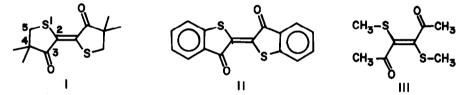
THE CRYSTAL STRUCTURE OF A MODEL FOR THE THIOINDIGO CHROMOPHORE. Δ<sup>2,2<sup>1</sup></sup>-BIS(4,4-DIMETHYLTHIOLAN-3-ONE) By Heinrich J. A. Hermann,\* Herman L. Ammon and Raymond E. Gibson Division of Natural Sciences, University of California Santa Cruz, California 95060

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In connection with investigations of the structure-color relationship in indigo dyes (1,2) the title compound (I) was synthesized (3) and found to have chemical and physical properties similar to those of thioindigo (II) (4). It was postulated (1) that a mesomeric interaction



of sulfur in one 5-membered ring with the carbonyl group in the other ring, through the central double bond, was primarily responsible for the basic thioindigo chromophore. Furthermore, differences in the electronic spectra and properties of I and III were attributed to steric interactions between the methyl groups of III, causing a loss of planarity in the sulfur-carbonyl moiety and hence a significant decrease in sulfur-carbonyl mesomeric stabilization of the ground state.

We have undertaken an X-ray crystallographic investigation of I to gain an insight into the extent of mesomeric interaction and to establish the conformation of the molecule. Our preliminary results are reported in this communication. (I) crystallizes from benzene as light yellow, hexagonal plates in the monoclinic space group  $P2_1/c$ . Unit cell parameters are  $\underline{a} = 10.91$ ,  $\underline{b} = 5.40$ ,  $\underline{c} = 11.56$  Å,  $\underline{\beta} = 113.3^{\circ}$ . Crystal density measurements gave two molecules per unit cell and indicated that each molecule must occupy a crystallographic center of symmetry (coincident with the center of the C(2)-C(2<sup>t</sup>) bond). Three-dimensional diffraction data were collected with a

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Weissenberg camera ( $CuK_{\Omega}$  radiation) and the film intensities were measured with a microdensitometer. The structure was solved with the symbolic addition procedure and has been refined with full matrix least-squares to an R index of 0.075.

Coplanarity of the central six atoms, S-C(2)-C(3)-S'-C(2')-C(3'), is guaranteed by the special position of the molecule; the two carbonyl oxygens deviate slightly (0.11 Å) from this plane. The short S-C(2) (1.734 Å)\* and long C(2)-C(2') (1.380 Å) bond lengths suggest an appreciable mesomeric interaction involving sulfur and the central double bond. The C(2)-C(3) and C(3)-O distances (1.480, 1.221 Å), which are normal for these kinds of bonds, give no evidence for a sulfur-carbonyl interaction through the ethylenic linkage.\*\* These data could indicate that a sulfur to sulfur interaction via the central double bond makes an important mesomeric contribution to the ground state of L The carbonyl group may be necessary for the operation of this mechanism since a short S...O intramolecular distance (2,850 Å) is observed (the sum of the van der Waals radii for sulfur and oxygen is 3.25 Å).\*\*\* Several other compounds which are germane to these ideas are now being investigated.

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<sup>\*</sup> The brevity of this bond becomes striking when it is compared with the S-C(5) distance of 1.830 Å.

<sup>\*\*</sup> Bond lengths reported (5) for the S-C=C-C=0 moiety in 2-acetyl-2-methyl-4-(1-methylacetonylidene)-1,3-dithiacyclobutane (S-C = 1.718, C=C = 1.377, C-C = 1.441, C=O = 1.271 Å) suggest that a sulfur-oxygen mesomeric interaction is important in the ground state. The absence of such an effect can be seen in 2,4-diphenacylidene-1,3-dithiacyclobutane (6) (S-C = 1.765, C=C = 1.324, C-C = 1.462, C=O = 1.216 Å).

<sup>\*\*\*</sup> This is a further example of short, non-bonded distances between sulfur and oxygen atoms constrained to 5-membered rings (5).