

The Structure of 4-5 Dimethyl Phthalic Thio-Anhydride

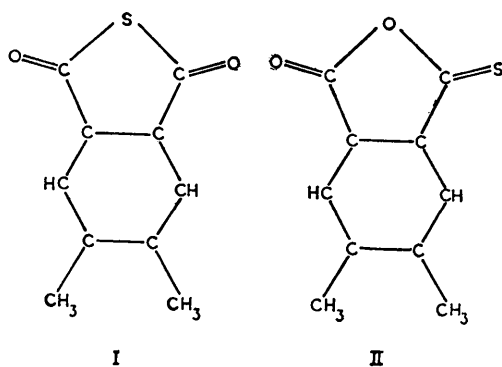
BY W. T. EYLES

Viriamu Jones Laboratory, University College, Cardiff, Wales

(Received 21 December 1955)

The crystal and molecular structure of 4-5 dimethyl phthalic thio-anhydride has been determined by X-ray methods. The lattice parameters are $a = 4.08$, $b = 13.6$, $c = 16.7$ Å, $\beta = 92^\circ$, with an accuracy of $\pm 1\%$. The space group is $P2_1/c$. The positions of the sulphur atoms were derived from Patterson projections, and a trial set of coordinates for the other atoms was obtained from a Buerger minimum function. Limited refinement has been achieved by means of Fourier projections and difference syntheses.

Two chemical formulae, I and II, were originally proposed for 4-5 dimethyl phthalic thio-anhydride, and recently some chemical evidence in favour of I was obtained by Burrows (private communication, 1952). An X-ray investigation was undertaken to decide conclusively which formula is correct.



It was hoped that the distinctive symmetry of I might have been indicated by nothing more elaborate than the determination of the unit-cell dimensions, space group and cell contents, but this was not found to be the case. The substance crystallizes from warm ethanol as needles, elongated along [100] and with the form {011} well developed.

The systematic absences ($0k0$ absent for k odd and $h0l$ absent for l odd) identify the space group uniquely as $P2_1/c$. The lattice parameters are

$$a = 4.08, b = 13.6, c = 16.7 \text{ \AA}, \beta = 92^\circ,$$

with an accuracy of $\pm 1\%$ in each case. The density, calculated on the assumption that there are four molecules per unit cell, is $1.365 \text{ g. cm.}^{-3}$, which agrees with that determined by flotation, $1.348 \text{ g. cm.}^{-3}$.

The relative intensities of $200\ 0kl$ reflexions and $60\ h0l$ reflexions were estimated visually from multiple-film Weissenberg photographs taken with $\text{CuK}\alpha$ radiation. After correction for Lorentz and polarization factors, the intensities were placed on an approx-

imately absolute scale by Wilson's method (Wilson, 1942). No absorption corrections were thought necessary because of the small dimensions of the crystals used.

Among the $h0l$ reflexions the 102 reflexion is outstandingly strong, and it was inferred, therefore, that the molecules lie roughly parallel to the (102) planes. The positions of the sulphur atoms were derived from the [100] (Fig. 1(a)) and [010] Patterson projections. The approximate fractional coordinates of a representative sulphur atom, referred to one of the crystallographic centres of symmetry, were deduced as

$$x = 0, y = 0.145, z = 0.$$

Only the [100] projection of electron density could be expected to yield a well-resolved picture of the structure, but the sulphur atoms are situated so that they make no contribution to $0kl$ reflexions when $k+l$ is odd. No attempt was made, therefore, to determine signs by the heavy-atom method. It was found that with the sulphur atoms in the above positions the permissible orientations of the molecules were severely restricted by packing considerations. These restrictions are such that a structure composed solely of molecules of formula II is not possible, and moreover, in a structure composed solely of molecules of formula I the molecular orientation is confined within narrow limits. A structure composed of both types of molecule is incompatible with the crystal symmetry.

A minimum function (Buerger, 1951) was derived from the [100] Patterson projection shown in Fig. 1(a). The peaks representing vectors between sulphur atoms are marked A , B and C . The vector OA , that between centrosymmetrically related sulphur atoms, was used as the image-seeking vector, and, because it is coincident with \mathbf{b} , the minimum function (Fig. 1(b)) has a mirror plane at $z = 0$ superimposed on the plane-group symmetry of the structure. Despite this, the minimum function was easily interpreted and led to a conclusion closely agreeing with that reached by packing considerations. The contour which shows the

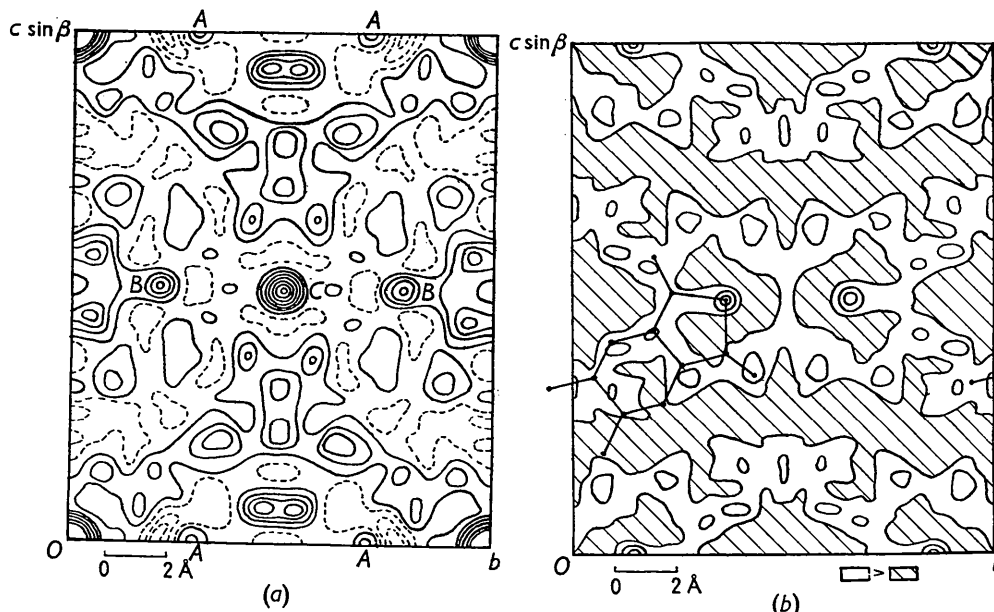


Fig. 1. (a) [100] Patterson projection, arbitrary scale, negative contours broken. (b) Minimum function derived from [100] Patterson projection.

broad outline of the structure is derived from the highest broken contour in Fig. 1(a). The atomic coordinates thus derived were refined by successive Fourier and difference syntheses until the electron-density map shown in Fig. 2 was obtained. At this stage the value of $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ was 0.165 for the 200 observed $0kl$ reflexions. This map establishes that the sulphur atom is incorporated in the five-membered ring.

Refinement of the [010] projection has been hampered by extensive overlapping. The x coordinates were obtained from the [100] projection in the fol-

lowing way. The orientation of the molecule was calculated from the y and z coordinates assuming that the molecule is planar and that the benzene ring is a regular hexagon. Errors in the calculated orientation due to deviations from regularity in the actual benzene ring were assumed to be negligible, though some slight deviations are apparent in the final atomic coordinates. The x coordinates of the atoms in the [010] projection were then adjusted by a Fourier-transform method (Taylor, 1954). The final value of R for the $h0l$ reflexions is 0.26.

The atomic coordinates relative to a centre of symmetry are given in Table 1. Standard deviations were

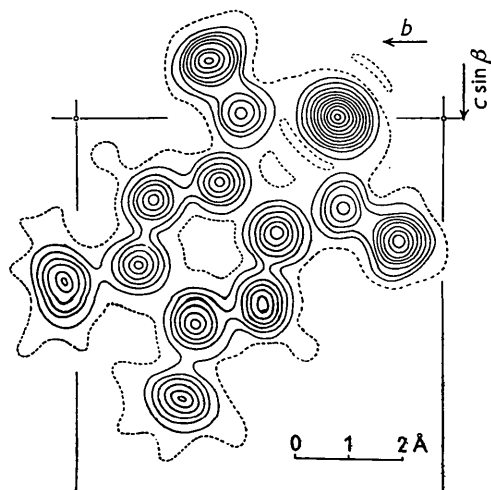


Fig. 2. Electron density projected down [100]. Contours at approximately $1 \text{ e.}\text{\AA}^{-2}$ intervals except at the sulphur atom, where, above $4 \text{ e.}\text{\AA}^{-2}$, they are at $2 \text{ e.}\text{\AA}^{-2}$ intervals. The $1 \text{ e.}\text{\AA}^{-2}$ contour is broken.

Table 1. Atomic coordinates

	X/a	Y/b	Z/c
S	0.120	0.1439	0.9976
O ₁	0.07	0.319	0.935
O ₂	0.95	0.062	0.136
C ₁	0.01	0.276	0.994
C ₂	0.85	0.306	0.070
C ₃	0.74	0.397	0.088
C ₄	0.59	0.416	0.163
C ₅	0.46	0.519	0.184
C ₆	0.40	0.357	0.301
C ₇	0.56	0.339	0.219
C ₈	0.67	0.247	0.201
C ₉	0.82	0.232	0.125
C ₁₀	0.95	0.134	0.099

estimated from the final difference syntheses in accordance with Cruickshank's formula (Cruickshank, 1949). For the sulphur atom $\sigma = 0.005 \text{ \AA}$ for the y and z coordinates and 0.002 \AA for the x coordinates. For the light atoms $\sigma = 0.03 \text{ \AA}$ for the x coordinates and 0.01 \AA for the y and z coordinates. The limited

accuracy of the x coordinates makes it impossible to quote accurate bond lengths and angles. The values calculated from the coordinates given in Table 1 are

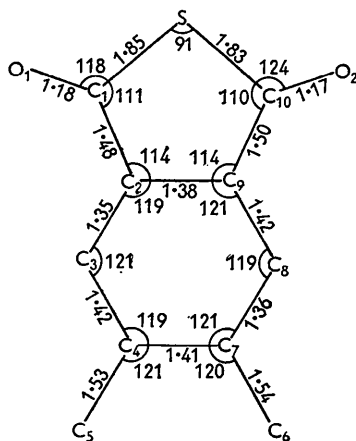


Fig. 3. Bond lengths, in Ångström units. Valence angles in degrees.

shown in Fig. 3. The intermolecular distances are nowhere less than 3.5 Å and are attributable to van der Waals forces. Fig. 2 shows quite clearly the positions of the two hydrogen atoms attached directly to the benzene ring, and there is markedly high electron density in the vicinity of the carbonyl bonds. The significance of the latter detail is, however, doubtful, as the standard deviation for the electron density in this projection is 0.3 e.Å^{-2} and the Fourier synthesis is subject to termination-of-series errors.

I am indebted to Prof. A. J. C. Wilson for guidance and for the use of apparatus purchased with a Royal Society grant, and to Mr G. Burrows for suggesting the problem and supplying the specimens.

References

- BUERGER, M. J. (1951). *Acta Cryst.* **4**, 531.
 CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
 TAYLOR, C. A. (1954). *Acta Cryst.* **7**, 757.
 WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.

Acta Cryst. (1956). **9**, 367

Compounds of Thorium with Transition Metals. II. Systems with Iron, Cobalt and Nickel*

BY JOHN V. FLORIO,† N. C. BAENZIGER‡ AND R. E. RUNDLE

Institute for Atomic Research and Department of Chemistry, Iowa State College, Ames, Iowa, U.S.A.

(Received 30 August 1955)

The compositions of the compounds of thorium with iron, cobalt, nickel and copper have been summarized in a previous paper. Details of the structures of these compounds, together with a brief description of the structure determinations of the new structural types, are given here. Certain relationships among the compounds are noted.

Methods

Studies of powder diagrams of the Th- M systems were made to determine the number and approximate compositions of the compounds stable (or metastable) at room temperature. Single crystals were subsequently found for almost all the observed phases. This was usually most easily accomplished for two-phase material, and seldom was enough strictly one-phase material obtainable to settle compositions precisely by chemical means. Final compositions were decided

by approximate chemical compositions, coupled with atomic volume and space-group considerations, and finally, in most cases, by complete structure determinations. The thermal and microscopic study of the Th-Ni system by Horn & Basserman (1948) is in reasonable agreement with our results.

Except for the Th₇M₃ compounds, described below, data were collected with Weissenberg cameras and copper radiation or precession cameras and molybdenum radiation. Intensities were estimated visually using multiple films for copper radiation and timed exposures for molybdenum. In the latter case a G. E. XRD-3 diffraction unit with current and voltage stabilization was used as an X-ray source.

Absorption was inevitably a complicating factor in these studies, especially since crystal fragments isolated from alloys often had peculiar shapes and were

* Contribution No. 425. Work was performed in part in the Ames Laboratory of the Atomic Energy Commission, and in part for the Manhattan Project.

† Present address: Sylvania Electric Products, Inc., Mineola, Long Island, N.Y., U.S.A.

‡ Present address: Department of Chemistry, State University of Iowa, Iowa City, Iowa, U.S.A.