\cdot}2\times10^{-12}$	c_{11}	$58{\cdot}2\times10^{9}$
s_{22}	73·6	c_{22}	35·9
s_{33}	98·3	c_{33}	25·5
$s_{44}{}^D$	61	$c_{44}{}^D$	16·4
$s_{44}{}^E$	64	$c_{44}{}^E$	15·8
s_{55}	215	c_{55}	4·63
s_{66}	175	c_{66}	5·7
s_{12}	−10·6	c_{12}	22·9
s_{13}	−6·1	c_{13}	17·4
s_{23}	−60	c_{23}	23·1

Superscripts *D* and *E* designate constant electric displacement or field.

The crystal shows interesting elastic behavior expressed in the coefficients relating to stress and strain in the (100) plane. The shear compliance s_{44} is unusually low compared to the compressional compliances s_{22} and s_{33}, while the cross compliance s_{23} is quite high, corresponding to a Poisson's ratio over 0·5. The behavior is qualitatively similar to that of ammonium dihydrogen phosphate in the (001) plane referred to *X* and *Y* axes in the symmetry planes.

Table 2. *Dielectric and piezoelectric coefficients*

Values of d in coulomb/newton

	$KB_5O_8.4\,H_2O$	$NH_4B_5O_8.4\,H_2O$
K_1	5·5	5·6
K_2	4·6	6·5
K_3	4·5	4·6
d_{31}	$\lvert< 1\rvert\times10^{-12}$	$-1{\cdot}9\times10^{-12}$
d_{32}	−5·4	−6·6
d_{33}	5·6	6·9
d_{24}	9·5	13
d_{15}	1·7	6·7

Table 2 shows dielectric and piezoelectric coefficients of the potassium as well as the ammonium salt. The piezoelectric coefficients were obtained by measurements of charge produced by compression of oriented blocks.

The elastic behavior of ammonium pentaborate was studied partially and found similar to that of the potassium salt; it also has a low value, $s_{44}^D=55\times10^{-12}$ m.^{2}/newton for one shear compliance.

The resonant frequencies controlled by the compliance s_{44} in both crystals show a maximum as a function of temperature at 25° C.

Frequency maxima in corresponding sections of rubidium pentaborate and of deuterated potassium pentaborate were found at 5° C. and 15° C. respectively. The anomalous temperature dependence of s_{44} giving rise to this frequency maximum apparently resides in the B–O framework rather than the hydrogen bonds since it is so little affected by substitution of *D* for *H*.

The maximum of frequency versus temperature in a strongly excited shear mode has made these crystals of interest in frequency-control applications. Unfortunately, both the potassium and ammonium crystals were found to show slow surface changes in ordinary atmospheres.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.*

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Preliminary single-crystal X-ray and optical study of nor-harman, $C_{11}H_8N_2$.

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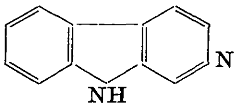
Introduction

Very few complete structure determinations of the heterogeneous ring compounds containing more than one benzene nucleus have been reported. The author has undertaken a systematic investigation of some ring compounds the complete determination of whose structure will give very valuable data for the study of *Rauwolfia* alkaloids. The preliminary crystal data of the compounds rauwolscane, $C_{19}H_{24}N_2$, and harmine, $C_{12}H_{13}N_2O$, have been reported (Ray, 1956, 1957), and the present paper reports the results of X-ray and optical measurements carried out with single crystals of nor-harman. A complete structure determination of this simple compound by the Fourier-synthesis method has been taken up and the results will be published in due course.

Experimental

Nor-harman, $C_{11}H_8N_2$, a colourless substance melting at 198–9° C., is of particular interest because it is the simplest of the series of the heterogeneous compounds mentioned above, having the structural formula



The crystals used in this investigation were from materials very kindly supplied by Dr Schlittler of the Ciba Pharmaceutical Products, New Jersey. The compound subsequently synthesized here by Dr (Mrs) A. Chatterjee and Dr P. Bagchi gave identical results. The substance was crystallized from a solution containing a mixture of alcohol and acetone. Thin plates and rod-like crystals, which are seldom well-formed, are usually obtained. The crystals exhibit the forms {011} and {110}; the faces {110} though present are not well developed.

Morphological and goniometric studies showed the crystal to be orthorhombic and gave

$$a:b:c = 0{\cdot}5982:1:1{\cdot}494\ .$$

The axial ratios calculated from the X-ray results were found to agree fairly well with those derived goniometrically.

Studies under a polarizing microscope showed that Nor-harman is optically positive. The refractive indices along the three principal directions are

$$\alpha = 1{\cdot}758,\quad \beta = 1{\cdot}759,\quad \gamma = 1{\cdot}806\ .$$

Single-crystal rotation and Weissenberg diagrams were obtained along the three crystallographic directions with a very small crystal, using copper radiation filtered through nickel foil of proper thickness. Rotation as well as Weissenberg diagrams gave

$$a = 5{\cdot}9,\quad b = 9{\cdot}8,\quad c = 14{\cdot}6\ \text{Å}\ .$$

A higher degree of accuracy is not claimed as no allowance has been made for the film shrinkage etc.

Complete sets of $h00$, $0k0$, $00l$, $h0l$, $0kl$, $hk0$ and hkl data were recorded on Weissenberg photographs. The planes $h00$, $0k0$ and $00l$ are absent when h, k and l, respectively, are odd. No other systematic absences were found. These conditions indicate the space group $P2_12_12_1$–D_2^4 with four molecules of nor-harman in the unit cell. The density of the crystal, determined by flotation, was 1·32 g.cm.$^{-3}$, and the calculated density, corresponding to four molecules of nor-harman in the unit cell, is 1·319 g.cm.$^{-3}$.

The author wishes to express her indebtedness to Prof. S. N. Bose under whose guidance and direction the project is being carried out. The author also wishes to record her thanks to the Atomic Energy Commission, Bombay, for the award of a scholarship and to Prof. H. Mark, Polytechnic Institute of Brooklyn, U.S.A., for the supply of tryptophan used in the synthesis of nor-harman.

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