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# Monoclinic glycine sulfate: crystallographic data.

By ELIZABETH A. WOOD and ALAN N. HOLDEN, *Bell Telephone Laboratories, Murray Hill, N.J., U.S.A.*

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## Introduction

Matthias, Miller & Remeika (1957) have recently discovered that glycine sulfate is ferroelectric. The ferroelectric properties of this material are being investigated by J. P. Remeika, and large crystals are being grown from aqueous solution by C. E. Miller.

## Unit cell and formula

Zero- and first-layer precession photographs were taken around $c$ and around $b$, and a zero-layer Weissenberg photograph was taken around $b$, all with molybdenum radiation. The lattice constants, checked by goniometric measurements, are:

$$a_0 = 9{\cdot}15,\quad b_0 = 12{\cdot}69,\quad c_0 = 5{\cdot}73 \pm 0{\cdot}03 \text{ Å};$$
$$\beta = 105^\circ\ 40' \pm 20'.$$

The volume of the unit cell is 640 Å$^3$ and the measured density is 1·69 g.cm.$^{-3}$. If the formula were $(CH_2NH_2COOH)_2H_2SO_4$, the calculated density for this volume would be 1·28 g.cm.$^{-3}$ for two formula-weights in the unit cell. The similarly calculated density would be 1·66 g.cm.$^{-3}$ if the formula were

$$(CH_2NH_2COOH)_2H_2SO_4 . 4H_2O$$

and 1·68 g.cm.$^{-3}$ for the formula $(CH_2NH_2COOH)_3H_2SO_4$. Chemical analysis by H. E. Johnson gave 12·77 weight% nitrogen and 9·93 weight% sulfur (atomic ratio, 2·94) in agreement with the second formula but not the first. This result was confirmed by C. F. Miller by isolating and weighting the glycine from a weighed sample of glycine sulfate. Both chemical analyses indicate that the correct formula is $(CH_2NH_2COOH)_3H_2SO_4$.

## Space group

The Laue symmetry is $2/m$, with $0k0$ reflections present only for $k = 2n$. The monoclinic space groups with this condition alone are $C_2^2$–$P2_1$ and $C_{2h}^2$–$P2_1/m$. The absence of a center of symmetry, as shown by ferroelectricity and etch-pit shapes, eliminates the second alternative, leaving $C_2^2$–$P2_1$ as the most probable space group.

## Optical properties

The optic plane makes an angle of approximately 93° with the $c$ axis, and the acute bisectrix, $X$, is parallel to $b$. The optic plane is thus approximately parallel to $(\bar{1}02)$. $(-)2V = 40 \pm 5^\circ$.

## Cleavage

There is good cleavage parallel to (010), i.e. normal to the ferroelectric axis.

## Discussion of the unit cell and structure

The lattice constants are such that certain special relationships obtain, as illustrated in Fig. 1. The plane $(\bar{1}02)$ makes an angle of about 93° with the $c$ axis, as does the optic plane, within experimental error. The short diagonal of the reciprocal cell is almost the same length as $c^*$ and makes an angle with $a^*$ that is close to $\beta^*$ (see Fig. 1). We therefore consider whether this short diagonal should be chosen as $c^*$. In real space this means choosing the $a$ axis along $[\bar{1}0\bar{1}]$ instead of [100]. The pertinent data are shown in Table 1.

Table 1

| Spacing | Angle '$\beta$' | Translation $t = \frac{d(100)}{\cos(\beta - 90^\circ)}$ |
|---|---|---|
| $d_{(100)} = 8{\cdot}81$ Å | (001) : (100) = 105° 40′ | Along [100] 9·15 Å |
| $d_{(100)} = 8{\cdot}81$ Å | $(\bar{1}01)$ : (100) = 110° 20′ | Along $[\bar{1}0\bar{1}]$ 9·40 Å |

Since $\beta$ is nearer 90° and the $a$ translation is shorter for the present choice than for the alternative with the $a$ axis along the present $[\bar{1}0\bar{1}]$ direction, the present choice is retained. The morphology of most of the large crystals currently being grown would favor the other

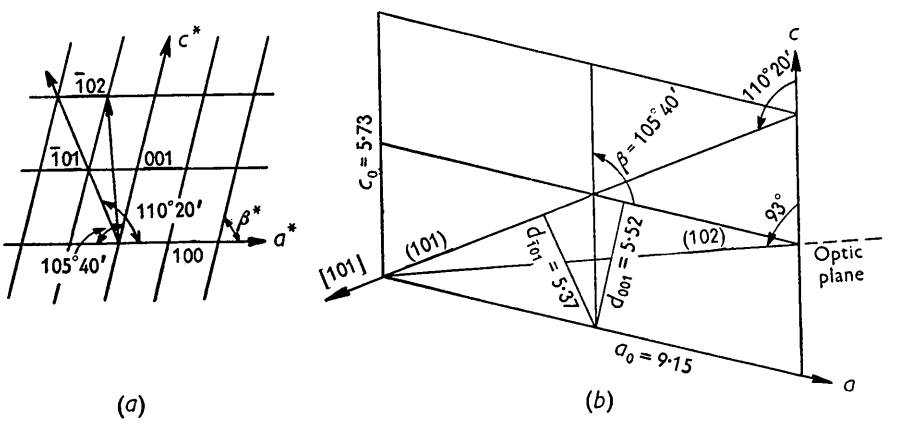


Fig. 1.

choice since their prominent faces are {*hk*0} faces, terminated by large {$\bar{1}$01} faces. However, a smaller crystal on which most of the X-ray work was done showed only {*hk*0} and {001} faces.

Glycine has the lattice constants

$$a = 5{\cdot}10,\ b = 11{\cdot}96,\ c = 5{\cdot}45\ \text{Å};\ \beta = 111°\ 38'$$

and the crystals have good cleavage parallel to (010). The nearly flat glycine molecules lie in sheets, parallel to (010), with four molecules to the unit cell (Albrecht & Corey, 1939). That the sheet-like structure is also present in the glycine sulfate described here is indicated by the good (010) cleavage and is suggested by the optical properties.

When crystals are grown from a solution containing glycine and sulfuric acid in equal molecular proportions, they are orthorhombic with the formula

$$(CH_2NH_2COOH)_2H_2SO_4\ .$$

These crystals are not ferroelectric and may correspond to an orthorhombic glycine sulfate listed by Groth (1909). Crystals of the orthorhombic

$$(CH_2NH_2COOH)_2H_2SO_4\ ,$$

the orthorhombic $(CH_2NH_2COOH)_2H_2SeO_4$, and the monoclinic $(CH_2NH_2COOH)_3H_2SeO_4$ have all been grown and are currently under investigation. The selenates and the sulfates are isomorphous.

The writers wish to thank Mr Val Bala for assistance in obtaining the data reported.

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## Atomic form-factor curves for carbon and oxygen of >C=O bond of anthraquinone (25–35° C.).

By B. V. R. MURTY, *Physics Department, University of Allahabad, India*

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The crystal structure of anthraquinone, $C_{14}H_8O_2$, was determined by Banerjee & Sen (1938) and by Sen (1945) by the two-dimensional Fourier synthesis method. In deriving $F_c$, Sen (1948) used the carbon scattering-factor curve of benzoquinone (Robertson, 1935) and the oxygen scattering-factor curve of magnesium oxide (Wollan, 1930). The agreement between $F_o$ and $F_c$ was not very satisfactory: the $R$ value was 21% for the (*h*0*l*) projection, which is very well resolved. In spite of careful intensity measurements at temperatures ranging between 25° C. and 35° C., and refinement of the atomic positions by a difference synthesis, $F_c$'s being calculated by Hartree curves corrected for temperature, it was still found that the $R$ value remained quite high ($R$ was 23% before refinement and 24% after refinement). This necessitated the determination of $f$ curves for carbon and oxygen in anthraquinone. The publication of $f$ curves for oxygen where it is bonded to a carbon atom of an aromatic benzene ring is expected to be useful for the determination of structures of aromatic compounds with C=O bonds.

Considering a particular atom, its scattering factor in any direction is given by

$$f = \int_{-r_0}^{+r_0} \varrho(r) \exp\,[i\mu r]\, dr\ ,$$

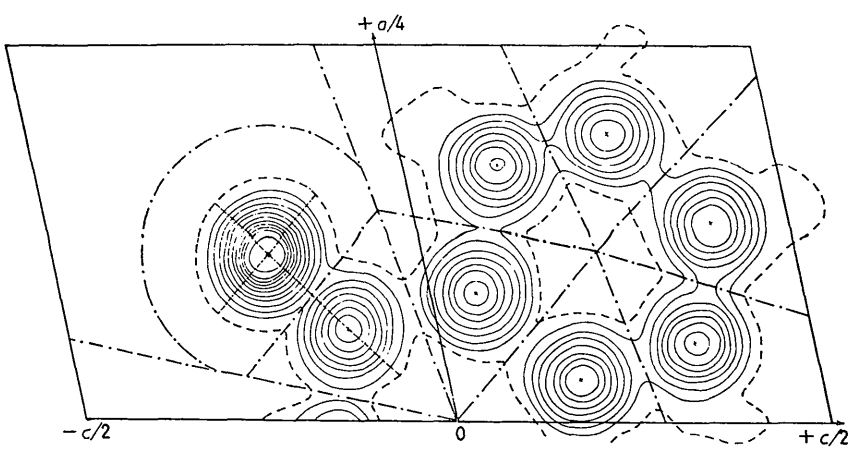


Fig. 1. The (*h*0*l*) projection of anthraquinone. Contours are drawn at intervals of 1 e.Å$^{-2}$, the 1-electron line being broken. The division lines for different atoms, the projected >C=O bond and the major axis of the oxygen atom are shown as chain lines.