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The First Dithiono Derivative of an Indigoid System

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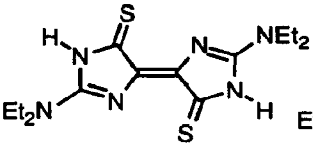
Abstract: X-ray crystallographic analysis reveals that 2,6-bis-diethylamino-3,4,7,8-tetrahydro-1,3,5,7-tetraaza-fulvalene-4,8-dithione **3** is the first dithiono derivative of an indigoid system.

The outstanding properties of indigo as a dye and prototype of a cross-conjugated π-electron system have caused numerous investigations leading among other things to the basic indigo chromophore.[1] Dithiono derivatives of indigoid compounds are expected to absorb at longer wavelengths than indigo but to the best of our knowledge compounds of this sort have never been synthesized up to now. The preparation of dithionothioindigo has been reported in 1969.[2] It has been shown later, however, that the correct structure was that of a 1,2-dithiine derivative[3] which is stabilized as a consequence of the resonance energy of the thiophene rings.

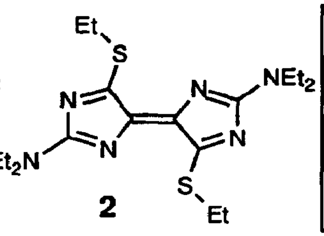
In 1990 we reported on the synthesis of the dithiono derivative **1** of an imidazole isoindigo.[4] The trans-isoindigoid structure of **1** was derived from the fact that **1** could be alkylated to produce the tetraazafulvalene derivative **2**. Only recently we were in a position to obtain single crystals of **1** (or **3**, for that matter. The X-ray crstallographic analysis shows that the compound has the indigoid structure **3**. The unit cell (figure 1) contains two molecules of **3** in a centrosymmetrical arrangement. In contrast to, e. g., N,N'-dimethylindigo the central C=C bond of **5** is neither twisted or folded.

The almost identical lengths of the bonds C3-N1 (135.4 pm) and C3-N2 (135.4 pm) are indicative of a strong resonance interaction in the guanidine moiety of the imidazole rings.The central C=C bond (132.7 pm) is somewhat shorter than that of indigo (137.0 pm)[5].

In conclusion, the structure of **3**, the first dithiono derivative of an indigoid system, proves that the formation of valence isomers of indigoid compounds (C=O replaced by: C=S → 1,2-dithiines,[3]



1



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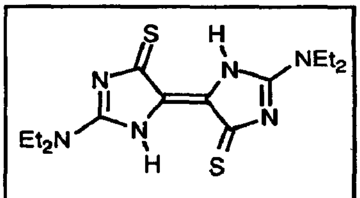

3

C=NR → dihydropyridazines, C=CR$_2$ → cyclohexadienes) depends on the aromaticity of the heterocyclic rings (benzothiophene, indole, imidazole etc.) that are formed in the process.

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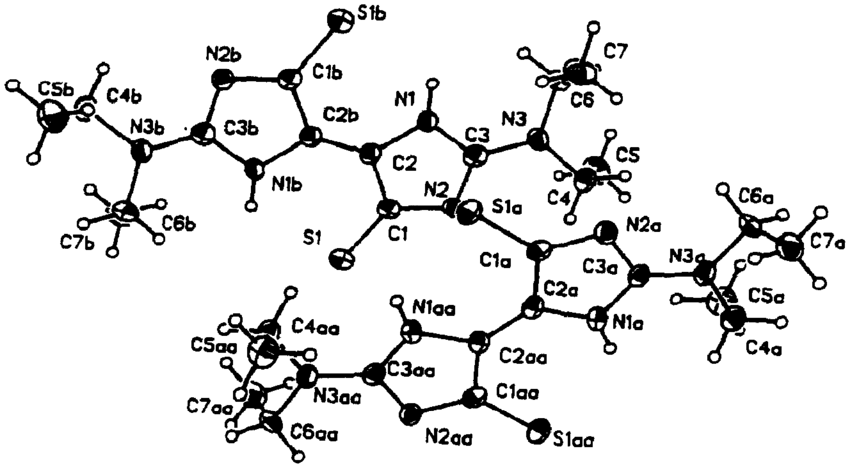

Fig. 1 Structure of **5** in the crystal (ORTEP).[6] Selected bond lengths [pm] and angles [°]: C1-S1 165.3(4), C1-N2 136.1(5), C1-C2 148.7(4), C2-C2b 132.7(8), C3-N1 135.4(5), C3-N2 135.6(4), C3-N3 132.3(5); C1-C2-C2b 129.2(4), N1-C2-C2b 126.4(4), C1-N2-C3 106.3(3), N1-C2-C1 104.3(3), N1-C3-N2 112.9(4), C2-N1-C3 108.0 (3), N2-C1-C2 108.3(3).

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6 Crystal data for **5**: $C_{14}H_{22}N_6S_2$, M = 338.50, monoclinic, space group $P2_1/n$, a = 1062.5(2), b = 1252.5(3), c = 1406.4(4) pm, β = 111.09(2)°, V = 1.7463 nm^3, Z = 4, D_c = 1.287 g cm^{-3}, μ (Mo-K$_\alpha$) = 2.974 cm^{-1}, $2\Theta_{max}$ = 4-46°, ω-scan, crystal dimensions 0.13 × 0.13 × 0.10 mm, maximum measuring time 180 s. Enraf-Nonius CAD4 diffractometer. 2677 measured (±h, +k, +l), 2176 independent reflections, 1774 classed as observed [$I > 2\sigma(I)$]; refined parameters: 199. Solution of structure: SHELXS-86, refinement with SHELXTL-PLUS. R = 0.0408, R_W = 0.0406; largest residual electron density ρ = +0.25/-0.23 e pm^{-3} 10^6. - Supplementary material on the X-ray structure determination are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-58706, the names of the authors and the journal citation.

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