THE SPECTRA OF 3-OXO-2, 3-DIHYDROTHIANAPHTHENE AND ITS DERIVATIVES.

X. Some Aliphatic Indogenides*

M. A. Mostoslavskii and I. N. Shevchuk

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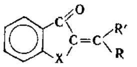
Condensation of isatin-α-anil with acetylacetone and with derivatives of malonic and acetoacetic acids in acetic anhydride has given 5 indogenides. It is observed that isatin-α-anil is readily acetylated by acetic anhydride. The acetyl derivative is very reactive, and is an intermediate in the condensation of isatin-α-anil with acetylacetone in acetic anhydride. The indogenides which have been synthesized are nonphototropic as a result of the presence of intramolecular hydrogen bonds.

It has previously been shown [2] that nonsymmetrical thioindogenides of the general formula A are capable of undergoing phototropic conversions. This paper describes the synthesis and spectral properties of the analogous indogenides B.



A X=S; B X=NH

The condensation of isatin-α-anil with acetylacetone in acetic anhydride [3], as we have found, proceeds mainly via the intermediate formation of the acetyl derivative. The reaction with acetic anhydride is complete in a few minutes at 120° C. The resulting acetyl derivative of isatin-α-anil can be isolated in a pure state and condensed with acetylacetone in acetic anhydride, to give only the nonacetylated compound II. This led to the conclusion that the acetyl derivative must have the structure Ia, and not Ib. When an excess of acetylacetone was used in the absence of acetic anhydride, the acetyl derivative condensed more rapidly than did isatin-α-anil itself.

Table 1 lists the compounds obtained by analogy with the indogenides [3]. None of them showed phototropic properties, apparently as a result of the presence of intramolecular hydrogen bonds. Prolonged boiling with acetic anhydride and acetyl chloride failed to introduce an acetyl group into II, while indigo itself is readily acetylated under these conditions [4]. This must be due either to the reduction in the basicity of the nitrogen atom under the influence of the three electron-acceptor carbonyl groups, or to intramolecular hydrogen bonding.

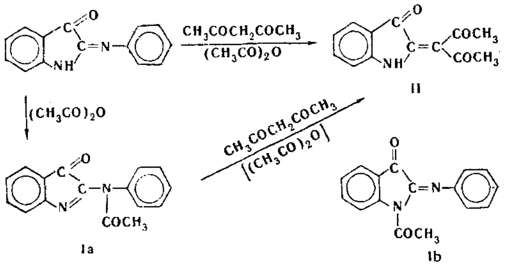


Table 2 compares the positions of the long-wavelength absorption maxima of the indogenides and the thioindogenides. In all cases, the indole derivatives absorb more strongly at longer wavelengths than the thianaphthene derivatives, the size of the bathochromic shift depending on the nature of the substituents R and R'. If the latter are acetyl or ethoxycarbonyl, the shift amounts to 20–25 nm. Even if one of the substituents is a cyano group, the shift amounts to 6–8 nm. Thus, the proportional shift [5] in the indogenides and thioindogenides is not observed. This is to be expected, since the presence of hydrogen bonds in the indogenide molecules must substantially influence the spectral

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*For part IX, see [1].

Table 1. Indogenides of General Formula B

Indogenide	R	R′	Reaction temperature °C	Reaction time, hr	Mp, °C	Molecular formula	Found, %			Calculated, %		
							C	H	N	C	H	N
II	$COCH_3$	$COCH_3$	At the boil	14	215—216[a]	$C_{13}H_{11}NO_3$	67.85	4.85	5.92	68.10	4.80	6.12
III	$COOC_2H_5$	$COOC_2H_5$	130	2	121.5—122.5[b]	$C_{15}H_{15}NO_5$	62.50	5.43	4.84	62.30	5.19	4.84
IV	CN	CN	105	2	260—262[a]	$C_{11}H_5N_3O$	67.66	2.62	21.20	67.69	2.56	21.54
V	$COOC_2H_5$	$COCH_3$	At the boil	1.5	120—121[c]	$C_{14}H_{13}NO_4$	65.16	4.86	5.22	64.85	5.02	5.40
VI	CN	$COOC_2H_5$	130	14	204.5—205.5[d]	$C_{13}H_{10}N_2O_3$	65.06	4.16	11.51	64.46	4.13	11.57

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[a] From chlorobenzene; [b] From benzene-light petroleum (1 : 1); [c] From hexane; [d] From alcohol.

Table 2. Comparison of the Absorption Spectra in the Visible Region of the Indogenides (B) and the Corresponding Thioindogenides (A).

R	R′	B		A		$\lambda^B_{max} - \lambda^A_{max}$, nm	$\frac{\varepsilon^B_{max}}{\varepsilon^A_{max}}$
		λ_{max}, nm	$\varepsilon_{max} \times 10^{-4}$	λ_{max}, nm	$\varepsilon_{max} \times 10^{-4}$		
$COOC_2H_5$	$COOC_2H_5$	466	0.58	445	0.34	21	1.70
$COCH_3$	$COCH_3$	486	0.60	461	0.36	25	1.66
CN	CN	468	0.56	462	0.35	6	1.60
$COOC_2H_5$	$COCH_3$	480	0.65	460	0.39	20	1.67
CN	$COOC_2H_5$	472	0.64	464	0.39	8	1.64

properties and destroy any correlation with the spectra of the thioindogenides. The IR spectra of the compounds referred to are considered in detail in [6].

EXPERIMENTAL

Acetyl derivative of isatin-α-anil, Ia or Ib. Ten grams (0.045 mole) of isatin-α-anil (mp 126° C) was heated for 10 min at 120° C with 35 ml (0.37 mole) of acetic anhydride. The mixture was cooled and filtered to give 8.42 g (70.9%) of product, mp 129–133° C. Recrystallization from toluene gave mp 133–133.5° C. Found, %: N 10.73; 10.78. Calculated for $C_{16}H_{12}N_2O_2$, %: N 10.6.

2-(Diacetylmethylene)indoline-3-one (II). A mixture of 0.5 g (0.0019 mole) of the acetyl derivative of isatin-α-anil and 2 ml (0.019 mole) of acetylacetone were heated for 6 hr at 130° C. The mixture was cooled, and 0.05 g of a dark-colored precipitate filtered off. Recrystallization from chlorobenzene gave a red substance, mp 208° C (decomp.). The IR spectrum and chromatogram showed it to be identical with II obtained according to [3]. Lit. [3] mp, 200° C.

2-(Diethoxycarbonylmethylene)indoline-3-one (III). Six grams (0.027 mole) of isatin-α-anil, 4.2 g (0.026 mole) of diethyl malonate, 35 ml of acetic anhydride and 5 drops of acetic acid were boiled for 2 hr. The mixture was cooled, decomposed with water, extracted with boiling light petroleum, and the residue from the extraction recrystallized from benzene–light petroleum (1:1). Reddish crystals, mp 121.5–122.5° C. Compounds IV–VI were obtained similarly (see Table 1).

Chromatography was carried out on type S paper, impregnated with a 5% solution of α-bromonaphthalene in alcohol. The eluent was pyridine–water (1:2). Absorption spectra were measured on an SF-2M recording spectrophotometer. The method of preparing the solutions has been described previously [7].

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Rubezhansk Branch, Scientific-Research Institute for
Organic Intermediates and Dyes