Ultraviolet Absorption of Some Di-9-anthrylalkanes

F. H. C. STEWART

Department of Organic Chemistry, Weizmann Institute of Science, Rehovoth, Israel

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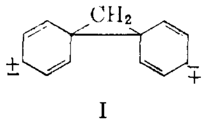
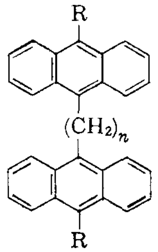
Electronic interaction between aromatic rings connected by a saturated bridge of one or two carbon atoms has been discussed by Braude.[1] In particular, the ultraviolet spectrum of diphenylmethane exhibited slight divergences from additivity when compared with that of ethylbenzene, which indicated that some conjugation occurred between the two rings either through the methylene group or directly by way of structures such as I. This effect has been examined quantitatively by Coffman and McClure[2,3] for diphenylmethane, dibenzyl, and some paracyclophanes, while Bartlett and Lewis[4] have postulated structures of type I to account for spectroscopic evidence of enhanced conjugation in triptycene, which is a favorable case sterically for the operation of this mode of interaction.



I



II

In this connection it seemed of interest to examine the spectra of several recently described di-9-anthrylalkanes (II)[5,6] in which the electronically active *meso* positions are connected by one or two methylene groups. The compounds concerned are di(10-*n*-butyl-9-anthryl)methane (II $n = 1$; $R = C_4H_9$),[5] the corresponding methyl analog (II $n = 1$; $R = CH_3$),[6] and 1,2-di(10-*n*-butyl-9-anthryl) ethane (II $n = 2$; $R = C_4H_9$).[5] The spectra of these derivatives in chloroform solution were compared with that of 9-ethyl-10-methylanthracene, and the wave lengths and intensities of the main peaks of the well defined anthracene Group II absorption pattern are collected in Table I.

TABLE I[a]

SPECTRA OF DI-9-ANTHRYLALKANES

	Absorption maxima (mμ) and ϵ_{max}[b]							
	E		F		G		H	
Compound	λ	ϵ_{max}	λ	ϵ_{max}	λ	ϵ_{max}	λ	ϵ_{max}
II $n = 1$; $R = CH_3$	347	3000	364	7,400	385	19,000	408	26,000
II $n = 1$; $R = C_4H_9$	348	5000	365	10,000	386	20,000	409	26,000
II $n = 2$; $R = C_4H_9$	348	4300	365	9,000	385	20,000	408	27,000
9-Ethyl-10-methylanthracene[c]	343	5400	360	12,000	380	22,000	401	20,000

[a] *The measurements were made with a Unicam SP 700 recording spectrophotometer.* [b] The maxima are designated according to the nomenclature of Jones.[7] [c] The intensities are $2\epsilon_{max}$.

The results show that a small bathochromic shift occurs with each of the four maxima of the di-9-anthrylalkanes (II), but that this is most marked (7–8 mμ) with the peak of longest wave length (H). The corresponding maxima for a number of simple 9,10-dialkylanthracenes have been listed by Jones,[7] and there is no significant variation in the series, the values being close to those found here for 9-ethyl-10-methylanthracene in Table I. The observed shifts with the compounds of structure II are consistent with an appreciable degree of conjugation between the anthracene nuclei.

The ϵ_{max} values, on the other hand, tend to be reduced for all the maxima with the exception of the H peak, which exhibits a marked increase in intensity. This has the effect of inverting the relative intensity of the G and H peaks from that found with simple anthracene derivatives.[7,8] Comparison of the extinction coefficients, however, is probably of limited significance with the present compounds owing to the effect of fluorescence-emission on the recorded absorption.[10] It is noteworthy that the visible fluorescence of solutions of the compounds II is qualitatively much weaker than with 9-ethyl-10-methylanthracene.

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(1) E. A. Braude, *J. Chem. Soc.*, 1902 (1949).

(2) R. Coffman and D. S. McClure, *Can. J. Chem.*, **36**, 48 (1958).

(3) D. S. McClure, *ibid.*, **36**, 59 (1958).

(4) P. D. Bartlett and E. S. Lewis, *J. Am. Chem. Soc.*, **72**, 1005 (1950).

(5) F. H. C. Stewart, *Aust. J. Chem.*, **13**, 478 (1960).

(6) F. H. C. Stewart, *ibid.*, **14**, 177 (1961).

(7) R. N. Jones, *Chem. Rev.*, **41**, 353 (1947).

(8) The spectrum of 1,2-di-(10-methyl-9-anthryl)ethane (II $n = 2$; $R = CH_3$) has been determined by Beckwith and Waters.[9] The bathochromic shifts and inversion of the G and H peaks found here are also evident, but the reported intensities are much less.

(9) A. L. J. Beckwith and W. A. Waters, *J. Chem. Soc.*, 1108 (1958).

(10) E. A. Braude, J. S. Fawcett, and C. J. Timmons, *ibid.*, 1019 (1950).