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Reactions of 5-Methyl-6-thioxo-5,6,11,12-tetrahydrodibenzo[*b*,*f*]azocin-12-one and a Novel Rearrangement to a Hydroximino-isothrochromene

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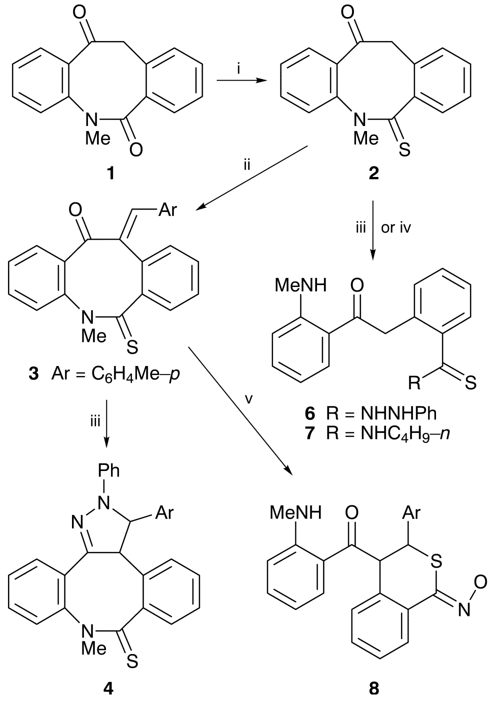
The synthesis of dibenzazocinone **2** and several of its reactions are described, including formation of a benzylidene derivative **3**, which with hydroxylamine undergoes a novel rearrangement to give the methanone **8**.

The multifunctional dibenzacocine **1** has been found to take part in rearrangement reactions to produce a wide variety of novel heterocycles.[1] We now report the synthesis of the azocinone **2**, the thioamide analogue of **1**. In an endeavour to synthesise novel sulfur-containing heterocyclic compounds the azocinone **2** has been subjected to a variety of reactions which are based on those reported for **1** and its derivatives.

The synthesis of **2** was achieved in good yield by treating dibenzazocine **1** with Lawesson's reagent as shown in Scheme 1 and its structure determined from spectroscopic data. With 4-methylbenzaldehyde and sodium ethoxide, the benzylidene derivative **3** was formed, and its stereochemistry shown to be (*E*) from the $^3J_{\mathrm{CO,H}}$ coupling constant.[3] When **2** was treated with phenylhydrazine, thioamide cleavage occurred to give **6**; similarly, **2** reacted with *n*-butylamine to give **7**, revealing the greater reactivity in these reactions of the thiocarbonyl (thioamide) relative to the ketone.

Treatment of the derivative **3** with phenylhydrazine gave the not unexpected pyrazolodibenzazocine **4** from a condensation reaction. Treatment of the benzylidene **3** with hydroxylamine, however, gave a (1 + 1) adduct, with spectra showing that a reaction quite different from a simple condensation had occurred. As no single structure for the adduct could be deduced from the known chemistry of thioamides, and because of the high proportion of groups containing elements which could not be identified from spectroscopy (*viz.* N_2O_2S), a single crystal X-ray structure determination (Fig. 1) was carried out, which revealed the structure to be **8**.



Scheme 1 *Reagents and conditions*: i, $P_2S_4(C_6H_4OMe\text{-}p)$, 76%; ii, ArCHO, NaOEt, 60%; iii, $PhNHNH_2$, 100 °C, 54% for **4**, 34% for **6**; iv, $n\text{-}C_4H_9NH_2$, reflux, 20% for **7**; v, $NH_2OH{\cdot}HCl$, pyridine, reflux, 37%

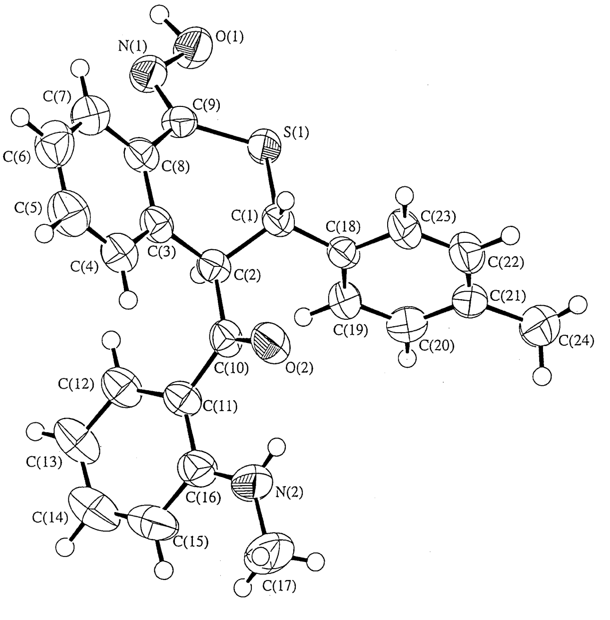


Fig. 1 ORTEP diagram of the molecular structure with crystallographic numbering scheme for **8**

Data Collection and Processing.—Rigaku AFC7R diffractometer, ω–2θ scan, scan width $(0.73 + 0.35 \tan\theta)^\circ$, $4 < 2\theta < 45^\circ$, h: $0 \rightarrow 30$, k: $\rightarrow 5$, l: $-30 \rightarrow 30$; graphite-monochromated Mo-Kα radiation; 3058 unique reflections measured, giving 1754 with $I > 3\sigma(I)$.

Structure Analysis and Refinement.—A direct method (SIR92) was employed.[5] A full-matrix least-squares refinement on F (TEXSAN)[6] was carried out with all non-hydrogen atoms anisotropic, H(1) bonded to O(1), and H(2) bonded to N(2) positional parameters, and other hydrogen atoms in calculated positions using the riding model with $B_{\mathrm{iso}}(\mathrm{H}) = 1.3\,B(\mathrm{eq})$ for the attached atom. The final $R = 0.046$ and $wR = 0.056$ for 1754 data, GOF = 2.00, and maximum residual electron density was 0.27 e$\mathrm{\AA}^{-3}$. An ORTEP[7] drawing of the molecule is shown in Fig. 1.

Crystal Data.—$C_{24}H_{22}N_2O_2S$, $M_r = 402.5$. Monoclinic, $a = 28.445(5)$, $b = 5.177(6)$, $c = 28.209(6)$ Å, $\beta = 93.86(2)^\circ$, $V = 4114(3)$ Å, $\lambda = 0.71073$ Å, space group $C2/c$ (no. 15), $Z = 8$, $D_x = 1.290$ g cm^{-3}. Yellow prisms, dimensions $0.15 \times 0.15 \times 0.35$ mm, $\mu(\text{Mo-K}_\alpha) = 1.79$ cm^{-1}.

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Techniques used: ^{1}H and ^{13}C NMR, mass spectrometry, IR, X-ray diffraction

References: 7

Schemes: 1

Figure: 1

Supplementary material: Tables of atomic coordinates and anisotropic displacement parameters, bond lengths and angles, structure factors, and a packing diagram

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