C–H bond to a lesser degree than will the more evenly distributed electrons in the C–C bond, causing the C–C–H angle to be larger than the N–C–H angle.

A similar effect would be expected in the Cl-sydnone, and the angles N(13)–C(14)–Cl(17) and C(15)–C(14)–Cl(17) actually show a difference of about 7°; however, the corresponding angles at C(4) do not differ appreciably. A possible explanation of this dissimilar behavior arises from the difference in orientation of the two rings with respect to the ethylene group as described above. Cl(7) is 'eclipsed' with respect to one of the methylene hydrogen atoms, H(9), while Cl(17) is in the 'staggered' configuration relative to its neighboring methylene group.

The angles associated with the nitrogen–methylene carbon bond differ from each other by amounts (8–11°) which are commonly encountered in planar groups where an exocyclic atom is flanked by another exocyclic atom on one side but not on the other.

The C–Cl distance in Cl-sydnone (1·68 Å) is 0·06 Å shorter than the normal C(aromatic)–Cl distance (Palenik, Donohue & Trueblood, 1968). The charge distribution implied in our proposed formula leads to a situation in which considerable delocalization of the chlorine lone-pair electrons onto the positive nitrogen is to be expected with consequent shortening of the C–Cl bond.

All intermolecular distances found in both structures are normal with the exception of one between O(18) and Cl(7′) which is 2·98 Å, or about 0·2 Å less than the sum of van der Waals radii. This contact does not seem to have any appreciable effect on the geometry around the carbonyl carbon.

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The Crystal Structure of Tetronic Acid Derivatives. II. α,γ-Dimethyltetronic Acid

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The structure of α,γ-dimethyltetronic acid, $C_6H_7O_3$, has been determined by obtaining the equation of the molecular plane by the method of Lawrence & MacDonald (*Acta Cryst.* (1968) A**24**, 579), and refined by least-squares techniques in three dimensions. The molecule is very similar in structure to that of α-methyltetronic acid, and the resonance across the OH–C=C–CO chain and the strong hydrogen bonding found in the latter are again present.

Introduction

Tetronic acid derivatives occur in a wide range of natural products, and their importance is discussed in a previous paper (McDonald & Alleyne, 1963) in which the structure of α-methyltetronic acid is described. The second member of the series to be investigated, α,γ-dimethyltetronic acid (see Fig. 3) differs from the previous one only in the addition of a methyl group in the γ position. The molecule of α-methyltetronic acid is planar, but it was believed that the carbon atom C(6)

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of the additional methyl group and possibly atom C(3) would not lie in the plane of the rest of the molecule in α,γ-dimethyltetronic acid.

Experimental

The crystals used were kindly supplied by the Natural Products Unit attached to the Chemistry Department of the University of the West Indies. As with all the tetronic acid derivatives studied, the crystals often exhibited severe twinning, and the specimens used in the X-ray investigation were selected after careful examination under the polarizing microscope.

By use of Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å), oscillation and equi-inclination Weissenberg photographs of the *a*, *b* and *c* axis zero layers and all obtainable upper layers were taken. Multiple film techniques were employed and the relative intensities were estimated visually with the aid of a calibration strip produced with the X-ray set under carefully controlled conditions. These intensities were corrected for Lorentz and polarization factors and the factors applicable to upper layers, sets of intensities being correlated by common spots. The intensities were put on an approximately absolute scale by the use of Wilson's statistical method (Wilson, 1942).

The unit-cell parameters were calculated from zero-layer Weissenberg photographs by analytical extrapolation.

Unit cell and space group

The unit cell has dimensions:

$$a = 6{\cdot}66 \pm 0{\cdot}02, \quad b = 14{\cdot}18 \pm 0{\cdot}02, \quad c = 6{\cdot}58 \pm 0{\cdot}02 \text{ Å}; \quad \beta = 100{\cdot}3° \pm 0{\cdot}1°.$$

The experimentally obtained density is (1·78 ± 0·01) g.cm^{-3}, the calculated density is (1·775 ± 0·01) g.cm^{-3}, assuming four molecules per unit cell. The absent spectra are $h0l$ for l odd and $0k0$ for k odd. The space group is therefore $P2_1/c$.

Structure determination

On the basis of the structure of α-methyltetronic acid, the molecule was assumed to be planar with the exception of the additional carbon atom C(6). Vectors between atoms in the planar part of the molecule must all lie in the same plane in Patterson space. This plane was detected by use of a method devised by Lawrence & McDonald (1968), and was found to have the equation $0{\cdot}18x + 0{\cdot}98y = 0$.

The section through the Patterson function in the orientation of the molecular plane was calculated by use of a program written by D.W. Young for the I.B.M. 1620 computer. A theoretical Patterson for the molecule, obtained by drawing the vector set of the atoms in the structure, excluding the atom which was not expected to lie in the same plane as the rest of the molecule, was superimposed on the Patterson section and rotated until the peaks in the two Pattersons coresponded. The coordinates of the atoms relative to an arbitrary origin were thus found. Fig. 1 shows the Patterson section in the molecular plane with the theoretical Patterson superimposed in the correct orientation.

The absolute location of the atoms in the unit cell was determined using the modified *Q*-function defined by Tollin (1966). The symmetry operations between atoms at (x,y,z) and $(-x,\frac{1}{2}+y,\frac{1}{2}-z)$ give rise to a two-dimensional summation from which the x and z coordinates of the arbitrary origin were obtained, the y coordinate being determined from the one-dimensional summation resulting from the symmetry operation between atoms at (x,y,z) and $x,\frac{1}{2}-y,\frac{1}{2}+z)$.

With the coordinates of the planar part of the molecule thus obtained a structure factor calculation was performed using *f* values taken from *International Tables for X-ray Crystallography* (1962). Vol. III. An *R* value of 0·36 resulted, the *R* value being defined as $\Sigma\,|F_o - F_c| / \Sigma\,F_o$, and only the structure amplitudes of observed reflexions being included. The corresponding Fourier summation yielded an electron density map which showed atoms in the expected positions and one other peak which corresponded to the remaining carbon atom C(6), which was out of the plane of the rest of the molecule. With this atom included, an *R* value of 0·28 was obtained. The structure was then

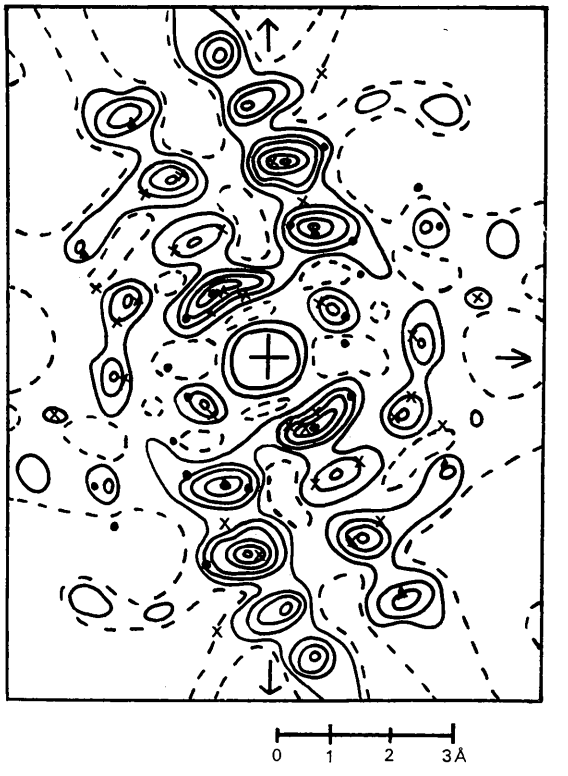

Fig. 1. The Patterson section in the plane of the molecule with the theoretical Patterson superimposed. ▲: O–O; ×: C–O; ●: C–C.

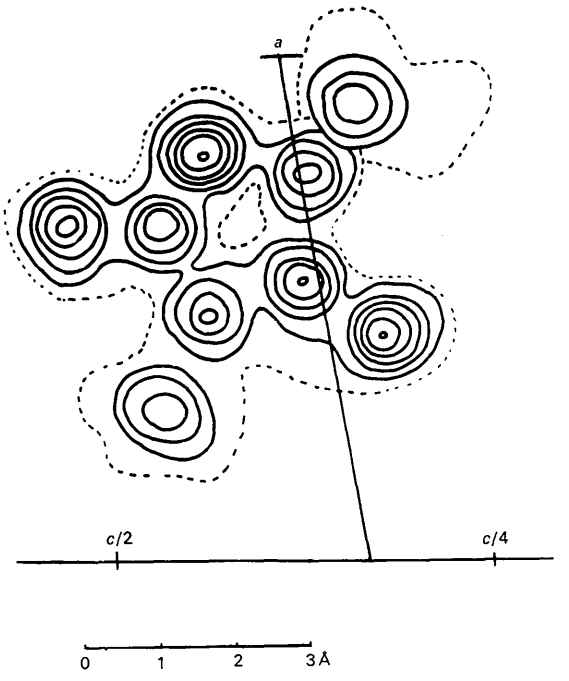

Fig. 2. The section of the three-dimensional electron density distribution in the molecular plane with atom C(6) superimposed. Contours are at intervals of 1 e.Å^{-3}, the broken contour being at 1 e.Å^{-3}.

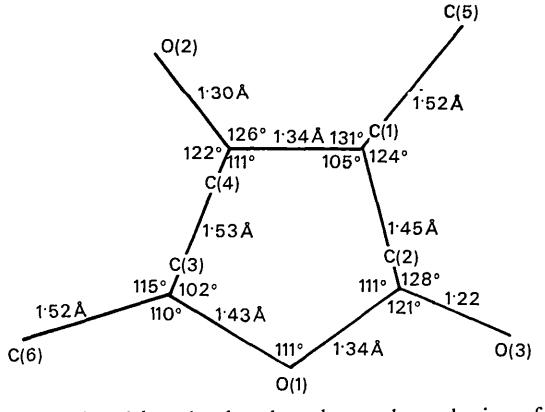

Fig. 3. The bond lengths, bond angles, and numbering of the atoms of α,γ-dimethyltetronic acid.

refined by least-squares by use of a Hughes weighting scheme in a program written by J. C. Schoone (Rogers, 1961) for the Stantec Zebra computer, which refines the positional parameters and isotropic temperature factors. Refinement was discontinued when the shifts obtained were of the same order as the standard deviations. There was evidence of all the hydrogen atoms in the three-dimensional Fourier summation but only three of them were in any way resolved. A final R value of 0·13 was obtained, and this was felt to be satisfactory in view of the poor quality of the crystals, for which reason also no anisotropic temperature factor refinement was attempted. The section in the molecular plane of a three-dimensional electron density map with atom C(6) superimposed is shown in Fig. 2. The final coordinates, standard deviations, and isotropic temperature factors are shown in Table 1, the standard deviations being calculated by the method due to Cox & Cruickshank (1948). Table 2 shows the observed and calculated structure factors.

Discussion of the structure

Fig. 3 shows the bond lengths and angles between the bonds for α,γ-dimethyltetronic acid. The angles are within 2° of the corresponding angles in the α-methyltetronic acid molecule, and the bond lengths are within 0·2 Å with three exceptions.

(1). The distance from C(3), where the additional methyl group was added, to the adjacent carbon atom C(4) in the ring has been shortened from 1·59 Å to 1·52 Å.

(2). The distance from C(4) to O(2) has been lengthened from 1·24 Å to 1·30 Å.

(3). The distance between C(3) and the carbon atom of the other methyl group C(5) has been shortened from 1·57 Å to 1·52 Å.

In view of the standard deviations obtained, these differences were not considered to be highly significant.

As in the case of α-methyltetronic acid it is clear that C(1)–C(4) and C(2)–C(3) are not pure double bonds and that C(4)–O(2) and C(1)–C(2) are not pure single bonds. Resonance is clearly taking place across the OH–C=C–CO chain.

The shortest distance between atoms in different molecules was 2·63 Å between the oxygen atoms O(2)

Table 1. *Final fractional coordinates, standard deviations and isotropic temperature factors for α,γ-dimethyltetronic acid.*

	x/a	$\sigma(x)/a$	y/b	$\sigma(y)/b$	z/c	$\sigma(z)/c$	B (Å^2)
C(1)	0·4962	0·0016	0·1182	0·0013	−0·2342	0·0017	2·5
C(2)	0·6654	0·0016	0·0932	0·0017	−0·3303	0·0017	2·8
C(3)	0·7838	0·0017	0·0845	0·0013	0·0176	0·0014	2·7
C(4)	0·5632	0·0019	0·1117	0·0014	−0·0289	0·0017	2·4
C(5)	0·2935	0·0022	0·1448	0·0015	−0·3545	0·0015	3·5
C(6)	0·9239	0·0021	0·1568	0·0013	0·1320	0·0015	3·7
O(1)	0·8256	0·0014	0·0718	0·0010	−0·1882	0·0011	3·2
O(2)	0·4606	0·0012	0·1286	0·0011	0·1179	0·0011	3·4
O(3)	0·6712	0·0011	0·0883	0·0012	−0·5154	0·0011	3·6

and O(3′) in molecules whose atoms are situated at positions $(x,y,z)$and $(x,y,1+z)$ respectively. Hydrogen bonding must, therefore, take place and there was evidence of a hydrogen atom between two oxygen atoms. By this means, the molecules form chains parallel to the z axis, and the packing is the same as in α-methyltetronic acid.

Apart from the carbon atom C(6), the molecule was approximately planar as had been predicted. The equation of the mean plane through these atoms was

$$0{\cdot}284x+0{\cdot}958y-0{\cdot}038z=2{\cdot}674,$$

no atom being more than 0·02 Å from it. This plane is 4° away from the plane initially obtained from the Patterson function. There was no evidence to show that the carbon atom C(3) had been lifted from the plane of the rest of the molecule by the addition of the methyl group as had been suggested.

Table 2. *Measured and calculated values of the observed structure factors*

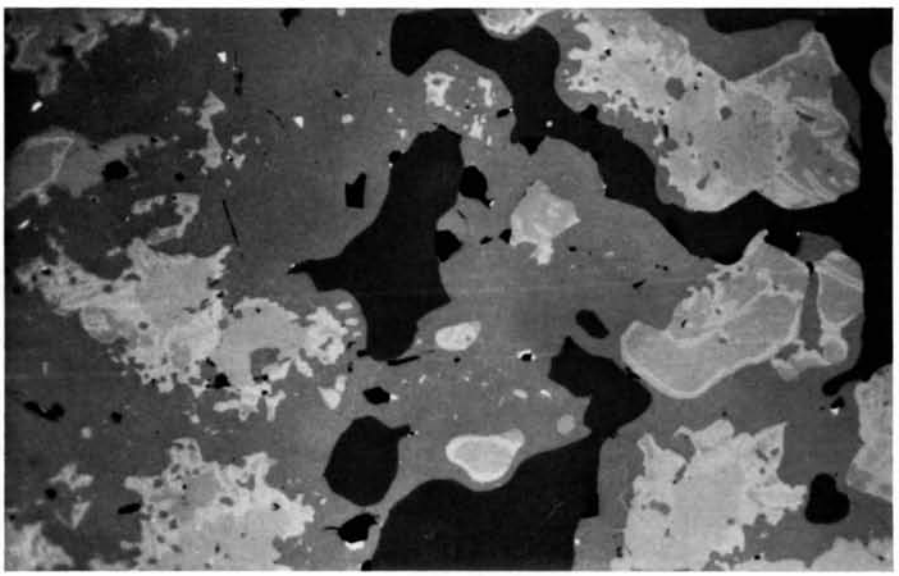

Fig. 1. Photomicrograph of a polished section showing fayalite (dark grey) and magnetite-wustite (light grey) in a matrix of iscorite (medium grey) × 250.

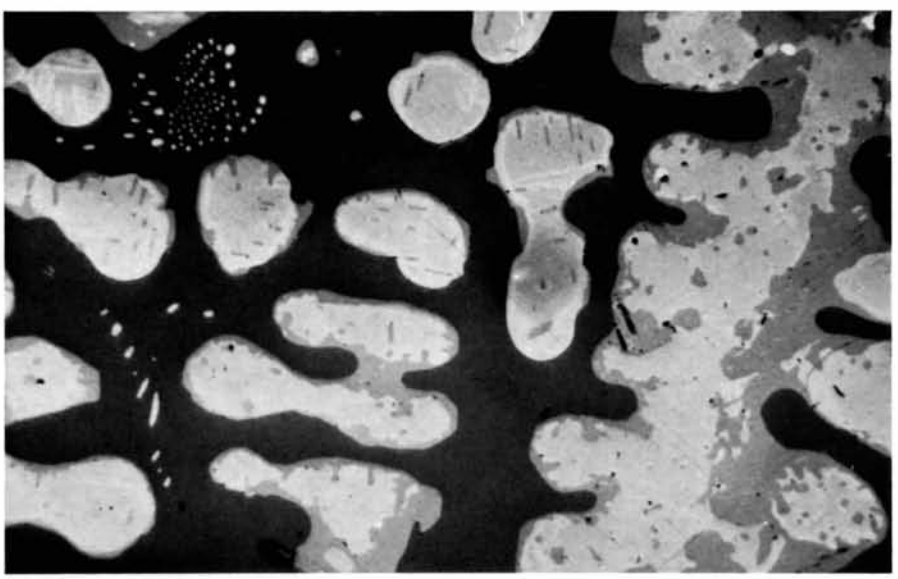

Fig. 2. Photomicrograph of a polished section showing iscorite (medium grey) along the contact between magnetite-wustite units (light grey) and fayalite (dark grey) × 320.

We wish to express our thanks to Dr J. R. Plimmer for supplying the crystals and to Mr P. J. Jutsum for obtaining most of the intensity data.

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The Crystal Structure of an Iron Silicate, Iscorite

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The crystal structure of an iron silicate (Fe_7SiO_{10}), which has been found in material from the floor of a reheating furnace of a steel plant, has been determined by X-ray diffraction methods. The structure is based on a cubic close-packed arrangement of oxygen atoms with ferrous ions in octahedral interstices. Si^{4+} occurs in a tetrahedral environment while Fe^{3+} ions are distributed evenly between octahedral and tetrahedral sites. This structure represents a variety not encountered before.

Introduction

The mineral Fe_7SiO_{10}, for which we propose the name Iscorite, occurs in material from the floor of a reheating furnace of the Pretoria Works of the South African Iron and Steel Industrial Corporation (ISCOR). This furnace is normally kept at a temperature of ~ 1300 °C. Although the refractories used in this type of furnace are supposed to be silica-free (magnesite and chrome-magnesite), the material in which iscorite occurs is rich in silica. It consists mainly of magnetite, wustite and fayalite ($2FeO.SiO_2$). Preliminary crystallographic investigations showed that iscorite was not isomorphous with any of the known silicates (Wyckoff, 1960). Existing phase diagrams of the system Fe–Si–O (Levin, Robbins & McMurdie, 1964; Muan & Osborn, 1964) do not indicate the existence of any phase with which iscorite can be identified. This is probably due to iscorite being formed only under exotic conditions. It has not been synthesized directly as yet. A detailed study of the crystal structure of this mineral was thus undertaken.

Mineralogical properties

The mineral is associated mainly with fayalite, magnetite and wustite. It occurs most commonly in irregularly shaped units (Fig. 1) as well as in narrow zones between crystals of fayalite and magnetite (Fig. 2), and occasionally as lath-shaped crystals. The mineral is opaque to transmitted light. In incident light it is slightly pleochroic and strongly anisotropic. The reflectance pleochroism is from bluish to grey with a brownish tinge and the polarization colours are dark-blue and reddish-brown. Its reflectivity is lower than that of magnetic and wustite, but higher than that of fayalite.

The mineral was extracted magnetically. Although the magnetic susceptibility of iscorite is considerably lower than those of wustite and magnetite, it is only slightly less than that of fayalite. The best recovery was obtained from powders of particle size 15–38 micron which were separated by air elutriation.

The composition was established, by chemical analysis of a material of 98% estimated purity, to be as given in Table 1.

Table 1. *The chemical analysis and calculated composition of an iscorite sample of* 98% *estimated purity*

	Experimental	Theoretical
SiO_2	10·1%	10·3%
Fe^{2+}	47·2	48·3
Fe^{3+}	19·4	19·3
MgO	0·2	–
Cr_2O_3	0·2	–
Al_2O_3	1·3	–

* Mineralogical properties, separation and density measurement.