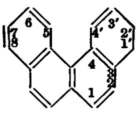
Substituted Anthracene Derivatives. Part VIII. The Conjugating Powers of the Substitution Positions in* 3 : 4-*Benzophenanthrene.*

By G. M. Badger and I. S. Walker.

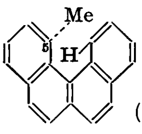
[Reprint Order No. 5229.]

The absorption spectra of 3 : 4-benzophenanthrene (I) and of its six monomethyl derivatives have been examined. The bathochromic shifts produced by methyl substitution have been compared with the conjugating powers of the six substitution positions calculated by the method of molecular orbitals.

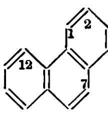
Methyl substitution in benzenoid aromatic hydrocarbons normally produces a shift in the ultra-violet absorption bands to longer wave-lengths, the extent of the bathochromic shift depending on the degree of electronic interaction between the substituent and the ring (Jones, *J. Amer. Chem. Soc.*, 1945, **67**, 2127; *Chem. Reviews*, 1943, **32**, 1; Doub and Vandenbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714). Many of the polycyclic compounds have several positions available for substitution, and in the case of 1 : 2-benzanthracene an attempt has already been made to estimate the relative conjugating abilities of the various positions by measuring the bathochromic shifts produced by methyl substitution (Badger, Pearce, and Pettit, *J.*, 1952, 1112). Although this method is only very approximate, the greatest shifts are produced by methyl substitution at positions of greatest self-polarisability as calculated by the method of molecular orbitals. We have therefore now examined the absorption spectra of 3 : 4-benzophenanthrene (I) and of all six possible monomethyl derivatives.



(I)



(II)



(III)

The bands in the absorption spectrum of 3 : 4-benzophenanthrene (see Figure) fall into three main groups: group I, bands *A*—*E*; group II, bands *F*—*I*; group III, bands *J*—*L*. All the monomethyl derivatives show similar absorption spectra (see Table 1) except that the bands are shifted to somewhat longer wave-lengths, and in some cases (notably 5-methyl-3 : 4-benzophenanthrene) there is a certain loss of fine structure. For the two most prominent bands (*E* and *H*) the bathochromic shifts are given in Table 2.

According to Coulson and Longuet-Higgins (*Proc. Roy. Soc.*, 1947, *A*, **191**, 39; 1948, *A*, **195**, 188), the conjugating power of a given position is defined as β times the self-polarisa-

---

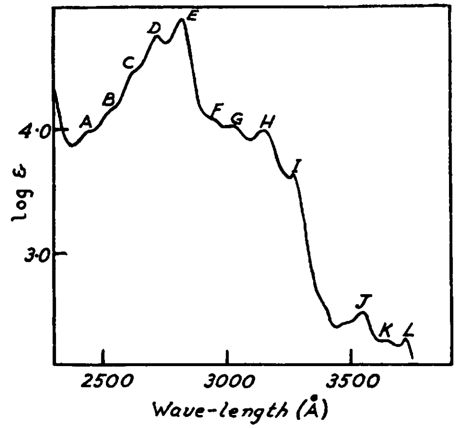
* Part VII, *J.*, 1954, 3151.

TABLE 1. *Positions of the maxima and corresponding intensities* (log $\varepsilon_{max.}$) *in the ultra-violet absorption spectra of* 3 : 4-*benzophenanthrene and of the methyl*-3 : 4-*benzophenanthrenes* (*in ethanol*).*

Position of Me	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	*J*	*K*	*L*
†	(2450)	(2540)	(2635)	2715	2815	(2945)	3020	3145	3265	3545	3630	3720
	3·99	4·16	4·48	4·76	4·90	4·09	4·03	4·00	3·63	2·52	2·29	2·30
1	(2460)	(2545)	(2655)	2745	2835	2985	(3045)	3160	(3270)	3590	—	3770
	4·02	4·16	4·45	4·71	4·83	4·16	4·09	4·01	3·62	2·57	—	2·41
2	2455	2545	(2650)	2735	2835	(2955)	3050	3175	3300	3565	—	3745
	4·00	4·14	4·43	4·74	4·89	4·10	4·02	4·01	3·71	2·60	—	2·38
5	—	—	—	2775	2865	(3000)	3085	3210	(3330)	3625	—	—
	—	—	—	4·73	4·83	4·08	3·99	3·95	3·67	2·49	—	—
6	2470	(2550)	(2645)	2735	2830	2990	(3035)	3160	(3265)	3570	—	3750
	4·00	4·17	4·45	4·72	4·85	4·14	4·09	4·00	3·60	2·72	—	2·65
7	(2465)	(2540)	(2640)	2730	2830	(2955)	3035	3160	(3275)	3560	—	3735
	4·00	4·14	4·43	4·75	4·91	4·08	4·03	4·01	3·64	2·54	—	2·26
8	(2480)	(2575)	(2670)	2760	2855	(2970)	3055	3180	3300	3575	(3655)	3745
	4·03	4·23	4·49	4·73	4·84	4·18	4·06	4·00	3·69	2·51	2·33	2·19

* Figures in parentheses are points of inflexion. † Parent compound.

bility of that position. The self-polarisabilities for the various positions in 3 : 4-benzophenanthrene have now been calculated, a simplified mathematical technique being used (Potts, *J. Chem. Phys.*, 1953, **21**, 758; Potts and Walker, unpublished work), and are included in Table 2, together with the free valence numbers for the various positions. As in other cases (Badger, Pearce, and Pettit, *loc. cit.*) there is a satisfactory linear relation between the self-polarisabilities and the free valence numbers, so that either set of figures may be used to estimate relative conjugating abilities. Unfortunately the bathochromic shifts produced by methyl substitution in 3 : 4-benzophenanthrene are rather small, and the results must therefore be interpreted with caution. However, in agreement with the theoretical work, it seems that the 2- and the 8- have greater conjugating powers than the 6- and the 7-position. On the other hand, the greatest bathochromic shift was produced by



Absorption spectrum of 3 : 4-*benzophenanthrene in ethanol.*

TABLE 2. *Bathochromic shifts* (*E and H bands*) *for methyl substitution, calculated conjugating powers, and free valence numbers for* 3 : 4-*benzophenanthrene.*

Position	Δ*E* (Å)	Δ*H* (Å)	Self-polarisability [a] (M.O. method)	Free valence number M.O. method [b]	Free valence number V.B. method [c]
6	15	15	0·408	0·089	0·173
7	15	15	0·409	0·086	0·167
5	50	65	0·435	0·127	0·190
1	20	15	0·438	0·131	0·202
8	40	35	0·440	0·132	0·196
2	20	30	0·442	0·133	0·208

[a] These values should be multiplied by $1/\beta$. [b] Based on $N_{max.} = 3 + \sqrt{2}$; cf. Berthier, Coulson, Greenwood, and Pullman, *Compt. rend.*, 1948, **226**, 1906. [c] Pullman, *Ann. Chim.*, 1947, **2**, 5.

5-methyl substitution, though the self-polarisability and the free valence numbers indicate only moderate conjugating power. In 5-methyl-3 : 4-benzophenanthrene (II) the methyl substituent cannot be in the plane of the ring system (Newman and Wheatley, *J. Amer. Chem. Soc.*, 1948, **70**, 1913) and there seems little doubt that the anomalous bathochromic shift is associated with this fact. Several other cases have been recorded in the literature where methyl groups which are not coplanar with the ring system have been shown to give very large bathochromic shifts. For example, very large shifts are produced in 1-methyl-, 6-methyl-, and 1 : 12-dimethyl-chrysene (III), and a large shift is also evident for 4 : 5-dimethylphenanthrene (Brode and Patterson, *J. Amer. Chem. Soc.*, 1941, **63**, 3252; Jones, *ibid.*, 1941, **63**, 313; Friedel and Orchin, " Ultra-violet Spectra of Aromatic Compounds," Wiley, 1951; see also Brockmann and Dorlars, *Chem. Ber.*, 1952, **85**, 1168). However, more data are required, for 1′-methyl substitution in 1 : 2-benzanthracene produces only a very small bathochromic shift and steric hindrance must be involved also in this case.

EXPERIMENTAL

Spectra.—Spectra were determined, in absolute ethanol, with a Hilger Uvispek Spectrophotometer. The positions of the peaks were checked by examination of the spectra in hexane. Little if any solvent effect was apparent.

We are very grateful to Professor Melvin S. Newman for gifts of all the compounds used in this investigation.

UNIVERSITY OF ADELAIDE, SOUTH AUSTRALIA. [*Received, March 23rd*, 1954.]