

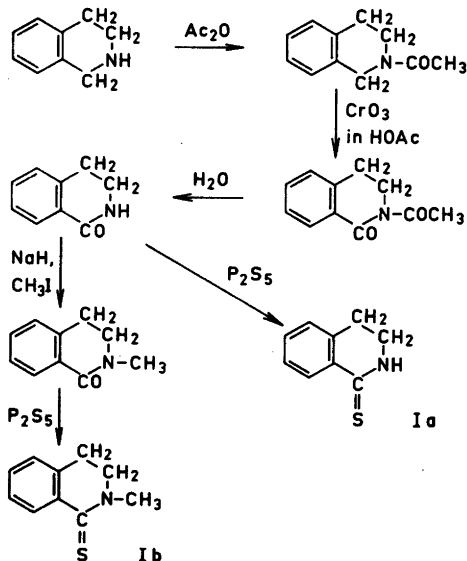
The Electronic Spectra of Thioamides and Thiohydrazides

Part VII.* 1,2,3,4-Tetrahydroisoquinoline-1-thiones

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In Part I of this series,¹ it was shown that successive hypsochromic shifts of the $n \rightarrow \pi^*$ and the $\pi \rightarrow \pi^*$ bands of the thio-benzamides occurred when first one and then two methyl groups were introduced on the nitrogen atom. It was proposed that this was due to a departure from coplanarity caused by interference between the methyl groups and the ring hydrogen atoms. In the hope of demonstrating this effect more firmly, the ultraviolet-visible spectra of 1,2,3,4-tetrahydroisoquinoline-1-thione, Ia, and its N-methyl derivative, Ib, have now been investigated. These compounds have been synthesized by the following reaction path:



The structure of the oxidation product was demonstrated by its PMR spectrum,

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which shows a singlet for the acetyl protons at $\delta = 2.66$ and two triplets for the adjacent CH_2 groups at $\delta = 2.97$ and 4.22 with $J = 7$ cps. The aromatic protons give signals in the region 7.2–8.2 ppm. Also for the other compounds the PMR spectra are in complete agreement with the assigned structures.

In Ia and Ib the chromophoric system will be forced to near-coplanarity by the ring closure, and this was found to have a considerable influence on the absorption spectrum.

In non-polar solvent the $n \rightarrow \pi^*$ band appeared at somewhat shorter wavelength in Ia than in thio-benzamide, whereas the reverse was found for Ib. The effect on the $\pi \rightarrow \pi^*$ bands was more striking. In the spectrum of thio-benzamide the first strong absorption band at 298 nm is a doublet, which was explained as slight vibrational fine structure.¹ However, it is more likely that it is due to two close lying electronic transitions, since in the spectra of Ia and Ib it is split into two bands, one displaced 25–30 nm towards longer wavelengths, the other remaining close to the previous position. This bathochromic shift of the $\pi \rightarrow \pi^*$ band gives strong support to the hypothesis of a steric effect in thio-benzamides. However, the series thio-benzamide, Ia, Ib, does not show exactly the same order of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands as the series thioacetamide (IIa), N-methylthioacetamide (IIb), and N,N-dimethylthioacetamide (IIc), which has the order IIb, IIc, IIa for the $n \rightarrow \pi^*$ transitions and IIb, IIa, IIc for the $\pi \rightarrow \pi^*$ transitions.^{1,2} The differences in the band positions are small, however, and the divergences may well be due to the difference in hyperconjugating ability of the methyl and methylene groups, and also to the interplay between these groups and the phenyl ring.

The effect of changing the solvent from heptane to ethanol is the same as for the thio-benzamides described in Ref. 1, *i.e.* hypsochromic shifts of both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands. In the series thio-benzamide, N-methylthio-benzamide, N,N-dimethylthio-benzamide an increase in oscillator strength of the $n \rightarrow \pi^*$ band was observed, and this was ascribed to the increasing departure from coplanarity between the thioamide group and the benzene ring, which caused an increased mixing of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.¹ In the spectra of Ia and Ib, the $n \rightarrow \pi^*$ bands are

Compound	Solvent	$n \rightarrow \pi^*$		$\pi \rightarrow \pi^*$					
		λ_{\max} nm	log ϵ	λ_{\max} nm	log ϵ	λ_{\max} nm	log ϵ	λ_{\max} nm	log ϵ
Ia	Heptane	412	2.06	328.5	3.84	303	3.74	259	3.97
	Ethanol	395sh	2.2	326	3.85	302.5	3.79	260	3.97
Ib	Heptane	425	2.09	323	3.81	299	3.71	258	4.04
	Ethanol	395	2.22	317.5	3.85	299.5	3.87	261	4.04

weaker than in thiobenzamide, which is also in agreement with the theory.

Experimental. 1,2,3,4-Tetrahydroisoquinoline (50 g) and acetic anhydride (82 g) were refluxed for 1 h. Acetic acid and remaining anhydride were removed *in vacuo*, and then the product distilled at 3 Torr, 152°C. The product (54.3 g, 82 % yield) was a colourless crystalline solid, m.p. 26–27°, consisting of *N*-acetyl-1,2,3,4-tetrahydroisoquinoline. (Found: C 74.8; H 7.37; N 8.07. $C_{11}H_{13}NO$ (175.25) requires C 75.4; H 7.49; N 7.99). A solution of this compound (31.2 g) in glacial acetic acid (450 ml) was kept at 0°, and chromic trioxide (24.2 g) was added in portions with stirring during 2 h. After 48 h the acetic acid was evaporated, and the residue was dissolved in hot water (500 ml). On cooling, colourless crystals separated (18.6 g, 55 % yield), which crystallized from heptane as colourless plates, m.p. 99–100°, of *N*-acetyl-1,2,3,4-tetrahydroisoquinolone-1. (Found: C 69.3; H 5.86; N 7.55; O 17.2. $C_{11}H_{11}NO_2$ (189.23) requires C 69.8; H 5.87; N 7.40; O 16.9). The crude acetyl derivative (58.7 g) and aqueous N NaOH (400 ml) were refluxed with ethanol (1400 ml) for 15 min. The filtered solution was evaporated to about 100 ml volume, and then extracted with three portions of chloroform (200 ml each). Evaporation of the chloroform gave a solid residue (43.6 g, 95 % yield), which crystallized from a mixture of carbon tetrachloride and light petroleum (b.p. 40–60°) as colourless plates, m.p. 67–68°, of 1,2,3,4-tetrahydroisoquinolone-1 (Found: C 73.2; H 6.13; N 9.51; O 11.1. C_9H_9NO (147.19) requires C 73.4; H 6.18; N 9.52; O 10.9) This amide (3.0 g) and phosphorus pentasulphide (4 g) were refluxed in toluene (100 ml) for 2 h. The solution together with a toluene extract of the undissolved residue, was subjected to chromatography on activated silica. Elution with ether gave a solid product (1.1 g, 33 % yield), which crystallized from toluene-heptane as pale yellow prisms, m.p.

97–98°, of 1,2,3,4-tetrahydroisoquinoline-1-thione (Ia). (Found: C 66.2; H 5.65; N 8.56; S 19.7. C_9H_9NS (163.23) requires C 66.2; H 5.56; N 8.58; S 19.6).

Tetrahydroisoquinolone-1 (31.3 g) was added in portions to a suspension of sodium hydride (5.1 g) in dry toluene (700 ml) during 15 min. Then the mixture was refluxed for 40 min, and after cooling methyl iodide (36.3 g) was added with stirring during 15 min. After refluxing for 1 h, the solution was filtered and evaporated, and the product was distilled at 2 Torr, 140°C (25.2 g, 74 % yield). Final purification was performed by chromatography on activated silica (elution with benzene:ether in the proportions 4:1) followed by distillation at 1 Torr and 132°C. The *N*-methyl-1,2,3,4-tetrahydroisoquinolone-1 was obtained as a colourless, hygroscopic liquid. (Found: C 73.5; H 6.88; N 8.39; O 10.6. $C_{10}H_{11}NO$ (161.22) requires C 74.5; H 6.89; N 8.69; O 9.92).

The crude *N*-methyl derivative (18 g) and phosphorus pentasulphide (18 g) were refluxed in toluene (180 ml) for 3 h. The solution and a toluene extract of the residue were evaporated, and the solid residue (13.4 g, 68 % yield) crystallized from methanol as bright yellow needles, m.p. 93–93.5° after two recrystallizations, consisting of *N*-methyl-1,2,3,4-tetrahydroisoquinoline-1-thione (Ib). Found: C 67.6; H 6.22; N 7.99; S 18.2. $C_{10}H_{11}NS$ (177.29) requires C 67.8; H 6.27; N 7.91; S 18.1).

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