Studies on Heterocyclic Compounds. *X*-Ray Crystal Structure of a Novel Addition Product of Benzothiazole and Dimethyl Acetylenedicarboxylate

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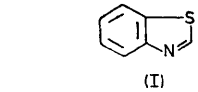
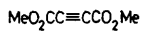
Summary From the cycloaddition of benzothiazole to dimethyl acetylenedicarboxylate, an abnormal addition product, dimethyl 4-formyl-2,3di-hydrobenzothiazine-2,3-dicarboxylate, was obtained; the structure of this compound was confirmed by an *X*-ray analysis.

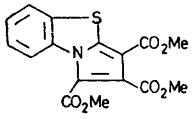
THERE is much confusing evidence[1,2] on the reaction products of benzothiazole (I) and dimethyl acetylenedicarboxylate II. Reid *et al.*[1] reported without giving spectral data that (III), m.p. 135—136°, was obtained from the reaction of (I) and (II) in methanol at room temperature.



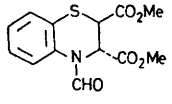
(I)



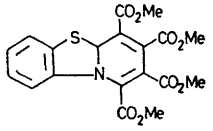
(II)



(III)



(IV)



(V)

We have re-examined the same reaction and obtained (IV), m.p. 135—136°. The structure of this compound was confirmed by ^1H and ^{13}C n.m.r., i.r., and mass spectra,[3] and the structure was further supported by an *X*-ray diffraction analysis.

Reaction of (I) with 2 molar equivalents of (II) in methanol at room temperature afforded (IV) (8%) accompanied by the known compound (V) (5%).[2]

The crystals of (IV) were obtained from ethanol as colourless needles, m.p. 135—136°. The crystals are triclinic, $a = 8{\cdot}11_6$, $b = 11{\cdot}17_2$, $c = 7{\cdot}97_5$ Å, $\alpha = 85{\cdot}0_4$, $\beta = 109{\cdot}7_9$, $\gamma = 99{\cdot}6_5°$; $Z = 2$, space group $P\bar{1}$.

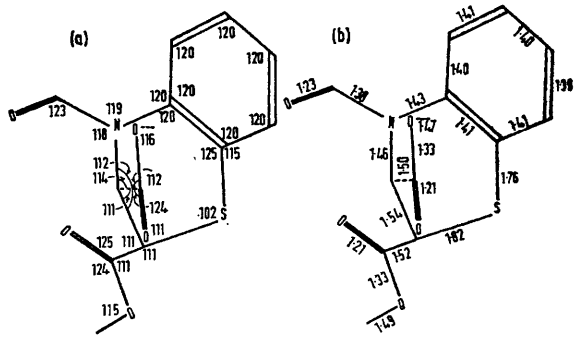


FIGURE. Crystal structure of (IV), (a) bond angles (°), (b) bond lengths (Å).

Intensity data were collected on a Philips 4-circle automatic diffractometer using monochromated Cu-K_α radiation ($\lambda = 1{\cdot}5418$ Å). A total of 2574 independent structure factors out of 2853 theoretically possible ones were obtained. The structure was solved by the heavy-atom method and refined by full-matrix least-squares to $R = 0{\cdot}089$. The structure of the molecule is shown in the Figure.

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[2] R. M. Acheson, M. W. Foxton, and G. R. Miller, *J. Chem. Soc.*, 1965, 3200.
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