195. *Substituted Anthracene Derivatives. Part V.* The Conjugating Powers of the Substitution Positions in* 1 : 2-*Benzanthracene.*

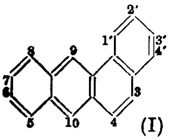
By G. M. Badger, R. S. Pearce, and R. Pettit.

The ultra-violet absorption spectra of several monomethyl-1 : 2-benzanthracenes are very similar to that of the parent hydrocarbon except that the bands are shifted to somewhat longer wave-lengths. The bathochromic shifts produced by methyl substitution in each of the twelve possible positions have been compared with the conjugating powers of these positions calculated by the method of molecular orbitals.

One of the most interesting problems in aromatic chemistry still awaiting adequate experimental investigation concerns the relative conjugating powers of the various positions in an aromatic ring system. In the case of naphthalene, evidence is accumulating that the conjugating power of the 1- is much greater than that of the 2-position. For example, Ketelaar and Oosterhout (*Rec. Trav. chim.*, 1946, **65**, 448) have examined the dipole moments of the halogenated naphthalenes and have concluded that the C–Cl bond in 1-chloronaphthalene has about 14·2% double-bond character as against 13·0% for 2-chloronaphthalene. Similarly, Badger (*Nature*, 1950, **165**, 647; see also Coulson, *J.*, 1950, 2252) has examined the rates of oxidation of the dinaphthylethylenes with osmium tetroxide, and has shown that an ethylenic double bond is conjugated to the 1- to a much greater extent than to the 2-position. For the azonaphthalenes, the rates of oxidation with perbenzoic acid indicate that an azo-group is conjugated to the 1- to a greater degree than to the 2-position (Badger and Lewis, *Nature*, 1951, **167**, 403). Furthermore, the basic strengths of 1- and 2-naphthylamines also confirm the superior conjugating ability of the 1-position. Very few data are available for other aromatic hydrocarbons, however, and it therefore seemed of interest to attempt to estimate the conjugating powers of the various substitution positions in 1 : 2-benzanthracene by a spectroscopic method.

Substituents in benzenoid aromatic compounds have long been known to produce shifts in the positions of the absorption bands to longer wave-lengths (bathochromic shifts), and it seems to be established that the magnitude of the shift produced depends on the extent of electronic interaction between the substituent and the ring (cf. Doub and Vandenbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714; Badger and Pearce, *J.*, 1950, 3072). Indeed, the magnitude of the bathochromic shift can be used to determine the relative degrees of conjugation of different substituents with the benzene ring (cf. Kiss, Molnár and Sandorfy, *Compt. rend.*, 1948, **227**, 724). It is therefore reasonable to suppose that the magnitude of the bathochromic shifts produced by a given substituent at the various possible positions of substitution should give a measure of the relative conjugating powers of the different positions.

1 : 2-Benzanthracene (I) seemed to be a suitable compound for examination as its spectrum shows a number of sharp bands, and as there are twelve possible positions of substitution. All twelve monomethyl derivatives have been described (Cook and Robinson, *J.*, 1938, 505), and the absorption spectra of six of these have already been reported in detail by Jones (*J. Amer. Chem. Soc.*, 1940, **62**, 148). Through the courtesy of Professor M. S. Newman, who has recently devised new and more satisfactory syntheses (Newman and Gaertner, *ibid.*, 1950, **72**, 264) and who has kindly presented us with samples of the remaining isomers, it has now been possible to complete the series.



(I)

The absorption bands in the spectrum of 1 : 2-benzanthracene (Fig. 1) have been labelled *A*—*K* in agreement with Jones and with previous work from this laboratory. These bands fall into three main groups: I, bands *ABCDE*; II, bands *FGHI*; III, bands *I'JK*. Most of the monomethyl derivatives show similar spectra except that the bands are shifted somewhat to longer wave-lengths. The data for six of the monomethylbenzanthracenes have been tabulated by Jones (*loc. cit.*); and the positions of the absorption peaks, together

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* Part IV, *J.*, 1950, 3072.

with the extinction coefficients of the remaining six isomers which have now been examined, are collected in Table 1. The spectra of some of the isomers show a certain loss of fine structure and this sometimes makes it difficult to identify all the bands with certainty. In every case, however, the *D* band is quite clear and distinct; and there is also little danger of wrong identification with the *H* band. The approximately constant frequency difference between the bands in each of the main three groups also assists identification (cf. Badger and Pearce, *loc. cit.*).

TABLE 1. *Positions of the maxima and corresponding intensities* (log $E_{max.}$) *in the ultra-violet absorption spectra of* 1 : 2-*benzanthracene and of the methyl*-1 : 2-*benzanthracenes* (*solvent, ethanol*).*

Position of methyl substituent	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*G′*	*H*	*H′*	*I*	*I′*	*J*	*K*
†	2560	2670	2770	2875	2995	3140	3265	—	3410	—	3585	(3635)	3755	3845
	4·56	4·62	4·90	4·99	3·95	3·67	3·81	—	3·87	—	3·72	3·46	2·73	2·95
2′-	2585	2690	2800	2910	3015	—	3270	3330	3425	3485	3590	3660	3765	3880
	4·57	4·63	4·87	4·92	3·93	—	3·79	3·80	3·87	3·77	3·74	3·46	2·79	3·16
3′-	2580	2685	2780	2890	3015	3150	3290	—	3435	—	3605	—	3760	3855
	4·45	4·55	4·81	4·89	4·03	3·75	3·83	—	3·84	—	3·64	—	2·66	2·69
4′-	2550	2720	2820	2930	3025	3160	3290	—	3445	—	3620	—	3780	3880
	4·57	4·63	4·89	4·95	4·09	3·73	3·87	—	3·93	—	3·78	—	2·73	3·03
3-	2570	2705	2800	2910	2995	3115	3260	3345	3405	3500	3570	3670	3770	3880
	4·63	4·68	4·90	4·96	4·22	3·71	3·82	3·79	3·86	3·70	3·71	3·27	2·76	3·12
6-	2570	2695	2790	2890	3010	3145	3300	—	3435	—	3600	—	(3770)	3850
	4·58	4·61	4·85	4·92	4·16	3·72	3·83	—	3·81	—	3·60	—	2·61	2·48
7-	2575	2680	2780	2885	3015	—	3255	3330	3405	3490	3570	3670	3770	3875
	4·63	4·66	4·90	5·01	4·04	—	3·80	3·80	3·84	3·74	3·67	3·39	2·78	3·18

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

TABLE 2. *Bathochromic shifts* (D *and* H *bands*) *for methyl substitution, calculated conjugating powers, and free-valence numbers for* 1 : 2-*benzanthracene.*

Position	Δ_D (in Å)	Δ_H (in Å)	Self-polarisability [a] (M.O. Method)	Free-valence number [b] (M.O. Method)	Free-valence number [c] (V. B. Method)
3′	15	25	0·404	0·352	0·164
6	15	25	0·409	0·355	0·168
7	10	−5	0·410	0·356	0·168
2′	35	15	0·410	0·357	0·171
1′	5	0	0·429	0·388	0·181
4′	55	35	0·439	0·399	0·192
4	15	10	0·441	0·403	0·200
8	30	50	0·449	0·404	0·196
3	35	−5	0·449	0·404	0·204
5	20	50	0·452	0·406	0·198
9	35	105	0·495	0·484	0·241
10	40	135	0·513	0·462	0·255

[a] These values should be multiplied by $1/\beta$. [b] Berthier, Coulson, Greenwood, and Pullman, *Compt. rend.*, 1948, **226**, 1906. [c] Pullman, *Ann. Chim.*, 1947, **2**, 5.

Three of the compounds in the present series (2′-, 3-, and 7-methyl-1 : 2-benzanthracenes) show a curious set of intermediate bands in the group-II region (see Fig. 2). These subsidiary bands are separated from the main bands by approximately 700 cm.$^{-1}$, and their origin is obscure. However, similar duplication of bands with methyl substitution has sometimes been observed in other cases, *e.g.*, in the visible spectrum of 2-methylazulene, but not in the spectra of the other methylazulenes (Plattner, *Helv. Chim. Acta*, 1941, **24**, 283E).

It is difficult to estimate the bathochromic shifts with any great accuracy. Some of the bands are relatively broad or irregular in shape, and it is not always possible to identify the complete set. In these circumstances, it has been thought best to study the shifts of the *D* and *H* bands only, especially as Jones (*loc. cit.*; *Chem. Reviews*, 1943, **32**, 1) has already examined the shifts in these bands produced by the six isomers previousy studied. The complete set of shifts is given in Table 2. The results certainly indicate that the 9- and the 10-position have the greatest conjugating power. With less certainty it may be said that the 2′-, 4′-, 3-, 5-, and 8-positions all have a moderate conjugating power, and that the remaining positions have relatively small conjugating power. The 1′- and the 4-isomer show smaller bathochromic shifts than expected; but in the former this may be due to steric effects.

It is instructive to compare these results with the quantitative estimates of the conjugating powers of the various positions as calculated by the method of molecular orbitals.

FIG. 1. *Absorption spectrum of* 1 : 2-*benzanthracene.*

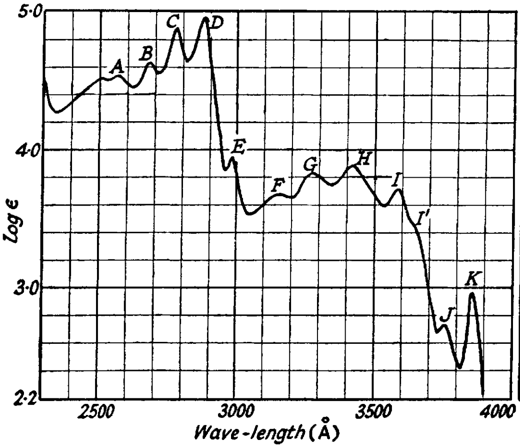


FIG. 2. *Absorption spectrum of* 2′-*methyl-*1 : 2-*benzanthracene.*

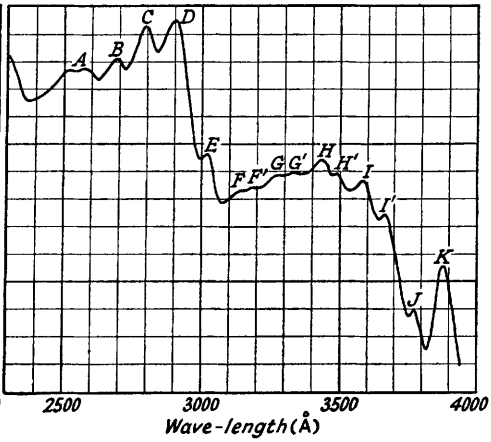
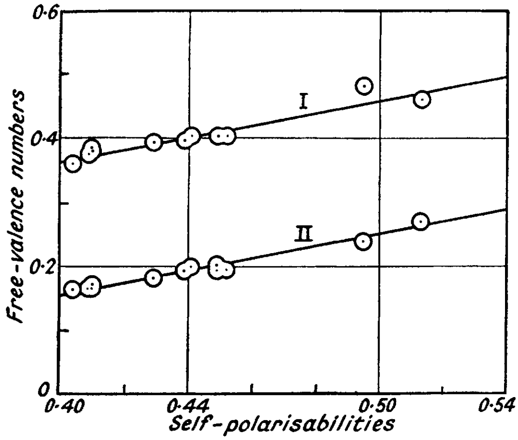


FIG. 3. *Curves showing the relationship between self-polarisabilities and free-valence numbers, M.O. method (curve* I*), and between self-polarisabilities and free-valence numbers, V. B. method (curve* II*).*



According to the treatment elaborated by Coulson and Longuet-Higgins (*Proc. Roy. Soc.*, *A*, 1947, **191**, 39; 1948, **195**, 188) the conjugating power of a given position is defined as β times the self-polarisability of that position. The self polarisability (π_{rr}) in an alternant hydrocarbon is given by the expression :

$$\pi_{rr} = 4 \sum_{j=1}^{n} \sum_{k=1}^{n} \frac{c_{rj}^{2}\, c_{rk}^{2}}{\varepsilon_j + \varepsilon_k}$$

where n is the number of occupied orbitals, c_{rj} (c_{rk}) is the coefficient of the atomic orbital r occurring in the j th (k th) molecular orbital and ε_j (ε_k) the difference in energy of the j th (k th) molecular orbital from H_{cc}, the coulomb integral for the carbon atom in, say, benzene.

The values of π_{rr} for the twelve positions in 1 : 2-benzanthracene have now been calculated and have been included in Table 2. There the compounds are arranged in increasing order of the positions as determined by this method. In view of the inaccuracies of the spectrographic method, no perfect correlation between self-polarizability and bathochromic shift can be expected, but with one or two exceptions a rough qualitative correlation does appear to exist. In particular, both methods indicate that the 9- and the 10-position have the greatest conjugating power.

Some studies have already been published on the relation between conjugating power and the free-valence number of a given position as determined by the valence-bond method. For example, B. Pullman (*Compt. rend.*, 1946, **222**, 1396) has pointed out that the extent of hyperconjugation of a methyl substituent is dependent on the free-valence number, and that the greater the free-valence number, the greater the conjugation. This has recently been supported by some work by Daudel (*Compt. rend.*, 1950, **230**, 99) who has shown that there is a linear relation between the free-valence numbers (as determined by the method of spin states) and the bond orders of the bonds linking the substituent to the various positions of substitution. A similar relation between the extent of conjugation and the free-valence number as determined by the method of molecular orbitals must also be expected for it can be shown that there is a smooth-curve relation between the free-valence numbers as determined by the V. B. and M.O. methods.

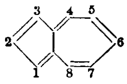
It is also noteworthy that A. Pullman (*Compt. rend.*, 1947, **224**, 1354; see also B. Pullman, *Bull. Soc. chim.*, 1948, **15**, 533) has found (for five monomethylbenzanthracenes) that there is an approximate correlation between the bathochromic shifts for methyl substitution and the " index of conjugation."

These relations all fall into place quite naturally when it is recognised that there are linear relations between the self-polarisabilities and the valence-bond free-valence numbers on the one hand, and between the self-polarisabilities and the M.O. free-valence numbers on the other. These linear relations are illustrated by Fig. 3, in which the various values for all twelve substitution positions are plotted.

TABLE 3. *Comparison between π-electron densities, and the observed shifts in the longest-wave-length band in the visible region when azulene is alkylated.*

Position of methyl group	π-Electron density	Observed shift (cm.$^{-1}$)	Position of methyl group	π-Electron density	Observed shift (cm.$^{-1}$)
1	1·173	−800	5	0·986	−360
2	1·047	+440	6	0·870	+380
3	1·173	−800	7	0·986	−360
4	0·855	+360	8	0·855	+360

In conclusion, reference may be made to the study of the bathochromic and hypsochromic shifts produced by methyl substitution in non-alternant aromatic hydrocarbons and in aromatic heterocyclic compounds. In these compounds, the annular carbon atoms normally have π-electron densities which are either greater than, or less than, unity. Brown and Lahey (*Austral. J. Sci. Res.*, 1950, **3**, *A*, 593) have claimed that a bathochromic shift is produced if the substituent is present in a position of (locally) high π-electron density, and that a hypsochromic shift is produced if the same substituent is present in a position of (locally) low π-electron density. They cite the case of the methylazulenes in support of the generalisation, but we believe that no such correlation exists in this case. Methyl substitution in the 1-, 3-, 5-, and 7-positions of azulene (II) (not the 1-, 5-, and 7-, as stated) shifts the visible absorption bands to longer wave-lengths, and similar substitution in the 2-, 4-, 6-, and 8-positions (not 2-, 3-, 6-, and 8-, as stated) has been shown to shift the visible absorption bands in the opposite direction (Plattner, *loc. cit.*; see also Haagen-Smit, "Fortschritte der Chemie Organischer Naturstoffe," Springer-Verlag, Vol. 5, 1948, p. 40). The extent of shift for the absorption band of longest wave-length is given in Table 3, which also includes the π-electron densities of the various positions as calculated by Brown (*Trans. Faraday Soc.*, 1948, **44**, 984). There seems to be no correlation between the two sets of figures. (The work of Pullman, Mayot, and Berthier, *J. Chem. Phys.*, 1950, **18**,



(II)

257, and of Mann, Platt, and Klevens, *ibid.*, 1949, **17**, 481, however, does appear to offer an explanation for the observed shifts.)

It is interesting that in the *ultra-violet* part of the spectrum, the shifts are *always* to longer wave-length whatever the position of substitution, and it may be significant that the greatest shifts are produced by substitution in the 1-, 2-, and 3-positions, which have high π-electron densities (Plattner and Heilbronner, *Helv. Chim. Acta*, 1948, **31**, 804).

Experimental.—The ultra-violet absorption spectra were determined, in absolute ethanol, by means of a Hilger Uvispek Spectrophotometer.

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