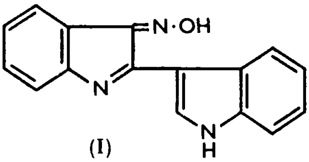
703. *Indoles. Part III.* The Structure of Zatti and Ferratini's " Dinitrosoindole."*

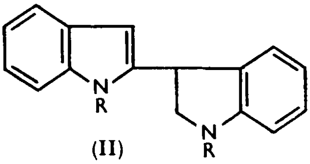
By H. F. Hodson and G. F. Smith.

Structure (IV) is proposed for " dinitrosoindole," mainly on the basis of ultraviolet spectra.

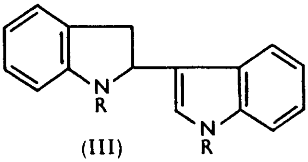
Nitrosation of indole in aqueous acetic acid, first studied systematically by Zatti and Ferratini in 1890,[1] proceeds in a complex manner to yield a very dark tar from which two compounds can be isolated : one is indole red, shown by Seidel [2] in 1944 to have structure (I), and the other is an almost colourless compound shown [3] to be $C_{16}H_{12}O_2N_4$ and called " dinitrosoindole." It is different from the deep yellow dinitrosoindole dimer prepared by Schmitz-DuMont *et al.*[4] by the nitrosation of indole dimer and formulated by them as (II; R = NO). Seidel[2] found that "dinitrosoindole" decomposes in pyridine solution to indole red (I) : this indicated the presence in " dinitrosoindole " of an αβ-di-indolyl skeleton, and led Seidel to propose the alternative structure (III; R = NO) for the compound. Indole dimer having been shown to have structure (III; R = H) (see preceding paper), the structure of its dinitroso-derivative must be (III; R = NO), that already given to " dinitrosoindole " by Seidel. This reopens the question of the structure of Zatti and Ferratini's " dinitrosoindole."



(I)

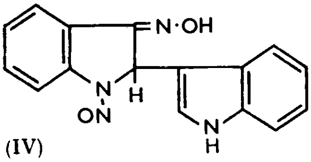


(II)

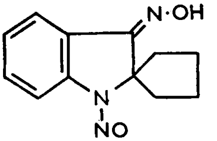


(III)

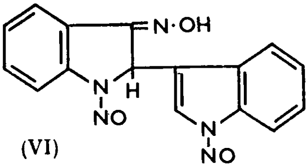
That " dinitrosoindole " cannot have structure (II; R = NO) is immediately shown by the strong and complex absorption this compound shows in the NH and OH stretching region of the infrared spectrum. It is profitable also to consider ultraviolet spectra : both compounds (II; R = NO) and (III; R = NO) contain unconjugated *N*-nitrosoindole and *N*-nitrosoindoline chromophores, and one would expect their ultraviolet spectra to be very similar.† The ultraviolet spectra of dinitrosoindole dimer and of " dinitrosoindole " are in fact markedly different (Fig. 1, curve *a*; Fig. 2, curve *a*). It was at this



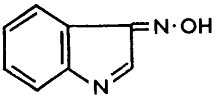
(IV)



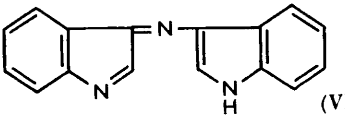
(V)



(VI)



(VII)



(VIII)

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* Part II, preceding paper.

† One of the Referees has drawn our attention to the fact that hyperconjugation through a saturated carbon atom (CH_2) has been found to affect ultraviolet absorption (Braude, *J.*, 1949, 1902). The effect is, however, only a minor one and for our purposes negligible.

[1] Zatti and Ferratini, *Ber.*, 1890, **23**, 2299.

[2] Seidel, *Ber.*, 1944—1946, **77—79**, 797.

[3] Zatti and Ferratini, *Gazzetta*, 1892, **21**, 19.

[4] Schmitz-DuMont, Hamann, and Geller, *Annalen*, 1933, **504**, 1.

stage found that a sum of the ultraviolet spectra of *N*-nitrososkatole and of 1-nitroso-2-methylindoline is very similar indeed to the spectrum of dinitrosoindole dimer (Fig. 1). From this it is clear that the deep yellow colour of dinitrosoindole dimer is due to the *N*-nitrosoindole system present in it.

That " dinitrosoindole " is colourless suggests that it does not contain an *N*-nitrosoindole system : this, and the formation of indole red (I) from it under mild conditions,[2] can be accounted for satisfactorily only by structure (IV). This view is supported by the fact that the sum of the ultraviolet spectra of cyclopentane*spiro*-2-(3-hydroxyimino-1-nitrosoindoline) (V) and skatole corresponds very closely to the spectrum of " dinitrosoindole " (Fig. 2). Further, we have found that " dinitrosoindole " forms a yellow nitroso-derivative which must have structure (VI) : in accord with this its ultraviolet spectrum is closely similar to the sum of the spectra of (V) and *N*-nitrososkatole (Fig. 3).

FIG. 1. FIG. 2.

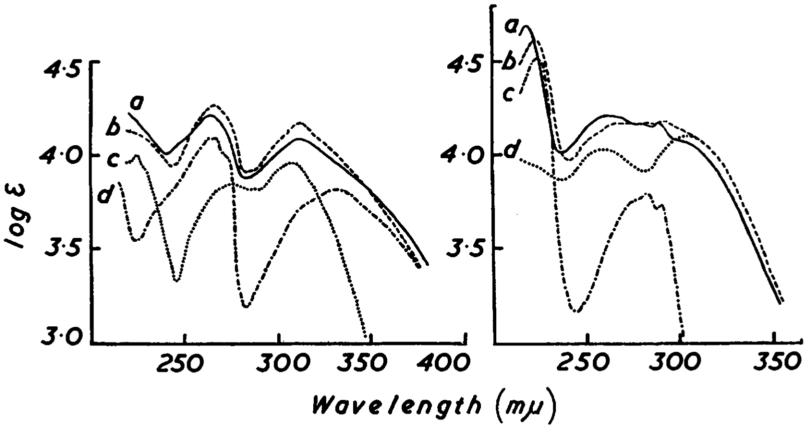

FIG. 1. *a, Dinitrosoindole dimer* (III; R = NO) *in* n-*hexane; b, sum of c and d; c, 2-methyl-*1-*nitrosoindoline in* n-*hexane; d,* N-*nitrososkatole in* n-*hexane.*

FIG. 2. *a, " Dinitrosoindole "* (IV); *b, sum of c and d; c, skatole; d,* cyclo*pentane*spiro-2-(3-*hydroxyimino*-1-*nitrosoindoline*) (V). *All in* EtOH.

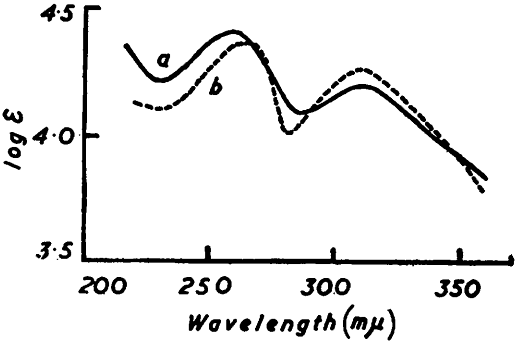

FIG. 3. *a, Nitroso-derivative of " dinitrosoindole "* (VI) *in* EtOH; *b, sum of* cyclo*pentane*spiro-2-(3-*hydroxyimino*-1-*nitrosoindoline*) (V) *in* EtOH *and* N-*nitrososkatole in* n-*hexane.*

To test the idea that " dinitrosoindole " (IV) is formed by acid-catalysed condensation of initially formed hydroxyiminoindolenine (VII) with indole, we studied the interaction of these two compounds in aqueous acetic acid. The only isolable product was a deep blue crystalline compound, $C_{18}H_{15}O_2N_3$, which is probably the acetate of di-3-indolylazamethine (VIII) : such a condensation of a hydroxyimino-group with a reactive position is well known in the formation of indophenols; a closer analogy is found in the formation of dipyrrylazamethines by condensation of nitrosopyrroles with pyrroles in acetic acid.[5]

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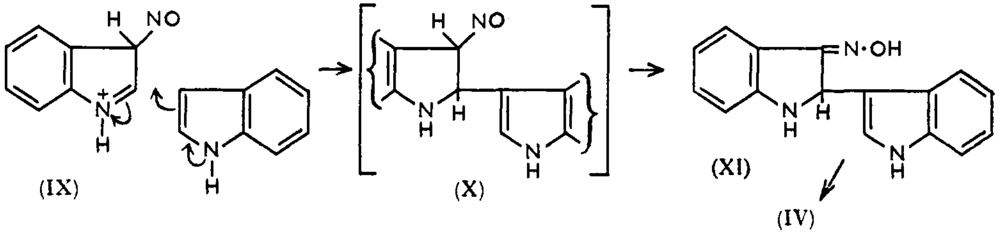
[5] Rogers, *J.*, 1943, 590.

It is evident, therefore, that " dinitrosoindole " (IV) is not formed by way of (VII); it is therefore likely that it is the immediate product of addition of a nitrosonium ion to indole (IX), which gives (X), which then rearranges to (XI), and is further nitrosated to " dinitrosoindole " (IV).

N-Nitrososkatole had previously been inadequately characterised:[6] we have now obtained it as a homogeneous product, m. p. 10—12°, which gives correct analyses.



EXPERIMENTAL

M. p.s are corrected.

N-*Nitrososkatole.*—To a solution of skatole (1·3 g.) in 90% aqueous acetic acid (12 c.c.) at 0° was added, dropwise and with swirling, a solution of sodium nitrite (2·0 g.) in water (4 c.c.) at 0°. The mixture was allowed to warm to room temperature during 15 min. and was poured into excess of cold saturated aqueous sodium hydrogen carbonate. The whole was extracted with *n*-pentane, the extracts were washed with 95% methanol (2 × 10 c.c.) and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was pure N-*nitrososkatole*, a yellow, very unstable, viscous liquid crystallising at 0° to a solid, m. p. 10—12° (Found: C, 67·5; H, 4·6. $C_9H_8ON_2$ requires C, 67·5; H, 5·0%), $\lambda_{max.}$ 264, 329—334 mμ (ε 12,560, 6515) in *n*-hexane.

cyclo*Pentane*spiro-2-(3-*hydroxyimino*-1-*nitrosoindoline*) (V).—*cyclo*Pentane*spiro*-2-(3-hydroxyiminoindoline)[7] (350 mg.) in methanol (5 c.c.) was added to a solution of sodium nitrite (160 mg.) in water (1 c.c.) and the solution cooled to 0°. 2N-Hydrochloric acid (1 c.c.) was added dropwise and the whole left at 0° for 30 min. On dilution with water and scratching, the *nitroso-compound* separated as very pale yellow prisms (312 mg., 78%), m. p. 110—113°, unchanged by recrystallisation from aqueous methanol or light petroleum (Found: C, 62·5; H, 5·5; N, 17·9. $C_{12}H_{13}O_2N_3$ requires C, 62·3; H, 5·67; N, 18·2%), $\lambda_{max.}$ 259—262, 305 mμ (ε 10,800, 12,600) in EtOH.

3-*Hydroxyimino*-1-*nitroso*-2-(1-*nitroso*-3-*indolyl*)*indoline* (VI).—To a solution of " dinitrosoindole " (500 mg.) in dimethylformamide (6 c.c.) and 95% aqueous acetic acid (6 c.c.) at 0° was added sodium nitrite (350 mg.) in water (1 c.c.). The whole was left at 0° for 1 hr., then poured into ice-water (100 c.c.), and the precipitated solid filtered off. This ochre-yellow powder (480 mg.) was digested with warm benzene (30 c.c.) for a short time, then filtered. The benzene was boiled off from the filtrate under reduced pressure, and the reddish residue (260 mg.) dissolved in ethanol (4 c.c.) at 50°: on cooling to 0°, the solution deposited the *nitroso-compound* (173 mg.) as a yellow crystalline powder, decomp. 130—132°, unchanged by further crystallisation (Found: C, 59·9; H, 3·8; N, 21·3. $C_{16}H_{11}O_3N_5$ requires C, 59·8; H, 3·5; N, 21·8%).

The work was carried out during the tenure of a grant from the Schunck Fund of the University of Manchester (to H. F. H).

THE UNIVERSITY, MANCHESTER. [*Received, April 12th*, 1957.]

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[6] Fischer, *Annalen*, 1886, **236**, 140.
[7] Beer, McGrath, and Robertson, *J.*, 1950, 2126.