

SPECTRA OF 3-KETO-2,3-DIHYDROTHIONAPHTHENE AND ITS DERIVATIVES

VIII. Thioindogenides of the Naphthoxyphenanthiophene (Comparison with 3-Keto-2,3-Dihydrothionaphthene Derivatives)*

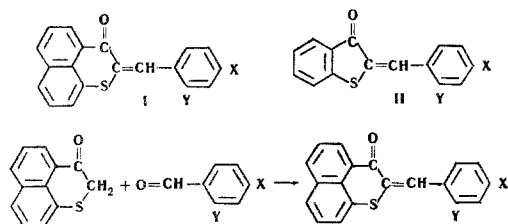
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A number of thioindogenides are synthesized by condensing 1,8-naphthoxyphenanthiophene with aromatic aldehydes, and their phototropic properties are investigated. It is shown that illumination of solutions of these compounds leads to shift of λ_{\max} toward the short wave region, and decrease in optical density.

Photochemical cis-trans isomerization of perinaphthothioindigo takes place considerably better than [2,3] the isomerization of thioindigo [4,5]. It was not impossible that thioindogenides of the 3-keto-2,3-dihydrophenanthiophene series I would have better photochemical properties than the thioindogenides of the 3-keto-2,3-dihydrothionaphthene series II which we previously investigated [6-8].

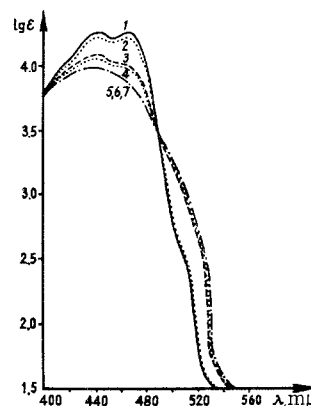


Some compounds of type I have now been prepared by condensing 2,3-dihydronaphtho[1,8-bc]thiopyran-3-one with the appropriate aromatic aldehydes. Absorption spectra measurements have been made on solutions of them, prepared in the dark, as well as on solutions exposed to daylight. In all cases illumination led to shift of λ_{\max} toward the short wave side, and decrease in optical density, and with the para-substituted compounds an isobestic point was clearly observed (figure), lacking with ortho-substituted ones, which are gradually decomposed by light. We previously observed a similar ortho effect with type II compounds [1].

Finally, we compared the effects of illumination on the spectra of perinaphthothioindigo, thioindigo, the thioindogenide I (X=H; Y=H) and thioindogenide II (X=H; Y=H). It is seen from Table 2 that illumination shifts λ_{\max} towards the short wave direction in all cases except the last. The reason for this is not altogether clear, and will be considered in a subsequent publication.

EXPERIMENTAL

2-(4'-Nitrobenzylidene)-3-keto-2,3-dihydroperinaphthopenthiophene. 13.3 ml AcOH, 0.8 (~0.4 mmole) 1,8-naphthoxyphenanthiophene, 0.604 g (~0.4 mmole) p-nitrobenzaldehyde, and 1.3 ml water were heated together to 60° C, then at that temperature 0.8 ml conc. HCl added. The whole was then kept at 75°-80° for 3 hr. After cooling the crystals were filtered off (yield 1.12 g, or 84.2%), and recrystallized from benzene-hexane, mp 221.7°-222.7°.



Absorption spectrum of 2-(4'-chlorobenzylidene)-3-keto-2,3-dihydroperinaphthopenthiophene in hexane. 1) Solution prepared in the dark; solutions illuminated with daylight: 2) 1 min; 3) 5 min; 4) 15 min; 5) 30 min; 6) 4 hr; 7) 24 hr.

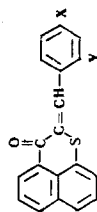
The other compounds given in Table 1 were prepared similarly.

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*For Part VII see [1].

Table 1
Constants of the Thioindogenides



Experiment no.	X	Y	Mp, °C	Formula	Found, %						Calculated, %				Solvent in which the spectrum was measured	λ_{max} , m μ		Yield, %
					C	H	Cl	N	S	C	H	Cl	N	S		Before illumination	After illumination	
1	H	H	123.5—125.2	C ₁₉ H ₁₂ OS	78.46 78.83	4.20 4.33	—	—	—	—	79.14	4.16	—	—	—	441 465	436	20.0
2	NO ₂	H	221.7—222.7	C ₁₉ H ₁₁ NO ₃ S	—	—	—	3.99 4.03	—	—	—	—	—	4.20	—	475	460	84.2
3	Cl	H	145.3—147.3	C ₁₉ H ₁₁ ClOS	—	—	10.50 10.31	—	9.98 10.26	—	—	—	10.99	—	9.97	443 466	439	59.4
4	OCH ₃	H	177.0—178.6	C ₂₀ H ₁₄ O ₂ S	—	—	—	—	10.15 10.19	—	—	—	—	—	10.07	451 474	449	40.0
5	N(CH ₃) ₂	H	164.0—165.0	C ₂₁ H ₁₇ NOS	—	—	—	—	9.65 9.40	—	—	—	—	—	9.65	480 500	479	38.0
6	H	NO ₂	189.0—190.0	C ₁₉ H ₁₁ NO ₃ S	—	—	—	—	—	—	—	—	—	4.20	—	448	445	60.2
7	H	Cl	145.3—147.3	C ₁₉ H ₁₁ ClOS	—	—	10.82 10.71	—	10.10 10.00	—	—	—	10.99	—	9.97	440 460	430	78.7

Table 2
Effect of Illumination on the Spectra of Compounds.

Compound	λ_{max} , m μ	
	Before illumination	After illumination
Thioindigo	546	485
Perinaphthoindigo	626	501
I (X=H; Y=H)	441	436
II (X=H; Y=H)	465	420
	420	443
	430	

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