

Table 1. *Crystallographic data*

Compound	Space group	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$	Density (g.cm. <sup>-3</sup> )		No. of formula units/unit cell
						Obs.	Calc.	
Brucine	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	7.6	11.6	26.6	—	1.31	1.32	4
Brucine sulphate	<i>C</i> 222 <sub>1</sub>	12.3	14.4	26.9	—	1.41	1.41	4
Gelsemine hydrochloride	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	7.3	9.0	26.4	—	1.37	1.37	4
$\alpha$ -Lobeline hydrochloride	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	8.1	14.2	18.0	—	1.24	1.25	4
Pilocarpine hydrochloride	<i>P</i> 2 <sub>1</sub>	6.7	9.2	10.8	105½°	1.26	1.26	2
Pilocarpine hydrobromide	<i>P</i> 4 <sub>1</sub>	6.9	6.9	37.6	—	2.12	2.11	8

consisted of long tapering needles; the other of square plates. The latter when viewed in convergent plane-polarized light shows a uniaxial brush. Crystals of both habits are reddish-brown in colour and give identical X-ray diffraction patterns. The Laue symmetry is 4/*m* and the reflexions (00*l*) are absent when *l* is not a multiple of 4. The possible space groups are *P*4<sub>1</sub> and *P*4<sub>1</sub>/*m*, but as the base from which the compound was prepared is optically active the space group must be *P*4<sub>1</sub>. Up to the present time it has not proved possible to obtain the hydrobromide in a form isomorphous with the hydrochloride.

A detailed investigation of the structure of pilocarpine

hydrochloride is in progress and similar investigations are to be started in the near future of  $\alpha$ -lobeline hydrochloride and gelsemine hydrochloride.

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#### Reference

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**Sayre's equation and Zachariasen's method.** By W. COCHRAN, *Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England*

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A recent note by Krogh-Moe (1953) provides a derivation, in a modified form, of an equality relation between structure factors first obtained by Sayre (1952). The new derivation is of interest in that Krogh-Moe appears to obtain his equation (12) (referred to here as (12-K.-M.)) without imposing Sayre's condition of equal atoms. The purpose of the present note is to point out that (12-K.-M.) is valid only in the equal-atom case, and that Zachariasen's (1952) equation (11-Z.) is also not generally valid. The derivation of this equation, on which Zachariasen's method is based, has already been criticised by Lavine (1952).

We define a unitary structure factor

$$U(\mathbf{h}) = 2 \sum_{j=1}^{\frac{1}{2}N} n_j \cos 2\pi \mathbf{h} \cdot \mathbf{r}_j \quad (1)$$

There is a corresponding distribution in crystal space

$$\sigma(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{h} < H} U(\mathbf{h}) \cos 2\pi \mathbf{h} \cdot \mathbf{r} \quad (2)$$

If we now put

$$\sigma^2(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{h} < 2H} G(\mathbf{h}) \cos 2\pi \mathbf{h} \cdot \mathbf{r} \quad (3)$$

it may readily be shown (see, e.g. Sayre, 1952) that

$$G(\mathbf{h}) = \frac{1}{V} \sum_{\mathbf{h}' < H} U(\mathbf{h}') U(\mathbf{h} - \mathbf{h}') \quad (4)$$

Equation (4) is true in all circumstances. If, however, the limits of the Fourier series (2) are set sufficiently high for the 'atoms' of  $\sigma(\mathbf{r})$  to be completely resolved from one another, those of  $\sigma^2(\mathbf{r})$  are also resolved and corresponding to

$$U(\mathbf{h}) = 2 \sum_{j=1}^{\frac{1}{2}N} n_j \cos 2\pi \mathbf{h} \cdot \mathbf{r}_j \quad (1) \quad \left. \vphantom{U(\mathbf{h})}} \right\} \quad (5)$$

we have

$$G(\mathbf{h}) = 2 \sum_{j=1}^{\frac{1}{2}N} g_j(h) \cos 2\pi \mathbf{h} \cdot \mathbf{r} \quad \left. \vphantom{G(\mathbf{h})}} \right\}$$

Each  $g_j$  is proportional to  $n_j^2$ .

If, furthermore, all values of  $n_j$  are the same, it may be shown along the lines of Sayre's (1952) derivation that it now follows that

$$U(\mathbf{h}) = N\overline{U(\mathbf{h}')U(\mathbf{h}-\mathbf{h}')}. \quad (6)$$

The average is over all values of  $h'$  less than  $H$ . This establishes the limits within which Krogh-Moe's result is valid in the equal-atom case, as (12-K.-M.) then reduces to (6). To show that (12-K.-M.) is incorrect when the atoms are unequal, we consider a structure in which  $N-2$  atoms are equal, but the remaining two at  $\pm r_0$  are  $m$  times heavier.

Then

$$\left. \begin{aligned} U(\mathbf{h}) &= 2 \sum_{j=1}^{\frac{1}{2}N-1} n \cos 2\pi\mathbf{h} \cdot \mathbf{r}_j + 2mn \cos 2\pi\mathbf{h} \cdot \mathbf{r}_0 \\ \text{and} \\ G(\mathbf{h}) &= 2 \sum_{j=1}^{\frac{1}{2}N-1} g(h) \cos 2\pi\mathbf{h} \cdot \mathbf{r}_j + 2m^2g(h) \cos 2\pi\mathbf{h} \cdot \mathbf{r}_0. \end{aligned} \right\} (7)$$

Now if

$$\left. \begin{aligned} |m \cos 2\pi\mathbf{h} \cdot \mathbf{r}_0| &< \left| \sum_{j=1}^{\frac{1}{2}N-1} \cos 2\pi\mathbf{h} \cdot \mathbf{r}_j \right| \\ \text{but} \\ |m^2 \cos 2\pi\mathbf{h} \cdot \mathbf{r}_0| &> \left| \sum_{j=1}^{\frac{1}{2}N-1} \cos 2\pi\mathbf{h} \cdot \mathbf{r}_j \right| \\ \text{while} \\ \cos 2\pi\mathbf{h} \cdot \mathbf{r}_0 \text{ and } \sum_{j=1}^{\frac{1}{2}N-1} \cos 2\pi\mathbf{h} \cdot \mathbf{r}_j \end{aligned} \right\} (8)$$

are opposite in sign it is clear that  $U(\mathbf{h})$  and  $G(\mathbf{h})$  are opposite in sign, or, using (4),

$$S\{U(\mathbf{h})\} = -S\left\{ \sum_{h' < H} U(\mathbf{h}')U(\mathbf{h}-\mathbf{h}') \right\},$$

for the particular values of  $\mathbf{h}$  for which conditions (8) happen to be satisfied.  $S\{U\}$  is used to denote the sign of  $U$ . In these circumstances the two sides of equation (12-K.-M.) are of opposite sign! The only step not rigorously established in Krogh-Moe's derivation is

(6-K.-M.), which must therefore be incorrect, except in the equal-atom case.

In the notation used here, Zachariasen's equation (11-Z.) is

$$S\{U(\mathbf{h})\} = S\left\{ \overline{S\{U(\mathbf{h}')\}S\{U(\mathbf{h}-\mathbf{h}')\}} \right\}. \quad (9)$$

Since Zachariasen stipulated that only large unitary structure factors are to be involved in the averaging process, and since these  $U$ 's will be approximately equal in magnitude, we may write (11-Z.) as

$$S\{\overline{U(\mathbf{h})}\} = S\left\{ \overline{U(\mathbf{h}')U(\mathbf{h}-\mathbf{h}')} \right\}. \quad (10)$$

This result is incorrect when conditions (8) are satisfied, so that (11-Z.) cannot be generally valid. Why then was Zachariasen able to apply it so successfully in practice? The explanation is that while

$$S\{G(\mathbf{h})\} = S\left\{ \overline{U(\mathbf{h}')U(\mathbf{h}-\mathbf{h}')} \right\} \quad (11)$$

is rigorously true when the average is over all unitary structure factors within a limiting sphere, the result is still true when only the larger  $U$ 's appear on the right-hand side of (11). Taking these  $U$ 's to be equal in magnitude, we obtain

$$S\{G(\mathbf{h})\} = S\left\{ \overline{S\{U(\mathbf{h}')\}S\{U(\mathbf{h}-\mathbf{h}')\}} \right\}. \quad (12)$$

Comparison of (9) with (12) shows that Zachariasen's procedure really gives the sign of  $G(\mathbf{h})$ , not of  $U(\mathbf{h})$ . When the atoms are equal, or nearly so,  $S\{U\} = S\{G\}$  (see equations (5)), and even when they are very unequal this will usually be true for the larger structure factors (see equations (7)). In such circumstances (11-Z.) is correct, but, as we have shown, exceptions may in principle occur.

## References

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**The unit cell and space group of ethyl nitrolic acid.** By D. JUNE SUTOR, *Department of Chemistry, Auckland University College, Auckland, New Zealand*

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Ethyl nitrolic acid ( $C_2N_2O_3H_4$ ) was prepared by the action of potassium hydroxide and sodium nitrite on nitroethane (Meyer & Constam, 1882). The crystals were pale yellow, orthorhombic, and two habits were observed, both of which gradually decomposed with the evolution of nitrous fumes. Recrystallization from chloroform, ether or water gave needles elongated along  $[c]$ , and exhibiting the forms  $\{100\}$ ,  $\{010\}$ ,  $\{001\}$ ,  $\{110\}$  and  $\{210\}$ , while small plates exhibiting  $\{011\}$  and  $\{100\}$  were obtained by slow evaporation of a chloroform solution. Both habits were consistent with the 222 class.

From rotation photographs taken with Cu  $K\alpha$  radiation, and from an optical examination, the crystal was found to be orthorhombic with axial lengths

$$[a] = 11.28, [b] = 8.06, [c] = 4.85 \text{ \AA}.$$

Reflexions were indexed on oscillation photographs and the only systematic absences were  $(h00)$ ,  $(0k0)$  and  $(00l)$  for  $h$ ,  $k$  and  $l$  odd respectively. The space group is therefore  $D_2^2-P2_12_12_1$ .

The density measured by flotation was  $1.555 \text{ g.cm}^{-3}$ . This agrees with a calculated value of  $1.567 \text{ g.cm}^{-3}$  for four molecules in the unit cell.

## Reference

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