364. *The Relative Reactivity of Aromatic Double Bonds. Part III. The Relation between Double-bond Character and the Velocity of Addition of Osmium Tetroxide.*

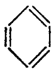
By G. M. Badger.

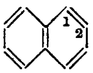
The relation between the double-bond character, or order of a bond, and the velocity of addition reactions is discussed, with special reference to the addition of osmium tetroxide to the 3 : 4-bond of alkyl derivatives of 1 : 2-benzanthracene and 1 : 2-benzacridine.

It has often been assumed that the reactivity of a double bond as exemplified by the velocity of an addition reaction is directly related to its double-bond character, or bond order. However, Gold (*Trans. Faraday Soc.*, 1949, **45**, 191) has recently pointed out that as the order of a bond is essentially a " static " property, it cannot provide an index of " dynamic " double-bond character. This is, of course, strictly true; but the present paper attempts to show that the error in making this assumption is, in suitable cases, not significant.

The double-bond character, or the order of a bond, has been variously defined (see for example, Pauling, Brockway, and Beach, *J. Amer. Chem. Soc.*, 1935, **57**, 2705; Penney, *Proc. Roy. Soc.*, 1937, *A*, **158**, 318; Coulson, *ibid.*, 1939, **169**, 413; Pullman, *Ann. Chim.*, 1947, **2**, 5; Daudel and Daudel, *J. Chem. Physics*, 1948, **16**, 639; Walsh, *Trans. Faraday Soc.*, 1946, **42**, 779) and although it is essentially a theoretical concept, its physical reality has been well established by a study of bond-length variations (*e.g.*, Wheland, " Theory of Resonance," John Wiley and Sons, New York; Robertson, *Acta Cryst.*, 1948, **1**, 101). On the other hand, although a general agreement between the results of the different methods has frequently been claimed (Coulson, Daudel, and Daudel, *Rev. Sci.*, 1947, **85**, 29; Buu-Hoï *et al.*, *ibid.*, p. 1041) all the methods are admittedly approximate, and in any particular series of bonds, wide variations in the relative magnitudes of the orders may be obtained by several methods.

This may be readily appreciated by a comparison of the orders obtained by different methods for a comparable bond in a series of closely related hydrocarbons. A suitable series would seem to be the C–C-bond in benzene (I), the 1 : 2-bond in naphthalene (II), and the 1 : 2-bond in anthracene (III). The calculated double-bond characters and bond orders for these three bonds are given in Table I. If the bond order as calculated by the molecular-orbital method is accepted as a satisfactory index of double-bond character, the relative magnitude in this series of bonds


(I.)



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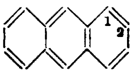

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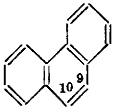

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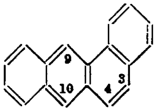

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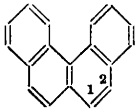


(VI.)

is : 1 : 2-bond of anthracene > 1 : 2-bond of naphthalene > C–C-bond of benzene. The same order of relative magnitude is obtained by Pauling's method involving resonance between all the possible Kekulé structures. If, however, one assumes that the total charge of π electrons on the bond and its terminal carbon atoms provides a satisfactory index of double-bond character (as was done by Pullman, *loc. cit.*), then the order of relative magnitude becomes : 1 : 2-bond of naphthalene > 1 : 2-bond of anthracene > C–C-bond of benzene. Again, if one accepts the bond order as determined by the method of Daudel and Daudel, the order of relative magnitude becomes : 1 : 2-bond of naphthalene > C–C-bond of benzene > 1 : 2-bond of anthracene. Similarly, a comparison of the relative magnitudes of the double-bond characters of the 9 : 10-bond in phenanthrene (IV), the 3 : 4-bond in 1 : 2-benzanthracene (V), and the 1 : 2-bond in 3 : 4-benzphenanthrene (VI) also reveals gross irregularities. The molecular-orbital method

TABLE I.

*Comparison of double-bond characters and bond orders for a comparable bond in a series of closely related hydrocarbons.**

		Double-bond characters and bond orders.			
Compound.	Bond.	Pauling (*a*).	Pullman (*b*) (Total charge π electrons).	Pullman–Daudel (*c*).	Coulson (*d*).
Benzene	—	1·50	1·073e	1·464	1·667
Naphthalene	1 : 2	1·67	1·274	1·527	1·725
Anthracene	1 : 2	1·75	1·259	1·452	1·738
Phenanthrene	9 : 10	1·80	1·291	1·446	1·775
1 : 2-Benzanthracene	3 : 4	1·86	1·283	1·440	1·783
3 : 4-Benzphenanthrene	1 : 2	1·71	1·293	1·442	1·762

[a] Double-bond character by summation of Kekulé structures (Pauling, " Nature of the Chemical Bond," Cornell University Press, 2nd edn., 1940). [b] Total charge of π electrons. Sum of the " charge de liaison " and the two " indices de valence libre " (Pullman, *Ann. Chim.*, 1947, **2**, 5). [c] Bond order, by the valence-bond method (Pullman, *Ann. Chim.*, 1947, **2**, 5; Daudel and Daudel, *J. Chem. Physics*, 1948, **16**, 639). [d] Bond order by the molecular-orbital method (Coulson and Longuet-Higgins, *Rev. Sci.*, 1947, **85**, 929; Berthier, Coulson, Greenwood, and Pullman, *Compt. rend.*, 1948, **226**, 1906).

* The various definitions of bond order, double-bond character, etc., are all basically different, and it is not to be expected that the different methods will give numerically equal values for any given bond. It is reasonable to expect, however, that all the methods will agree whether a given bond " A " is more like a double bond than another bond " B ", or *vice versa*. As all the various methods are based on different approximations, this is not always the case, as the table indicates. The exact definitions and the approximations used in the various methods are given in the references quoted.

places these three bonds in the series: 3 : 4-bond of benzanthracene > 9 : 10-bond of phenanthrene > 1 : 2-bond of benzphenanthrene. Pullman's total-charge method, on the other hand, places the series in the reverse order.

That there is, in most cases, a qualitative relation between double-bond character, or bond order, and the velocity of an addition reaction can hardly be doubted. It is well known, for example, that when electron-releasing groups are attached to, or in close proximity to the double bond, the reaction rate is increased, and when electron-attracting groups are present, the reaction is retarded (Swern, *J. Amer. Chem. Soc.*, 1947, **69**, 1692; Böeseken and Stuurman, *Rec. Trav. chim.*, 1937, **56**, 1034; De la Mare, *Quarterly Reviews*, 1949, **3**, 126). It is noteworthy that the rate of addition of osmium tetroxide to the dinaphthylethylenes is also consistent with the view that the greater the double-bond character (or density of π electrons), the more rapid the reaction (Badger, *Nature*, 1950, **165**, 647; cf. Chalvet and Daudel, *Compt. rend.*, 1949, **229**, 54).

In discussing the addition of ozone to aromatic double bonds however, Kooyman and Ketelaar (*Rec. Trav. chim.*, 1946, **65**, 859) pointed out that before the addition can be completed, the bond in question has to be converted into a " pure " double bond. More precisely, two π electrons have to be " localised." The initial degree of localisation is of great importance, as is evident from the fact that ozone always adds first to the bond having the greatest double-bond character, but it is conceivable that the polarisability will also be of significance; and that in certain cases it is of pre-eminent importance. This may be illustrated by reference to ethylene and its phenyl derivatives, for, as is well known, the phenyl group can act as an electron-donor or as an electron-acceptor, depending on the conditions. The rates of addition of halogens to ethylene and its phenyl derivatives decrease in the order, styrene > ethylene > stilbene, although the bond orders of the reactive bonds decrease in the order ethylene > styrene > stilbene. Furthermore, the rate of oxidation with peracetic acid decreases in the order styrene > stilbene > ethylene (Swern, *loc. cit.*; De la Mare, *loc. cit.*; Buu-Hoï *et al.*, *loc. cit.*).

Waters (*J.*, 1948, 727; see also Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900) has maintained that the correct method of assessing the reactivity at the various positions of an aromatic molecule is to estimate the energy difference between the normal state and the " quinonoid " transition state, and not merely to evaluate local electron densities. He points out that the oxidation–reduction potentials of the corresponding quinones can be used as indices of this energy difference, and it would seem therefore that the problem of the relationship between bond order and the " reactivity " may be approached indirectly through the oxidation–reduction potentials of the corresponding *o*-quinones. Indeed, following a study of the oxidation–reduction potentials of a number of *o*- and *p*-quinones derived from polycyclic aromatic hydrocarbons, Clar (*Ber.*, 1940, **73**, 104; " Aromatische Kohlenwasserstoffe," Berlin, 1941) pointed out that the quinones corresponding to the very reactive hydrocarbons have very little reactivity, and *vice versa*. The series: benzene, naphthalene, anthracene, naphthacene, and pentacene, is characterised by a very marked and progressive increase in " reactivity " and in the tendency to undergo addition rather than substitution reactions as the number of aromatic rings increases. The series of *p*-quinones: *p*-benzoquinone, α-naphthaquinone, anthraquinone, naphthacenequinone, and pentacenequinone, on the other hand, is characterised by an equally marked and progressive *decrease* in reactivity as the series is ascended. *p*-Benzoquinone has a potential of 0·71 volt, α-naphthaquinone of 0·48 volt, and anthraquinone, of 0·15 volt. Naphthacenequinone is less reactive still. It forms a vat (*i.e.* an alkaline solution of the quinol) only with difficulty, whilst pentacenequinone does not form a vat.

Some years previously, Fieser and Price (*J. Amer. Chem. Soc.*, 1936, **58**, 1838) called attention to the very great similarity between the addition of bromine to the 9 : 10-bond of phenanthrene, and the oxidation of phenanthraquinol. The substituents in the 2- and the 3-position of phenanthrene which were found to decrease the free energy of bromine addition (retard the reaction) are precisely those which were earlier (Fieser and Fieser, *J. Amer. Chem. Soc.*, 1935, **57**, 491) found to decrease the free energy of oxidation of quinols (increase the potential). Similarly, the substituents which increased the free energy of bromine addition also increased the free energy of oxidation of quinols. The free-energy change in the bromine addition was found to be much less than that in the oxidation, but Fieser and Price found that a given substituent has nearly the same *proportionate* influence in each case. It may be concluded, therefore, that there is a reasonably good correlation between the velocity of an addition to a suitable aromatic double bond, and the magnitude of the oxidation–reduction potential of the corresponding quinone. Clar's treatment, for example, predicts the 3 : 4-bond of 1 : 2-benzanthracene (V) to be more " reactive " than the 9 : 10-bond of phenanthrene (IV), and this has been confirmed experimentally for the addition of osmium tetroxide (Badger and Reed, *Nature*, 1948, **161**, 238). That there is a similar correlation between bond order and the oxidation–reduction potential of the corresponding *o*-quinone does not seem to have been noted previously. In Fig. 1 the bond orders of a series of aromatic bonds, as determined by the molecular-orbital method (Coulson and Longuet-Higgins, *Rev. Sci.*, 1947, **85**, 3280; Berthier, Coulson, Greenwood, and Pullman, *Compt. rend.*, 1948, **226**, 1906; Baldock, Berthier, and Pullman, *ibid.*, 1949, **228**, 931) are plotted against the " corrected " oxidation–reduction potentials (Branch and Calvin, " The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, 1941) of the corresponding *o*-quinones. The distribution of the points indicates a very satisfactory degree of correlation between bond order and oxidation–reduction potential. It may also be reported that there is a fair degree of correlation between the oxidation–reduction potentials of a series of *p*-quinones and the sum of the two indices of free-valence (molecular-orbital method) for the corresponding positions in the related hydrocarbons.

FIG. 1.

Relationship between bond order (molecular-orbital method) and corrected oxidation–reduction potential of the corresponding o-*quinone.*

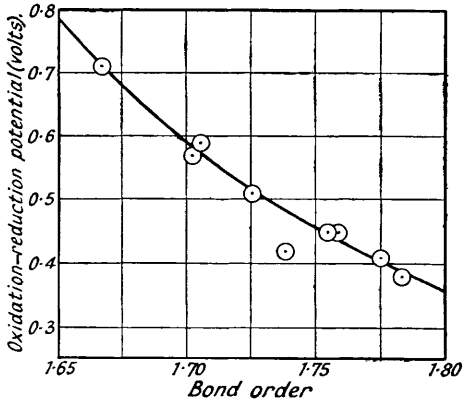


FIG. 2.

Ultra-violet absorption spectra, in alcohol.

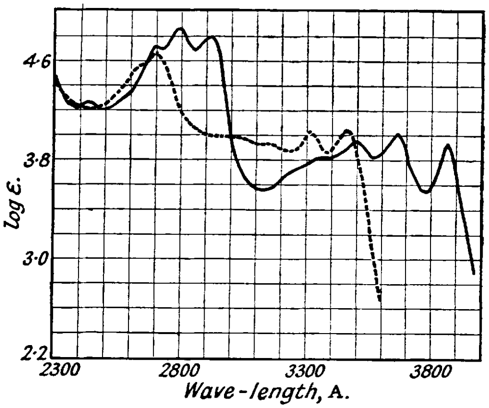


FIG. 2. ——— 5 : 7-*Dimethyl*-1 : 2-*benzacridine. Maxima at* 2440 (*log* ε 4·26), 2710 (4·71), 2790 (4·85), 2910 (4·80), 3490 (3·94), 3660 (4·01), 3860 (3·95).

\- - - - - - 3 : 4-*Dihydroxy*-5 : 7-*dimethyl*-3 : 4-*dihydro*-1 : 2-*benzacridine. Maxima at* 2700 (4·67), 3150 (3·95) 3310 (4·02).

Osmium tetroxide is the most satisfactory reagent for the determination of the relative reactivity of aromatic double bonds, for it reacts only with double bonds and does not attack reactive *centres*, as do most other electrophilic reagents. This reagent has already been used (Badger, *J.*, 1949, 456) to study the relative reactivity of the 3 : 4-bond in a series of cancer-producing compounds related to 1 : 2-benzanthracene, and this series has now been extended by the inclusion of 3-methyl- and 9-methyl-1 : 2-benzanthracene. The rate of addition of osmium tetroxide to 5 : 7-dimethyl-1 : 2-benzacridine (VII) has also been determined. These alkyl benzanthracenes provide a series of closely related compounds in which there is, almost certainly, very little difference in polarisability. For this reason these compounds would seem to provide a suitable series for an examination of the degree of correlation between double-bond character and the velocity of an addition reaction.

Several attempts to assess the changes in double-bond character, or density of π electrons, with the introduction of methyl substituents into benzanthracene have now been published (Table II). In order to examine the relation between the double-bond character of the 3 : 4-bond of benzanthracene and its methyl derivatives, and their cancer-producing potency, Pullman (*loc. cit.*) calculated the total charge of π electrons on this bond for an extensive series of derivatives. The method was admittedly very approximate, but in spite of this there is a remarkably good agreement between the rate of addition and the total charge. The only serious discrepancy is with 9-methyl-1 : 2-benzanthracene, which reacts more rapidly than expected. Daudel and Martin (see Daudel, *Bull. du Cancer*, 1948, **35**, 110) attempted to apply the valence-

TABLE II.

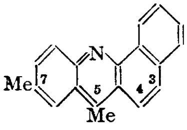
Comparison of the velocities of addition of osmium tetroxide to the 3 : 4*-bond of substituted benzanthracenes with calculated double-bond characters.*

Substituted 1 : 2-benzanthracene.	Rate constant (*a*), 10^3k_2.	Total-charge π electrons (*b*).	Free-valence numbers (*c*). $C_{(3)}$.	$C_{(4)}$.	Bond order (*c*).	Excess of charge on $C_{(3)}$ and $C_{(4)}$ (*d*).
1 : 2-Benzanthracene	0·48	1·283e	0·204	0·199	1·441	0
3-Methyl-	0·50·	1·298	—	—	—	—
6-Methyl-	0·64	1·294	0·185	0·134	1·460	0·013
5 : 6-Dimethyl-	0·64	1·307	0·168	0·154	1·476	0·029
5 : 7-Dimethyl-	0·80	1·304	0·141	0·114	1·479	0·024
2′ : 7-Dimethyl-	0·83	—	—	—	—	0·035
10-Methyl-	0·91	1·306	0·177	0·167	1·436	0·027
9-Methyl-	0·96	1·296	1·187	0·172	1·456	0·016
9 : 10-Dimethyl-	2·7	1·319	0·160	0·139	1·459	0·043
5 : 6 : 9 : 10-Tetramethyl- ...	2·9	1·343	—	—	—	0·072

See also Badger, *J.*, 1949, 456. [b] Pullman, *Ann. Chim.*, 1947, **2**, 5. [c] Dr. R. Daudel, private communication; see also Daudel, *Bull. du Cancer*, 1948, **35**, 110. [d] Daudel, *ibid.*, p. 110.

bond method rather more rigorously, and evaluated the bond orders and indices of free valence for a few selected compounds. Unfortunately, the valence-bond method seldom gives satisfactory results with substituted compounds, or with heterocyclic compounds, and several of the figures obtained would seem to be entirely unreasonable. For example, the calculated charge on the 3 : 4-bond of 1 : 2-benzanthracene was found to be *decreased* by the substitution of a methyl group in the 10-position. Indeed, in assessing the degree of correlation between these latter figures and the carcinogenic activity, Daudel was forced to conclude : " Il semble donc que l'accord entre la théorie et l'expérience soit moins bon dans le cas où l'évaluation des charges est plus correcte." However, by an alternative method, Daudel (*Bull. du Cancer*, 1948, **35**, 110; see also Daudel and Martin, *Bull. Soc. chim.*, 1948, **15**, 559) determined the " excess of charge " on the 3 : 4-positions produced by methyl substituents, or by the introduction of an annular nitrogen atom, as in the benzacridines. This treatment would seem to give a reasonable indication of the increase in double-bond character produced by a methyl substituent, and there is a fair degree of correlation between the rate of addition of osmium tetroxide and the magnitude of the " excess of charge." The case of 3-methyl-1 : 2-benzanthracene is interesting as the rate of addition is almost the same as with 1 : 2-benzanthracene itself. It seems likely that steric hindrance is a factor here. The rate of addition of osmium tetroxide to 9-methyl-1 : 2-benzanthracene was found to be comparable with that to the 10-methyl derivative, and more rapid than could be predicted by the " excess of charge." As was pointed out by Pullman (*Compt. rend.*, 1947, **224**, 1354) methyl groups in the *meso*-positions of this hydrocarbon are conjugated with the ring system to a much greater extent than methyl groups in other positions, and their effect on the 3 : 4-bond is therefore proportionately greater.

It is also noteworthy that osmium tetroxide adds to 5 : 7-dimethyl-1 : 2-benzacridine (VII) only slightly less rapidly than to the closely related 10-methyl-1 : 2-benzanthracene, and the degree of correlation between the velocity of the addition, and the " excess of charge " is, in this case, quite good.



(VII.)

The structure of the diols obtained by hydrolysis of the complexes of osmium tetroxide with various benzanthracenes has already been determined (Cook and Schoental, *J.*, 1948, 170; Badger, *J.*, 1949, 456, 2497). Hydrolysis of the complex with 5 : 7-dimethyl-1 : 2-benzacridine gave 3 : 4-dihydroxy-5 : 7-dimethyl-3 : 4-dihydro-1 : 2-benzacridine. The structure of this diol is confirmed by its ultra-violet absorption spectrum, which is similar to that expected for a derivative of phenyldimethylquinoline (Fig. 2). The ultra-violet absorption spectrum of 5 : 7-dimethyl-1 : 2-benzacridine, on the other hand, resembles that of 1 : 2-benzanthracene.

EXPERIMENTAL.

Reaction Rates.—Determinations of the rates of reaction with osmium tetroxide were carried out as previously described (Badger, *loc. cit.*).

3 : 4-*Dihydroxy*-5 : 7-*dimethyl*-3 : 4-*dihydro*-1 : 2-*benzacridine*.—Hydrolysis of the osmium tetroxide 5 : 7-dimethyl-1 : 2-benzacridine complex by Cook and Schoental's method (*loc. cit.*) gave 3 : 4-*dihydroxy*-5 : 7-*dimethyl*-3 : 4-*dihydro*-1 : 2-*benzacridine* as beautiful colourless needles (from alcohol), m. p. 244°

after sintering and darkening (Found: C, 78·6; H, 5·8. $C_{19}H_{17}O_2N$ requires C, 78·3; H, 5·9%). The ultra-violet absorption spectrum (Fig. 2) was determined with a Beckman DU spectrophotometer.

I am indebted to Dr. Ng.Ph. Buu-Hoï for a gift of 5 : 7-dimethyl-1 : 2-benzacridine, and to Mr. R. S. Pearce for the absorption spectra. Microanalyses were carried out by Mr. R. Howard.

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