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Crystallographic data for certain alkaloids. IV.

By D. C. Phillips,† *Viriamu Jones Laboratory, University College, Cardiff, Wales*

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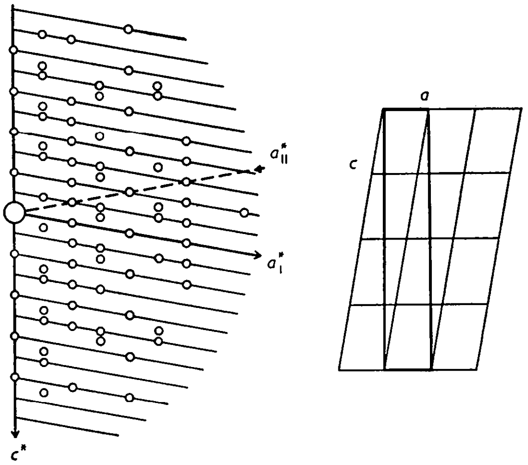
Arecoline hydrobromide, $C_8H_{13}NO_2.HBr$



(*a*) (*b*)

Fig. 1. (*a*) Observed *h0l* reflexions with reciprocal-lattice axes marked for normal twinning. (*b*) Monoclinic and pseudo-orthorhombic unit cells.

Crystals grown from solution in hot ethanol were very small prisms of too poor a quality for a useful optical examination. The Laue symmetry appeared to be *mmm*, but oscillation and Weissenberg photographs showed systematic peculiarities in the diffraction pattern which are not readily interpreted in terms of the orthorhombic crystal system. A diagram of the observed *h0l* reciprocal-lattice plane is shown in Fig. 1(*a*). The crystals are considered to belong to the monoclinic system and to be twinned polysynthetically with b^* and c^* in common and two orientations of a^*. The unit-cell dimensions (accurate to within about 1%) are then:

$$a = 9{\cdot}90,\; b = 7{\cdot}40,\; c = 14{\cdot}1\ \text{Å};\; \beta = 100\pm1^\circ$$

with 4 molecules per unit cell. Density: calculated 1·54 g.cm.$^{-3}$; observed 1·5±0·1 g.cm.$^{-3}$.

Reflexions *0k0* are present only when $k = 2n$. Not all the *h0l* reflexions can be indexed unambiguously because of the seemingly exact overlapping of independent reflexions from the twin components. The absences which can be established all comply, however, with the rule that reflexions *h0l* are present only when $h+l = 2n$. Reflexions *hkl* are present in all orders. The probable space group, therefore, is $P2_1/n$.

This appears to be an example of 'twinning by reticular pseudo-merohedry' (Friedel, 1905): a multiple lattice simulates a symmetry higher than that of the lattice. Here the axis [104] is very closely perpendicular to (001), $\cos\beta = -a/4c$, making possible the pseudo-orthorhombic unit-cell base outlined in Fig. 1(*b*).

The twin operation is one of the operations of orthorhombic pseudo-symmetry associated with this quadruple cell but not included in any possible monoclinic symmetry.

Sparteine sulphate pentahydrate, $C_{15}H_{26}N_2.H_2SO_4.5H_2O$

Crystals grown from dilute ethanol were plates with well formed pinacoids {001}. Oscillation and Weissenberg photographs showed the Laue symmetry to be 2/*m* and gave the monoclinic unit-cell dimensions:

$$a = 8{\cdot}03,\; b = 15{\cdot}2,\; c = 8{\cdot}84\ \text{Å};\; \beta = 91^\circ\,30'\pm1^\circ.$$

There are 2 molecules per unit cell. Density: calculated 1·30 g.cm.$^{-3}$; observed 1·28 g.cm.$^{-3}$.

Reflexions *0k0* are present only when $k = 2n$. All other classes of reflexions are present in all orders so that the space group is either $P2_1$ or $P2_1/m$. Since the compound is optically active, however, $P2_1$ must be chosen. This choice has been confirmed by an investigation of the distribution of intensities among the *h0l* and *0kl* reflexions (Wilson, 1951).

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† Present address: Physics Division, National Research Council, Ottawa, Canada.

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On the substantialization of sign sequences.

By I. J. Good, 25 *Scott House, Princess Elizabeth Way, Cheltenham, England.*

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Woolfson (1954) describes a method for the determination of the signs of the structure factors of a centrosymmetrical crystal. The method depends on a standard set of sixteen sequences of seven signs (7-sequences) such that each of the 128 possible 7-sequences differs from one of the set in at most one sign. In the present note the structure of the set is explained and is extended to a set, *S*, of 2048 15-sequences such that each of the 32,768 possible

15-sequences differs in at most one sign from one of the set of 2048. In the crystallographic application we may say that one member of S must be 'substantially correct', or that S *substantializes* the set of all possible 15-sequences. The use of S saves a work factor of 16 provided that we can stand one wrong sign. The general problem of substantialization remains open.

Denote a typical 15-sequence (an ordered sequence of fifteen signs, or of symbols $+1$ and -1) by $a_1, a_2, a_3, \ldots, a_{15}$, where each a_i is $+1$ or -1. Consider the set, S, of 15-sequences satisfying the relationships

$$\left.\begin{array}{l} a_1a_2a_3a_4a_5a_6a_7a_8 \quad = 1\,, \\ a_1a_2a_3a_4a_9a_{10}a_{11}a_{12} = 1\,, \\ a_1a_2a_5a_6a_9a_{10}a_{13}a_{14} = 1\,, \\ a_1a_3a_5a_7a_9a_{11}a_{13}a_{15} = 1\,. \end{array}\right\} \qquad (1)$$

Note first that S has precisely 2048 members; for $a_1, a_2, a_3, a_4, a_5, a_6, a_7, a_9, a_{10}, a_{11}, a_{13}$ can be selected arbitrarily (in 2^{11} ways) and then a_8, a_{12}, a_{14} and a_{15} can be determined uniquely from (1). Now if any pair of symbols is selected from $a_1, a_2, a_3, \ldots, a_{15}$, then one of the four relationships contains one of the pair and not the other, so a change of sign of two symbols in a member of S cannot transform this member into another one. Therefore the 16×2048 15-sequences obtained by taking the 2048 sequences of S, together with the ones obtained by changing one sign in each of them in all possible ways, must be all distinct. And since there are only 16×2048 possible 15-sequences they must each occur exactly once.

The relationships (1) were obtained by first writing down the numbers 1, 2, 3, ..., 15, expressed in the binary scale, into the columns of a four-by-fifteen rectangle, thus:

0 0 0 0 0 0 0 1 1 1 1 1 1 1 1
0 0 0 1 1 1 1 0 0 0 0 1 1 1 1
0 1 1 0 0 1 1 0 0 1 1 0 0 1 1
1 0 1 0 1 0 1 0 1 0 1 0 1 0 1 ,

then writing the symbols $a_{15}, a_{14}, a_{13}, \ldots, a_1$ at the tops of the columns (any order would have done just as well), and finally defining one relationship by each *row* of the rectangle using 1's to mean presence and 0's to mean absence. The process can clearly be applied to n-sequences, whenever n is 1 less than a power of 2, and in particular it covers the set presented by Woolfson, with $n = 7$.

The set S could be written down manually by the rule described in the proof that it has 2048 members. By making use of an electronic computer the set S could be used without actually being written down on paper. It is possible that it would sometimes be desirable to combine the use of S with other techniques that are appropriate for electronic computers, such as the one described by Cochran & Douglas (1953).

The general problem, $\gamma(n, r)$, of substantialization of sign sequences is that of finding economical sets of n-sequences such that every possible n-sequence differs from one of the set in at most r signs. The method given above solves the problems $\gamma(2^m-1, 1)$ and provides perfectly economical solutions for these problems. By simply abutting the sequences of k such solutions we can obtain reasonably economical, but not perfectly economical, solutions of $\gamma(2^{m_1}+2^{m_2}+\ldots+2^{m_k}-k, k)$. (This remark generalizes one made in Woolfson's paper.) For example we can obtain tolerable solutions of $\gamma(14, 2)$, $\gamma(21, 3)$, $\gamma(22, 2)$.

The problem of substantialization occurs in an even more general form in the filling up of coupons for 'football pools', a type of gambling that is popular in the United Kingdom. There are then three states (wins, draws and losses) for the components of the n-sequences instead of only two. Further generalizations may be of value in crystallography for crystals that are not centrosymmetrical. For example, if it is adequate to approximate to the phases to the nearest multiple of 60°, then we should be faced with the problem having six states instead of two or three.

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The unit cell of potassium borohydride, KBH_4, at 90° K.

By P. T. Ford and H. M. Powell, *Physical Chemistry Laboratory, South Parks Road, Oxford, England*

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In connexion with a nuclear magnetic resonance investigation of $NaBH_4$ and KBH_4, X-ray powder photographs of the two salts at 293° K. and 90° K. have been obtained, and lattice constants derived.

For the X-ray photographs copper radiation from a Metrovic generator was used, the specimen being mounted in a low-temperature camera similar to that described by Hume-Rothery (Hume-Rothery & Strawbridge, 1947), with a Unicam cassette of 19 cm. diameter. The low-temperature photographs were obtained by running a stream of liquid oxygen over the sample.

The $NaBH_4$, supplied by Light and Co., was recrystallized once from water below 5° C. and once, in a vacuum-tight vessel, from iso-propylamine previously dried over lithium hydride (Davis, Mason & Stegeman, 1949). Analysis by acid hydrolysis gave the theoretical quantity of hydrogen. The KBH_4, obtained from May and Baker, by a similar analysis gave 96·1% of the hydrogen required by the formula. Samples were packed into Lindemann glass tubes and sealed with picien. Both these operations were performed in a dry-box.

The following lattice constants were obtained. They are in Ångström units and previously published values are added in brackets.

$NaBH_4$ at 293° K.: face-centred cubic, $a = 6{\cdot}157$ (Soldate (1947), $a = 6{\cdot}151 \pm 0{\cdot}009$; Abrahams & Kalnajs (1954), $a = 6{\cdot}1635 \pm 0{\cdot}0005$).