

filter and a focusing lens, falls under an angle of about  $90^\circ$  on the quartz cell, which contains the sample. The fluorescence is observed under an angle of  $45^\circ$  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  $3500 \text{ \AA}$ .); on the photographic plate, the visible spectrum had a width of  $5 \text{ cm}$ .

### 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<sup>1</sup> has substantiated by a spectrographic investigation the assertion made by F. Bergmann and Israelashwili<sup>2</sup> 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<sup>3</sup> have given us the possibility of elaborating upon this statement. In exactly the same manner as *sym*-di-(9-phenanthryl)-ethylene (III) (Fig. 1),<sup>4</sup> 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,<sup>2</sup> is apt to lead to the *trans*-configuration. It is in

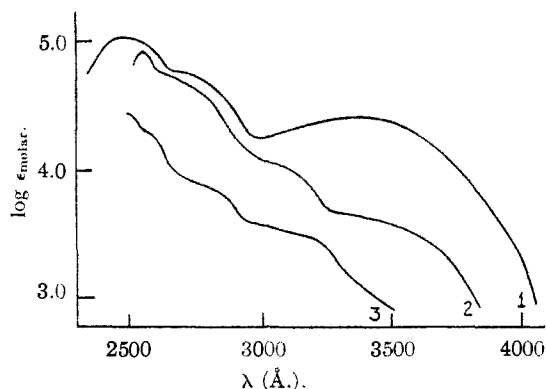


Fig. 1.—Absorption spectrum of *sym*-di-(9-phenanthryl)-ethylene (III): 1, original; 2, after irradiation for one hour; 3, after irradiation for two hours.

- (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.

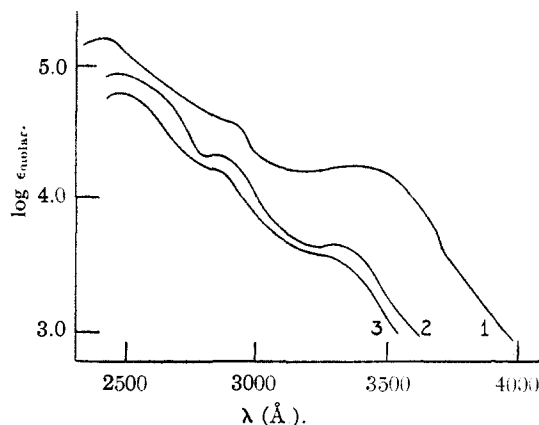
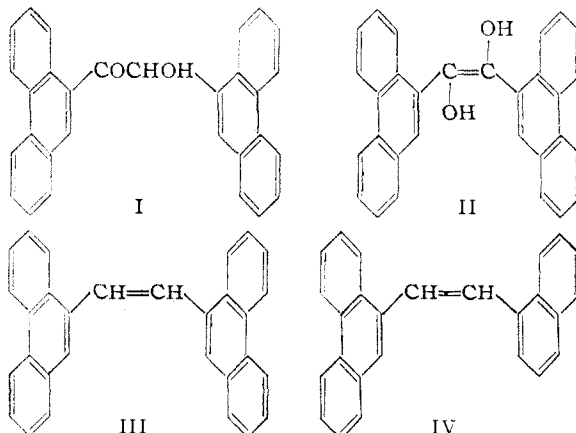


Fig. 2.—Absorption spectrum of 9,9'-phenanthroin (II): 1, original; 2, after irradiation for two hours; 3, after irradiation for three hours.

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-



tions prove that (I) cannot be an equilibrium mixture with (II), as then a continuous transition of the *trans*-form of (I) into the *cis*-form would have to be expected. The substance is a stable enediol, and stereoisomerization can be induced only photochemically. This recalls the observations by Fuson and his co-workers that certain substituted benzoin and even diarylacetaldehydes are stabilized in their enediol and enol forms, respectively, provided that at least one aryl is as highly substituted as in the mesityl or the isoduryl radical.<sup>5</sup>

In Table I Jones' and our own data for the spectra of 9,9'-phenanthroin and *sym*-di-(9-phenanthryl)-ethylene are compared.

TABLE I

9,9'-Phenanthroin				Di-(9-phenanthryl)-ethylene			
Jones	Present authors	Jones	Present authors	Jones	Present authors	Jones	Present authors
Maximum, Å.	log $\epsilon_{\text{max}}$ .	Maximum, Å.	log $\epsilon_{\text{max}}$ .	Maximum, Å.	log $\epsilon_{\text{max}}$ .	Maximum, Å.	log $\epsilon_{\text{max}}$ .
3300	4.4	3350	4.4	3420	4.4	3420	4.4
2880	4.3	2800	4.7	2670	4.8	2690	4.7
2520	4.95	2400	5.25	2480	5.0	2460	5.05

The spectrum of *sym*-di-(9-phenanthryl)-ethylene illustrates rather strikingly the fact that the 9,10-double bonds of the phenanthrene nuclei participate in the polyenic system: the absorption curve approaches closely the visible region of the

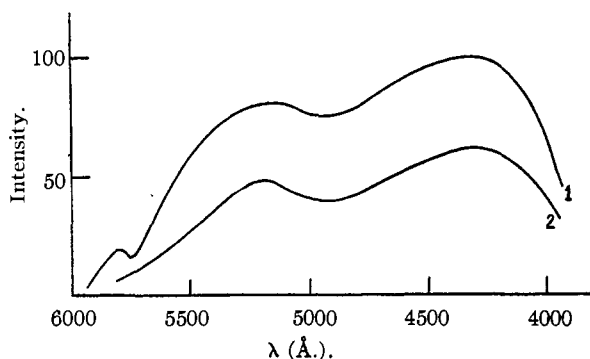


Fig. 3.—Fluorescence spectrum of *sym*-di-(9-phenanthryl)-ethylene (III): 1, original; 2, after irradiation for three hours.

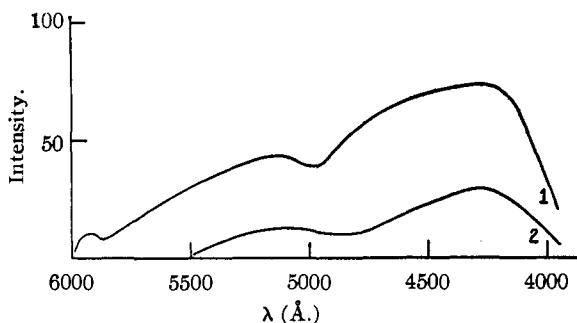


Fig. 4.—Fluorescence spectrum of 9,9'-phenanthroin (II): 1, original; 2, after irradiation for two hours.

(5) See, e. g., Fuson and co-workers, *THIS JOURNAL*, **65**, 915 (1943); **66**, 1109 (1944).

spectrum and resembles somewhat the spectrum of 1,6-diphenylhexatriene. This active extension of the resonating system is substantiated by the fact that the hydrocarbon as well as 9,9'-phenanthroin fluoresce distinctly. Figures 3 and 4 show the fluorescence spectra of the two substances and equally their changes upon continued ultraviolet irradiation. The decrease in fluorescence intensity can be ascribed, as pointed out in the foregoing paper, to the steric hindrance in the *cis*-forms. The fact that both the absorption and the fluorescence spectrum change mainly in intensity but not very outspokenly in the position of the constituent bands is further proof that no deep-going change in the structure of the molecules occurs upon irradiation.

In the course of these experiments the absorption and fluorescence of 1-(1'-naphthyl)-2-(9'-phenanthryl)-ethylene<sup>6</sup> (IV) were also measured. The spectra and their changes with prolonged irradiation are presented in Figs. 5 and 6. The phenomena are analogous to those observed for *sym*-di-(9-phenanthryl)-ethylene (III).

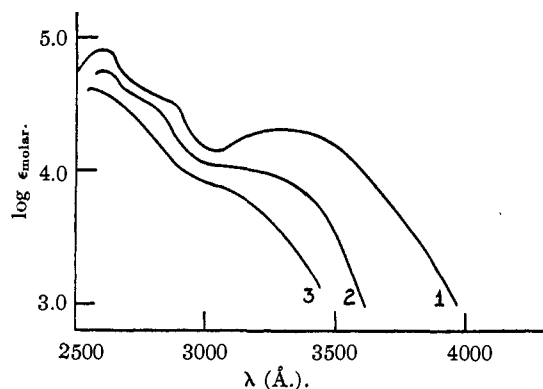


Fig. 5.—Absorption spectrum of 1-(1'-naphthyl)-2-(9'-phenanthryl)-ethylene (IV): 1, original; 2, after irradiation for one hour; 3, after irradiation for two hours.

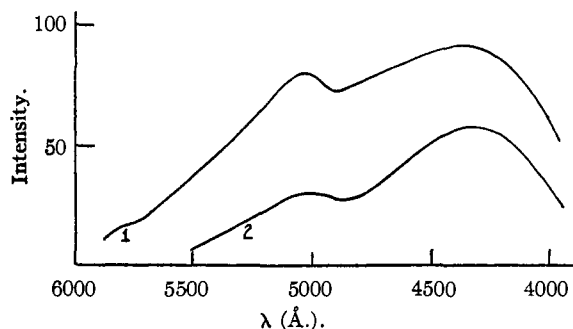


Fig. 6.—Fluorescence spectrum of 1-(1'-naphthyl)-2-(9'-phenanthryl)-ethylene (IV): 1, original; 2, after irradiation for two hours.

### Summary

9,9'-Phenanthroin, under the influence of ultraviolet light, undergoes a *trans* → *cis*-isomerization

(6) Prepared by Israelashwili and F. Bergmann, unpublished results (yellow crystals, m. p. 180°).

in the same manner as *sym*-di-(9-phenanthryl)-ethylene. This change proves that phenanthroin is a stable enediol and not a tautomeric equi-

librium mixture and illustrates the powerful "conjugating" influence of the 9-phenanthryl radical.

REHOVOTH, PALESTINE RECEIVED SEPTEMBER 13, 1947

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## Absorption Spectra and Photo-isomerization of Arylated Dienes

BY YEHUDA HIRSHBERG, ERNST BERGMANN AND FELIX BERGMANN

Zechmeister and co-workers<sup>1,2</sup> have shown that *trans-trans* 1,4-diphenylbutadiene, under the influence of ultraviolet light, isomerizes to the *cis-trans* isomer, and that the same is true for the *cis-cis* compound. They also showed that the *trans-trans* form has the most developed fine-structure and absorbs nearest to the visible spectrum, while the spectra of the (liquid) isomer—considered as *cis-trans*<sup>3</sup>—and of the *cis-cis* form have the maxima in the more remote part of the ultraviolet, and are characterized by absence of fine structure and low extinction coefficients.

Models show that only the *trans-trans* form is free of steric interference between groups on neighboring carbon atoms (no inhibition of resonance); in the isomerides, increasing interference appears between the *o*-hydrogen of the phenyl ring and hydrogen in the chain. In the latter cases, there occurs a marked deviation from that planar arrangement which is the necessary prerequisite of resonance.<sup>4</sup> These effects may well account for the differences in the spectra of the isomers.

The present paper is concerned with the influence substitution of the 1,4-diphenylbutadiene molecule, especially in the phenyl rings, exerts on its ability to resonate and, thereby, on the character of its absorption spectrum. The results are summarized in Table I, columns 2 and 3, and permit the following conclusions: (1)  $\beta$ -naphthyl is more effective than  $\alpha$ -naphthyl and phenyl, in shifting the absorption toward the visible and in causing a more elaborate fine-structure to appear. As  $\alpha$ - but not  $\beta$ -naphthyl can be considered as an ortho-substituted phenyl, only the former will cause steric interference and will, therefore, restrict resonance. Quantitatively,  $\alpha$ -naphthyl is equal to phenyl, in spite of its additional, formally conjugated, double bond, whilst 1,4-di-( $\beta$ -naphthyl)-butadiene has a spectrum very similar to that of 1,8-diphenyloctatetraene,<sup>5</sup> as the following figures show:

	$\lambda_{\text{Max}}$	Log $E_m$	$\lambda_{\text{Max}}$	Log $E_m$
1,4-Di-( $\beta$ -naphthyl)-butadiene	3610	4.84	3810	4.84
1,8-Diphenyloctatetraene	3600	4.79	3770	4.95

(1) Sandoval and Zechmeister, *THIS JOURNAL*, **69**, 553 (1947).

(2) Pinckard, Wille and Zechmeister, *ibid.*, **70**, 1938 (1948).

(3) Straus, *Ann.*, **342**, 190 (1905); compare Kelber and Schwarz, *Ber.*, **45**, 1946 (1912); Ott and Schroeter, *ibid.*, **60**, 624 (1927).

(4) Zechmeister and Ie Rosen, *Science*, **95**, 587 (1942); *THIS JOURNAL*, **64**, 2755 (1942); Lewis, Magel and Lipkin, *ibid.*, **62**, 2973 (1940).

(5) Hausser, Kuhn and Smakola, *Z. physik. Chem.*, **B29**, 384 (1935).

It may be recalled that according to Compton and W. Bergmann<sup>6</sup> also the 2-quinolyl group, which is analogous to  $\beta$ -naphthyl, is equivalent to styryl in its influence on the spectrum of the  $\alpha$ -phenyl- $\omega$ -(2-quinolyl)-polyenes.

(2) The first and only maximum of 1,4-di-(*o*-tolyl)-butadiene lies at 2740 Å. as compared with a wave length of 3450 Å. for the longest of the four maxima of 1,4-diphenylbutadiene. This difference may well be ascribed to resonance inhibition by the *o*-methyl groups. Conversely, 1,4-di-(*p*-methoxyphenyl)-butadiene reflects in the location of the longest of its (three) maxima (3590 Å.) and 1-phenyl-4-(*p*-biphenyl)-butadiene in the high extinction coefficient (4.9) of the first of its (three) maxima (3480 Å.), the extended resonating system present in the molecules.

(3) The three isomeric 1-phenyl-4-chlorophenyl-butadienes have practically identical absorption spectra, only in the number of absorption bands, not in their location distinguished from the parent compound. All three isomers show the same three bands; only in the para-compound, a fourth one is observed—with relatively low intensity—near the visible end of the ultraviolet spectrum. This unusual indifference to substitution has led to the investigation of 1,4-di-(*o*-chlorophenyl)-butadiene. In the spectrum of this substance, too, there occurs only a slight shift toward the remoter part of the ultraviolet; and the middle band in the spectrum of the monochloro compounds (3160–3200 Å.) disappears.

(4) Phenyl substitution in the diene system of 1,4-diphenylbutadiene leads to the disappearance of fine-structure and broadening of the absorption bands (Fig. 1). In 1,2,3,4-tetraphenylbutadiene, this is very probably due to interference between phenyl groups on neighboring carbon atoms. For the 1,1,2,4-tetraphenyl compound, an additional reason is that one of the *gem*-phenyl groups is forced out of the plane of the double bond.<sup>7</sup> This feature determines, obviously, the character of the absorption spectrum of 1,1,4,4-tetraphenylbutadiene.

(5) 1-Phenylbutadiene which is the *trans*-compound,<sup>8</sup> when prepared according to Muskat and Herrman<sup>9</sup> from cinnamaldehyde and methylmag-

(6) Compton and W. Bergmann, *J. Org. Chem.*, **12**, 363 (1947).

(7) Coates and Sutton, *J. Chem. Soc.*, 567 (1942); F. Bergmann and Israelashwili, *THIS JOURNAL*, **68**, 1 (1946).

(8) Grummitt and Christoph, *THIS JOURNAL*, **71**, 4157 (1949).

(9) Muskat and Herrman, *ibid.*, **53**, 252 (1931).