[CONTRIBUTION FROM THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL]

The Fluorescence of 1,4-Diarylbutadienes and its Relation to their Configuration

BY YEHUDA HIRSHBERG, ERNST BERGMANN AND FELIX BERGMANN

Kuhn and Winterstein[1] and Hausser, Kuhn and Smakula[2] have observed that 1,4-diphenylbutadiene exhibits a strong blue fluorescence. In connection with the investigation reported in the preceding paper, the fluorescence of a number of other arylated (mostly 1,4-diaryl) butadienes has been investigated. The table summarizes the results obtained, from which the following conclusions can be drawn:

(a) Fluorescence requires an extended resonating system. As expected, therefore, the *trans–trans* form of 1,4-diphenylbutadiene shows a more intense fluorescence than the *cis–trans* isomer, in which resonance is partly inhibited by steric interference (Fig. 1). The fluorescence observed for other arylated dienes is also in keeping with the *trans–trans* structure ascribed to them on the basis of their absorption spectra.[3]

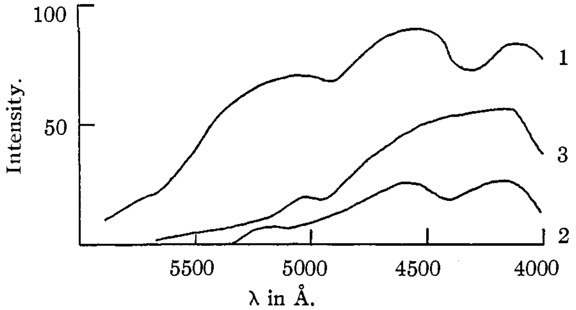

Fig. 1.—Fluorescence spectra of: 1, *trans–trans* 1,4-diphenylbutadiene; 2, same, after irradiation for 15 minutes; 3, *trans–cis* 1,4-diphenylbutadiene.

(b) Substituents which extend the resonating system in 1,4-diphenylbutadiene, increase the fluorescence intensity (methoxy and phenyl groups in para-position, α-, and especially β-naphthyl instead of phenyl), substituents which inhibit resonance (*e. g.*, *o*-methyl), decrease it (Fig. 2).

(c) Prolonged irradiation causes a decrease in fluorescence intensity (Fig. 1). This is in keeping with the inference drawn from the absorption spectra in the preceding paper, that irradiation causes stereoisomerization of the 1,4-diarylbutadienes.

As is customary, the intensities of the fluorescence maxima in the table are expressed in arbitrary units, taking the intensity of the intensest band as 100. All measurements have been carried out in benzene solution, using one of the methods briefly described by Hirshberg and Haskelberg.[4] In this arrangement, the exciting radiation of a mercury arc, after passing a Wood's

TABLE I

FLUORESCENCE SPECTRA OF ARYLATED DIENES AND THEIR CHANGE THROUGH ULTRAVIOLET IRRADIATION

Solvent: benzene; maxima in Å.; intensities in arbitrary units

-butadiene	Initial spectrum		Time, hours	Spectrum after irradiation	
	λ_{max}	E_m		λ_{max}	E_m
trans–trans-1,4-Diphenyl-	4120	85	1	4200	27
	4550	93		4430	27
	5100	74		(5200)	(7.5)
trans–cis-1,4-Diphenyl-	4170	60	2	4280	19
	5030	20			
1,4-Di-(*o*-tolyl)	4120	22	2	No fluorescence	
	4400	23			
1,4-Di-(*p*-methoxyphenyl)-	4220	100	2	4150	32
	4700	100		4640	32
	5170	80		(5320)	(8)
1-Phenyl-4-(*p*-biphenylyl)-	4100	98	2	4160	26
	4600	95		4700	25
	5150	90			
1-Phenyl-4-(β-naphthyl)-	4410	97	2	4300	19
	5220	75		(5000)	(4)
1,4-Di-(α-naphthyl)-	4400	90	3	4350	32
	5080	80		4900	25
	5830	64			
1,4-Di-(β-naphthyl)-	4500	100	3	4350	78
	5150	87		5150	50
	5870	71			
1-(α-Naphthyl)-4-(β-naphthyl)-	4340	94	3	4280	50
	5250	84		5200	30
	5810	69			
1,1,2,4-Tetraphenyl-	4250	36	2	No fluorescence	
1,2,3,4-Tetraphenyl-	4220	21.5	2	No fluorescence	
	4900	19			

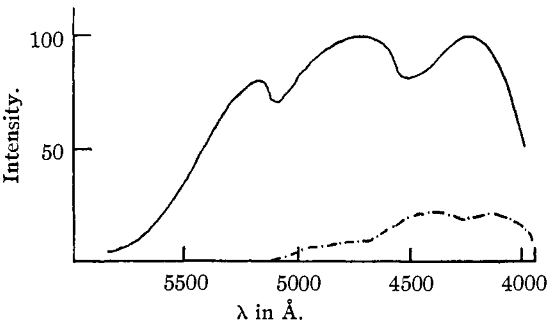

Fig. 2.—Fluorescence spectra of 1,4-di-(*p*-methoxyphenyl)-butadiene, —, and 1,4-di-(*o*-tolyl)-butadiene, —·—.

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[1] Kuhn and Winterstein, *Helv. Chim. Acta*, **11**, 87 (1928).

[2] Hausser, Kuhn and Kuhn, *Z. physik. Chem.*, **B29**, 417 (1935).

[3] The results regarding the fluorescence spectra of the 1,4-diphenylbutadienes have been described in a brief paper in 1944, which, however, was contained in a rather inaccessible publication: *Scientific Papers*, presented by the Palestine Chemists' Organization to Prof. Chaim Weizmann on the occasion of his 70th birthday, Jerusalem, 1944, p. 14.

[4] Hirshberg and Haskelberg, *Trans. Faraday Soc.*, **39**, 45 (1943).

filter and a focusing lens, falls under an angle of about 90° on the quartz cell, which contains the sample. The fluorescence is observed under an angle of 45° against the exciting radiation so that only the emission from the surface layer of the solution is measured and its self-absorption is not involved. The light is then concentrated by means of a second lens on the slit of the spectrograph. The latter was a Fuess instrument for the visible spectrum (extending to 3500 Å.); on the photographic plate, the visible spectrum had a width of 5 cm.

Summary

The fluorescence spectrum of a number of arylated (mostly 1,4-diaryl) butadienes has been measured and related to their constitution and configuration. The fluorescence intensity is parallel to the resonance of the molecules; inhibition of resonance decreases the intensity. Prolonged irradiation which causes rearrangement of the (most stable) *trans–trans* forms, therefore, also decreases the fluorescence intensity.

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[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

On the Photochemistry and Structure of 9,9'-Phenanthroin and *sym*-Di-(9-phenanthryl)-ethylene

BY YEHUDA HIRSHBERG AND FELIX BERGMANN

R. Norman Jones[1] has substantiated by a spectrographic investigation the assertion made by F. Bergmann and Israelashwili[2] that 9,9'-phenanthroin has not the "normal" structure (I), but rather that of an enediol (II) or of a tautomeric equilibrium mixture of (I) and (II). The observations recorded in the foregoing paper[3] have given us the possibility of elaborating upon this statement. In exactly the same manner as *sym*-di-(9-phenanthryl)-ethylene (III) (Fig. 1),[4] 9,9'-phenanthroin (Fig. 2) changes gradually under the influence of ultraviolet light. This change is likely to be caused by *cis-trans*-isomerization, so that to both (II) and (III) *trans*-configuration will have to be assigned. Indeed, the method used for the synthesis of (III), *viz.*, the desulfurization of phenanthrene-9-thioaldehyde with copper,[2] is apt to lead to the *trans*-configuration. It is in keeping with this hypothesis that the spectrum of tetra-(9-phenanthryl)-ethylene, like that of tetraphenylethylene, does not change even after prolonged irradiation. Furthermore, our observa-

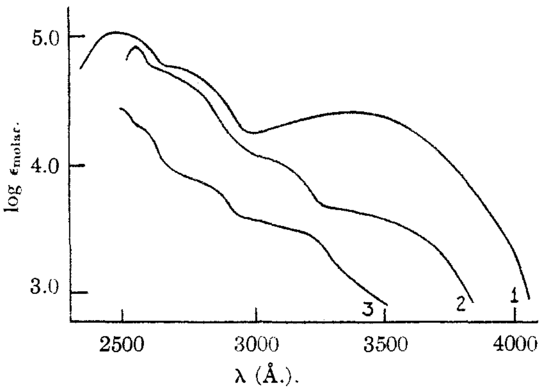


Fig. 1.—Absorption spectrum of *sym*-di-(9-phenanthryl)-ethylene (III): 1, original; 2, after irradiation for one hour; 3, after irradiation for two hours.

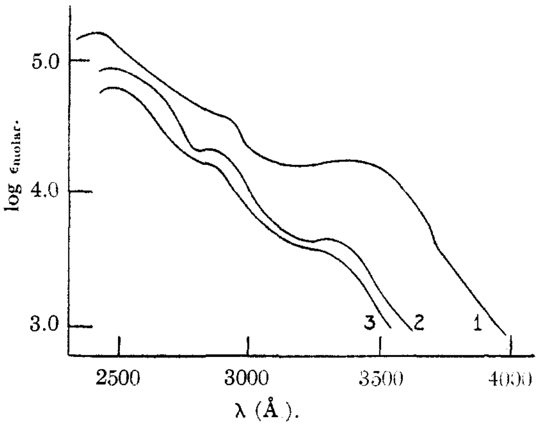
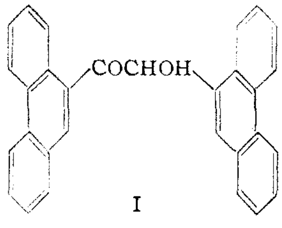
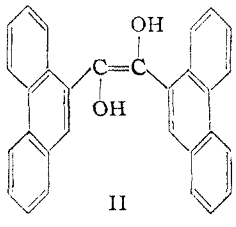


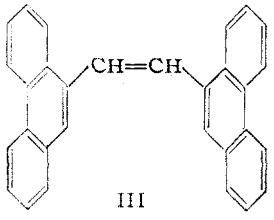
Fig. 2.—Absorption spectrum of 9,9'-phenanthroin (II): 1, original; 2, after irradiation for two hours; 3, after irradiation for three hours.



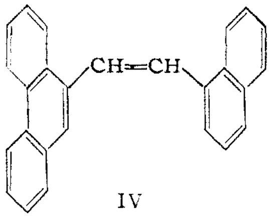
I



II



III



IV

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[1] R. N. Jones, THIS JOURNAL, **67**, 1956 (1945).

[2] F. Bergmann and Israelashwili, *ibid.*, **67**, 1951 (1945).

[3] Hirshberg, Bergmann and Bergmann, *ibid.*, **72**, 5117 (1950).

[4] All spectra were measured in dioxane solution.