THE AROMATIC BOND

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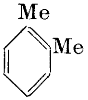
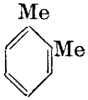
Although the Kekulé structure [1] for benzene, with alternate double and single bonds, explained many apparently disordered facts of aromatic chemistry, it has never been regarded as completely satisfactory. It does not, for example, explain the peculiar stability of benzene and, as Ladenburg [2] pointed out, *o*-disubstituted derivatives should exist in two isomeric configurations, such as (I) and (II); although it seemed possible that the physical properties of such isomers might preclude separation,[3] Kekulé [4] suggested rather that the double bonds are not fixed, but are " mobile ", oscillating very rapidly.



(I.)



(II.)

This concept of double-bond oscillation, although difficult to reconcile with the chemistry of the olefins, was widely accepted. Among other things, it explained the identity of the two positions *ortho* to the substituent in a monosubstituted benzene derivative. In certain polysubstituted benzenes, however, and in most di- and poly-cyclic aromatic compounds, the two *ortho*-positions are *not* equivalent: one is more reactive than the other, which led to the belief that, in some compounds, there is a partial or complete " fixation " of the double bonds.[5]

Considerable progress has been made in the study of the fine structure of aromatic compounds in recent years and, although complete bond fixation cannot be accepted today, there is a mass of experimental evidence which indicates that the carbon–carbon bonds in aromatic compounds are not all identical (except in benzene), but that some have greater " double-bond character " than others.

In this article an attempt is made to review the experimental evidence and to interpret it in terms of current theoretical concepts.

Apparent Bond Fixation.—The classical examples of apparent bond fixation are provided by the naphthalene molecule. By analogy with Kekulé's dynamic structure for benzene, the double bonds should oscillate between the positions shown in (III), (IV), and (V).[6] However, in 1893,

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[1] *Bull. Soc. chim.*, 1865, **1**, 98; *Annalen*, 1866, **137**, 129.

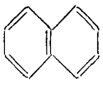
[2] *Ber.*, 1869, **2**, 140.

[3] Meyer, *Annalen*, 1870, **156**, 293.

[4] *Ibid.*, 1872, **162**, 77.

[5] For an excellent review of the earlier work, see Fieser's article in Gilman, " Organic Chemistry ", Vol. I, 2nd edn., John Wiley, 1943; also Fieser and Lothrop, *J. Amer. Chem. Soc.*, 1935, **57**, 1459; Wibaut and van Dijk, *Rec. Trav. chim.*, 1946, **65**, 413.

[6] Erdmann, *Annalen*, 1893, **275**, 184; cf. Ufimzew, *Ber.*, 1936, **69**, 2188.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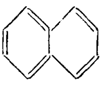
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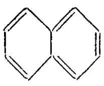
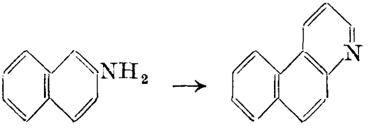
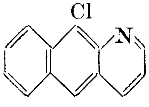

(V.)

Marckwald [7] called attention to the remarkable difference in reactivity between the two positions adjacent to the functional group in β-naphthol and β-naphthylamine (VI), notably the formation of the angular benzoquinoline (VII) in the Skraup reaction [8] which, with some 1-substituted 2-naphthylamines, even leads to elimination of the substituent. The simplest explanation, and that accepted by Marckwald, is that formation



(VI.) (VII.)



(VIII.)

of the new ring occurs so as to include a double bond of the original ring system, *i.e.*, that there is a double bond in the 1 : 2- and a single bond in the 2 : 3-position of naphthalene, and that these bonds are fixed.

Although angular cyclisation is by no means invariable [9, 10] [*e.g.*, (VIII) is obtained in reasonable yield], it is most common among naphthalene derivatives and also among heterocyclic analogues of naphthalene; [11] and it is paralleled by the angular cyclisation of β-2-naphthylpropionic acids, and of γ-2-naphthylbutyric acids, [12] although if the 1-position is hindered cyclisation may take place in the 3-position.[13]

It has been widely accepted in the past, particularly by Marckwald, by Fries, and by Fieser,[5] that the reactions of phenols are very similar to, and take place by the same mechanisms as, those of aliphatic enols: *e.g.*, halogenation and coupling with diazo-compounds may be used to demonstrate the presence or absence of a double bond in phenols. A *p*-alkylphenol is halogenated first at one of the positions *ortho-* to the hydroxyl group, and then at the other. If the reaction does involve an "enolic" double bond, then it must be supposed that the second substitution is preceded by a migration of the double bond. With 2-naphthol, however, the situation is very different. The first substituent enters the 1-position [14] and further halogenation of 1-chloro(or -bromo)-2-naphthol (IX) gives a keto-halogenide (X): [15] 1 : 3-dihalogeno-derivatives are not formed.

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[7] *Annalen*, 1893, **274**, 331; 1894, **279**, 1.

[8] See also Knueppel, *Ber.*, 1896, **29**, 703.

[9] Fries, Walter, and Schilling, *Annalen*, 1935, **516**, 285.

[10] Huisgen, *ibid.*, 1948, **559**, 101; see also Clemo and Legg, *J.*, 1947, 545.

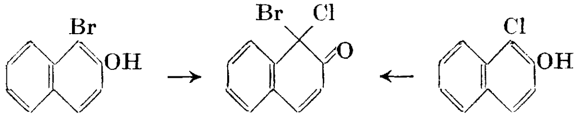
[11] Boggust and Cocker, *J.*, 1949, 355.

[12] Schroeter, Müller, and Huang, *Ber.*, 1929, **62**, 645; Cook and Hewett, *J.*, 1933, 1098; Haworth, *J.*, 1932, 1125; Bachmann and Edgerton, *J. Amer. Chem. Soc.*, 1940, **62**, 2219.

[13] Haworth and Sheldrick, *J.*, 1934, 1950; Hewett, *J.*, 1940, 293.

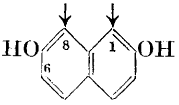
[14] Zincke, *Ber.*, 1888, **21**, 3378, 3540.

[15] Fries, *Annalen*, 1927, **454**, 121; Fries and Schimmelschmidt, *ibid.*, 1930, **484**, 245; Fries and Hübner, *Ber.*, 1906, **39**, 435; Fries and Hempelmann, *Ber.*, 1908, **41**, 2614.



(IX.) (X.) (IX.)

Similarly, 2-naphthol couples with diazotised amines at the 1-position, with elimination of a 1-carboxyl group or a 1-halogen atom ; 1-alkyl-2-naphthols do not react. It seems that the double bond which is evidently present in the 1 : 2-position cannot " migrate " to the 2 : 3-position. Further, Ruggli and Courtin [16] found that 2 : 7- dihydroxynaphthalene (XI) couples at the 1 : 8- and not at the 1 : 6-positions, so that naphthalene apparently has the symmetrical structure (III) ; and 1 : 8-dialkyl-2 : 7-dihydroxynaphthalenes (XII) and 1 : 5-dialkyl-2 : 6-dihydroxynaphthalenes (XIII) do not couple, even with particularly reactive diazo-compounds.[17]



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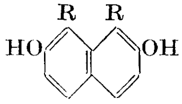

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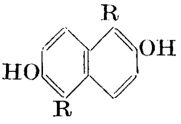

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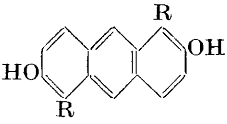

(XIV.)

The same technique has also been applied to the study of the double-bond distribution in anthracene, phenanthrene, pyrene, and other compounds. *E.g.*, 2 : 6-dihydroxyanthracene is brominated in the 1- and the 5-position,[18] and 1 : 5-dialkyl-2 : 6-dihydroxyanthracenes (XIV) do not couple with diazotised amines ; [19] it seems therefore that the 1 : 2-, 3 : 4-, 5 : 6-, and 7 : 8-bonds in anthracene are doubly linked, and that the 2 : 3- and 6 : 7-bonds are single. Similarly, in phenanthrene, it seems that the 1 : 2- and 3 : 4-bonds are double, and that the 2 : 3-bond is single.[20]

Unfortunately, the value of all this chemical work as evidence rests on the assumptions made regarding the reaction mechanisms. As McLeish and Campbell [21] have pointed out, the isolation of 5 : 6-benzoquinoline as the sole product of the Skraup reaction with β-naphthylamine, although clearly indicating the superior reactivity of the 1-position, may not *necessarily* depend on the presence of a double bond in the 1 : 2-position. Indeed, according to the modern view, such electrophilic reactions are probably dependent on the relative availability of two π-electrons at the 1- and the 3-position and not *per se* on the presence or otherwise of double bonds.

To a lesser extent this criticism may also be made with regard to the use of the Diels–Alder reaction [22] and of the Claisen rearrangement in the

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[16] *Helv. Chim. Acta*, 1932, **15**, 110.

[17] Fieser and Lothrop, *J. Amer. Chem. Soc.*, 1935, **57**, 1459.

[18] Fries, Walter, and Schilling, *Annalen*, 1935, **516**, 248.

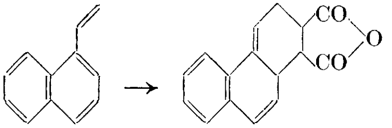
[19] Fieser and Lothrop, *J. Amer. Chem. Soc.*, 1936, **58**, 749.

[20] Fieser and Young, *ibid.*, 1931, **53**, 4120.

[21] McLeish and Campbell, *J.*, 1937, 1103.

[22] Kloetzel, " Organic Reactions ", Vol. IV, p. 1 ; Holmes, *op. cit.*, p. 60 ; Butz and Rytina, *op. cit*, Vol. V, p. 136.

study of bond fixation. 1-Vinylnaphthalene (XV) can function as a diene, giving with maleic anhydride the adduct (XVI).[23] Evidently the 1 : 2-bond in naphthalene functions as a double bond. For the present purpose, however, 2-vinylnaphthalene (XVII) is of even greater interest, for in this compound either the 1 : 2- or the 2 : 3-bond can conceivably function as a double bond : only the former does so, the adduct being (XVIII).[24]



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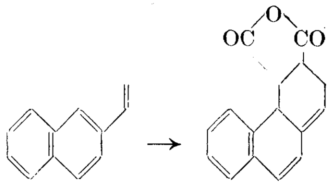
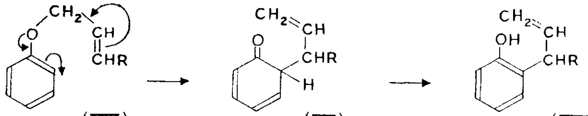
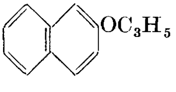


(XVII.) (XVIII.)

The Claisen rearrangement,[25] involving the conversion of allyl ethers of enols, and of phenols (as XIX), into *C*-alkyl derivatives (as XXI) on heating, almost certainly proceeds *via* a cyclic transition state and the intermediate (XX), for γ-substituted allyl groups become α-substituted in the product of rearrangement [cf. (XIX) ⟶ (XXI)].[26] The two double bonds (see XIX) seem to be an essential requirement for this mechanism, and for this reason the reaction has been extensively applied in the study of apparent bond fixation in aromatic compounds.



(XIX.) (XX.) (XXI.)



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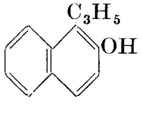

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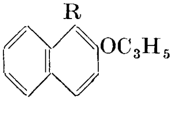

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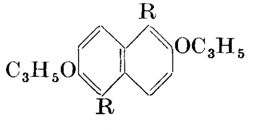

(XXV.)

The classical example is provided by 2-allyloxynaphthalene (XXII) which rearranges, in good yield, to 1-allyl-2-naphthol (XXIII) (and not to 3-allyl-2-naphthol). Similarly, 1-allyloxynaphthalene rearranges to 2-allyl-1-naphthol, a fact which indicates that there is no inherent resistance to reaction in the 2-position. However, 1-substituted 2-allyloxynaphthalenes (XXIV) do not rearrange, even when the 3-position is free and even under more vigorous conditions.[25] Here again, therefore, it seems that the 2 : 3- unlike the 1 : 2-linkage cannot function as a double bond. Further evidence

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[23] Cohen, *Nature*, 1935, **136**, 869 ; Bachmann and Scott, *J. Amer. Chem. Soc.*, 1948, **70**, 1462 ; Bachmann and Chemerda, *ibid.*, p. 1468.

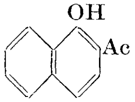
[24] Cohen and Warren, *J.*, 1937, 1315.

[25] Claisen, *Ber.*, 1912, **45**, 3157 ; Tarbell, " Organic Reactions ", Vol. II, p. 1.

[26] Claisen and Tietze, *Ber.*, 1925, **58**, 275 ; 1926, **59**, 2344 ; Ingold, *Ann. Reports*, 1926, 143.

of this nature is available from diallyloxynaphthalenes [*e.g.*, (XXV) does not rearrange [17]] and in the phenanthrene [20] and anthracene series [19] and among some heterocyclic aromatic compounds.[27]

In 1934, Baker [28] pointed out that the ability to form six-membered chelate rings containing co-ordinately linked hydrogen in *o*-hydroxyacetophenones and similar compounds, seems to depend on the presence of a double bond between the carbon atoms bearing the hydroxyl and acetyl groups. If naphthalene has a symmetrical arrangement of double bonds (as III), 1-hydroxy-2-acetylnaphthalene (XXVI) and 2-hydroxy-1-acetylnaphthalene (XXVII) should behave as chelated compounds, and 2-hydroxy-3-acetylnaphthalene (XXVIII) should be non-chelated. In fact, all three compounds are chelated,[29] apparently indicating that the 2 : 3-bond *can* function as a double bond. The results are, however, inconclusive as there is some evidence that the formation of a chelate ring is itself sufficiently powerful to overcome the normal arrangement of double bonds.[30]



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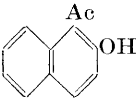

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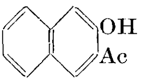

(XXVIII.)

On the other hand, the infra-red spectra of the nitronaphthylamines show that there is considerable hydrogen bonding in 2-nitro-1-naphthylamine, and in 1-nitro-2-naphthylamine, but that hydrogen bonding does not occur in 3-nitro-2-naphthylamine.[31]

Further evidence that the 1 : 2-bond of naphthalene behaves as a double and the 2 : 3-bond as a single bond has been obtained by a study of the transmission of the tautomeric (or resonance) effects of substituents. As required if the symmetrical Erlenmeyer structure (III) for naphthalene is correct, the bromine atom in 1-bromo-2-nitro-, 2-bromo-1-nitro-, and 4-bromo-1-nitro-naphthalenes is " reactive " towards piperidine but that in 3-bromo-2-nitronaphthalene is " non-reactive ".[21] Similarly, the methyl group in 1-methyl- but not in 3-methyl-*iso*quinoline is activated by the nitrogen, apparently indicating the presence of a double bond between the nitrogen and the carbon atom in the 1-position, but a single bond between the nitrogen and the 3-position.[32] For the same reason, the methyl group in 2-methylquinoline is reactive.[33]

The effects of *o*-substituents on the basicity of aromatic amines, and on the strengths of aromatic acids, are of interest in this connection. *o*-Nitroaniline is a much weaker base than aniline, and 1-nitro-2-naphthyl-

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[27] Ochiai and Kokeguti, *J. Pharm. Soc. Japan*, 1940, **60,** 271 ; Ochiai and Nisizawa, *Ber.*, 1941, **74,** 1407 ; Mander-Jones and Trikojus, *J. Amer. Chem. Soc.*, 1932, **54,** 2570 ; *J. Proc. Roy. Soc., N.S. Wales*, 1932, **66,** 300.

[28] *J.*, 1934, 1684.

[29] Baker and Carruthers, *J.*, 1937, 479.

[30] Baker and Lothian, *J.*, 1935, 628 ; 1936, 274 ; Shah and Laiwalla, *J.*, 1938, 1828 ; Shah and Shah, *J.*, 1939, 132.

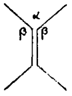
[31] Hathway and Flett, *Trans. Faraday Soc.*, 1949, **45,** 818.

[32] Mills and Smith, *J.*, 1922, **121,** 2724.

[33] Henrich, *Ber.*, 1899, **32,** 668.

amine is much weaker than β-naphthylamine. 3-Nitro-2-naphthylamine, on the other hand, is only *slightly* weaker than the parent amine.[34] Finally, Bergmann and Hirshberg [35] have shown that a chlorine atom in the 3-position has a much smaller influence on the strength of 2-naphthoic acid than when it is in the 1-position.

The Mills–Nixon Effect.—Until fairly recently, it was thought that the angle (α in XXIX) between the single bonds in ethylene and its derivatives is the same as that between the carbon valencies of methane (*i.e.*, $109\tfrac{1}{2}^{\circ}$), and that the angle (β) between each single bond and the double bond is, by difference, $125\tfrac{1}{4}^{\circ}$. Assuming this to be the case, Mills and Nixon [36] pointed out that, if benzene has alternate single and double bonds, then the external valency bonds cannot be directed from the centre of the hexagon, but must lie (as in XXX) alternately to either side.



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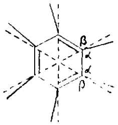
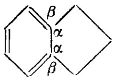
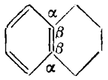


(XXX.)

It was recognised that the inclusion of double bonds in a cyclic system might affect the magnitude of the angles, but it was maintained that the angle α would certainly be smaller than the angle β, as in (XXX). In these circumstances, Mills and Nixon reasoned that a five-membered ring can be fused on to a benzene ring without distortion of the valency angles *only if it includes two of the smaller* (α) *angles* (as in XXXI); that is, if it is attached to two carbon atoms which are joined by a single bond. On the other hand, a six-membered ring can be attached without distortion of the valency angles *only if it includes two of the larger* (β) *angles* (as in XXXII), that is, if it is attached to two carbon atoms which are linked by a double bond. It was thought that the net effect would be to stabilise the double bonds of indane as in (XXXI), and that the double bonds in tetralin would be stabilised or fixed as in (XXXII).



(XXXI.)



(XXXII.)

The experimental methods which have been used in attempts to demonstrate bond fixation in these two compounds are similar to those already described. For example, as predicted by the hypothesis, bromination and diazo-coupling of 5-hydroxyindane (XXXIII) and of 6-hydroxytetralin (XXXIV) occurred predominantly at the positions shown by the arrows, but as 3 : 4-dimethylphenol (XXXV) reacts [37] in the same way as 5-hydroxyindane the results were inconclusive. Mills and Nixon were forced to

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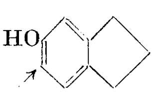
[34] Bryson, *Trans. Faraday Soc.*, 1949, **45**, 257.

[35] *J.*, 1936, 331.

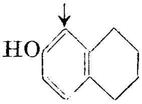
[36] *J.*, 1930, 2510.

[37] Diepolder, *Ber.*, 1909, **42**, 2916.

conclude that the arrangement of double bonds in 5-hydroxyindane is the " normal " arrangement, whereas the tetramethylene chain in 6-hydroxytetralin causes an " abnormal " arrangement.



(XXXIII.)



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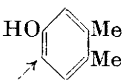
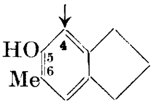


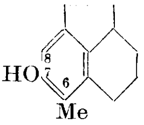
(XXXV.)

The evidence for bond fixation in indane and tetralin has been still further weakened since Parkes[38] found the relative reactivity, towards diazo-coupling, of the two positions *ortho* to the hydroxyl group of 3 : 4-dialkylphenols to depend on the alkyl group. Further, although 6-hydroxytetralin couples and brominates in the 5-position, it nitrates in the 7-position ;[39] and the Skraup reaction with 6-aminotetralin gives the linear, and not the angular, compound.[40]

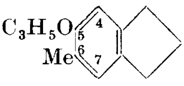
The coupling experiments of Fieser and Lothrop[41, 42] are also inconclusive : 6-hydroxy-5 : 8-dimethyltetralin readily couples with diazo-compounds, and 5-hydroxy-6-methylindane (XXXVI) also couples if the reaction is carried out in weakly alkaline solution, indicating that there is no bond fixation in indane comparable with that observed in naphthalene. Further, in tetrahydroacenaphthylene (as XXXVII), where the straining effects (if any) of the two exocyclic rings should reinforce one another, no definite evidence for bond fixation was obtained, for the 7-hydroxy-, the 8-hydroxy-, and the 7-hydroxy-6-methyl compounds (XXXVII) all couple comparatively readily.[43]



(XXXVI.)



(XXXVII.)



(XXXVIII.)

No bond fixation could be demonstrated by the Claisen rearrangement, for 5-allyloxy-6-methyl- (XXXVIII) and 5-allyloxy-4 : 7-dimethyl-indane both rearrange without difficulty.[42] If the hypothesis of Mills and Nixon were correct the former compound would not be expected to rearrange.

Other methods have also failed to detect bond fixation in indane and in tetralin. Baker[44] found that 4- and 6-acetyl-5-hydroxyindane are both chelated ; little weight can, however, be given to this observation, for the formation of a chelate ring may itself affect the ring system.[30] The acidities of the three nitrophenols (XXXIX—XLI) are almost identical,[45] although considerable difference would certainly exist if the bonds are fixed as postu-

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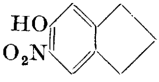
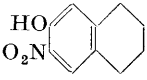
[38] *J.*, 1948, 2143.
[39] Thoms and Kross, *Arch. Pharm.*, 1927, **265,** 336.
[40] Von Braun and Gruber, *Ber.*, 1922, **55,** 1710.
[41] *J. Amer. Chem. Soc.*, 1936, **58,** 2050 ; 1937, **59,** 945.
[42] Lothrop, *ibid.*, 1940, **62,** 132.
[43] Johnson and Glenn, *ibid.*, 1949, **71,** 1087.
[44] *J.*, 1937, 476.
[45] Arnold and Evans, *J. Amer. Chem. Soc.*, 1940, **62,** 556.

lated by Mills and Nixon; and the heats of hydrogenation of alkylbenzenes and of indane are almost identical, entirely precluding bond fixation.[46]

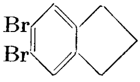


(XXXIX.)

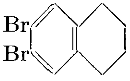


(XL.)

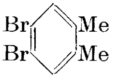
(XLI.)



(XLII.)



(XLIII.)



(XLIV.)

Attempts have also been made by using physical methods. Sidgwick and Springall[47] suggested that the considerable difference between the dipole moment of 5 : 6-dibromoindane (XLII) and those of 6 : 7-dibromotetralin (XLIII) and 4 : 5-dibromo-*o*-xylene (XLIV) might be associated with bond fixation in indane with a consequent increase in the bromine–bromine distance. This has, however, been invalidated by electron-diffraction measurements which show the bromine–bromine distances in 5 : 6-dibromoindane, 6 : 7-dibromotetralin, and 4 : 5-dibromo-*o*-xylene to be identical.[48] An alternative explanation for the differences in dipole moments must therefore be sought.[49]

It seems therefore that there is little or no physical or chemical evidence to support the hypothesis of bond fixation in indane and in tetralin. On the other hand, there is ample evidence that the steric requirements of a five-membered ring *do* result in a distortion of the angles α and β from the normal aromatic figure of 120°, as predicted by Mills and Nixon. Arnold and his collaborators[50] have pointed out that a distortion of the Mills–Nixon type would diminish the steric influence of the methylene groups adjacent to the benzenoid ring, and that the steric effect of a five-membered ring would therefore be smaller than that of a six-membered ring. This has been conclusively demonstrated[50] by several different experimental methods.

However, this distortion of the valency angles does not necessarily support the concept of bond stabilisation. Mills and Nixon's hypothesis was based on the assumption that the angle (α) between the single bonds in ethylene is $109\frac{1}{2}$°, and that the angle (β) between the double and single bonds is, by difference, $125\frac{1}{4}$°. Evidence has now accumulated[51] that this assumption has no basis in fact, but that all the angles in ethylene are very

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[46] Dolliver, Gresham, Kistiakowsky, and Vaughan, *J. Amer. Chem. Soc.*, 1937, **59**, 831.

[47] *J.*, 1936, 1532.

[48] Kossiakoff and Springall, *J. Amer. Chem. Soc.*, 1941, **63**, 2223; see also Springall, *Chem. and Ind.*, 1943, **21**, 149.

[49] Springall, Hampson, May, and Spedding, *J.*, 1949, 1524.

[50] Arnold and Rondestvedt, *J. Amer. Chem. Soc.*, 1945, **67**, 1265; 1946, **68**, 2176; Arnold and Craig, *ibid.*, 1948, **70**, 2791; 1950, **72**, 2728; Arnold and Richter, *ibid.*, 1948, **70**, 3505.

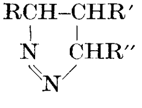
[51] Penney, *Proc. Roy. Soc.*, 1937, *A*, **158**, 306; Thompson, *Trans. Faraday Soc.*, 1939, **35**, 697; Gallaway and Barker, *J. Chem. Physics*, 1942, **10**, 88; see also Coulson, *Quart. Reviews*, 1947, **1**, 149.

nearly 120°. The argument as originally put forward by Mills and Nixon [36] is therefore entirely untenable, as also is the explanation by Sutton and Pauling [52] which is based on the same assumption. As a matter of fact, calculations by Longuet-Higgins and Coulson [53] indicate that, although the bonds in indane are very similar to those in benzene, any slight differences are in the direction opposite to those commonly postulated.

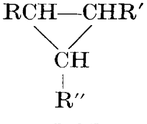
The problem therefore becomes one of finding why 5-hydroxyindane (XXXIII) couples in the 6-position, and 6-hydroxytetralin (XXXIV) in the 5-position. Several explanations have been advanced,[54, 55] but the recent contribution by Berthier and Pullman [56] seems to be important in this respect. The essence of their theory is that the activating influence of a saturated five-membered ring is not identical with that of a six-membered ring and that, although the electronic charge density on the 5-position of 6-hydroxytetralin exceeds that on the 7-position, the charge on the 4-position of 5-hydroxyindane exceeds that on the 6-position. It is, of course, a fundamental assumption that electrophilic reagents (such as diazo-compounds) seek out the positions of greatest electronic charge for attack.

The Double-bond Reagents.—For a study of the bond structure of aromatic compounds, no substitution reaction can be an entirely acceptable method. The same criticism cannot, however, be applied to the use of reagents which *add* only to double bonds. Several substances appear to function as " double-bond reagents ",[57] particularly osmium tetroxide, ozone, and certain aliphatic diazo-compounds such as diazomethane and diazoacetic ester, and all these reagents may be used to investigate the nature of aromatic double bonds.

Reactions with Diazo-compounds. Certain diazo-compounds, such as diazomethane and diazoacetic ester, add to ethylenic double bonds without difficulty, to give pyrazolines (XLV) ; but at moderately high temperatures such pyrazolines are often decomposed, with elimination of nitrogen, to give *cyclo*propane derivatives (XLVI). The reaction often provides a suitable method for the preparation of such compounds.[58]



(XLV.)



(XLVI.)

With aromatic compounds the reaction proceeds only with difficulty, and at the elevated temperatures normally used nitrogen may be eliminated *before* the addition, in which case the reacting molecule may be the radical $\overset{*}{*}$CHR.[59] Alternatively, the reaction (at least with diazomethane) can be

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[52] *Trans. Faraday Soc.*, 1935, **31**, 939.

[53] *Ibid.*, 1946, **42**, 756.

[54] Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900 ; Pullman, *Bull. Soc. chim.*, 1947, **14**, 337.

[55] Waters, *J.*, 1948, 727.

[56] *Bull. Soc. chim.*, 1950, **17**, 88.

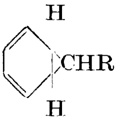
[57] Badger, *J.*, 1949, 456.

[58] Smith, *Chem. Reviews*, 1938, **23**, 193 ; Fieser and Peters, *J. Amer. Chem. Soc.*, 1931, **53**, 4080 ; Hancox, *J. Proc. Roy. Australian Chem. Inst.*, 1949, **16**, 282.

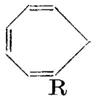
[59] Buchner and Hediger, *Ber.*, 1903, **36**, 3502.

carried out at ordinary temperatures, but under illumination with ultraviolet light,[60] and it is possible that a radical reagent is also involved under these conditions.

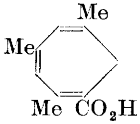
The reaction of diazoacetic ester with benzene and its derivatives was investigated by Buchner and his co-workers [59, 61, 62] who found that the primary product is the ester of norcaradienecarboxylic acid (XLVII; R = CO_2H), the structure of which was proved by its oxidation to *cyclo*propane-1 : 2 : 3-tricarboxylic acid, and by other degradations. It seems, therefore, that the acetic ester radical *adds* to one double bond. Norcaradienecarboxylic acid was also found to undergo rearrangement, especially at elevated temperatures, to *cyclo*heptatrienecarboxylic acid (XLVIII; R = CO_2H), and to phenylacetic acid. By the action of diazoacetic ester on methyl derivatives of benzene, phenylpropionic acids were also obtained. The addition of diazomethane to benzene is evidently very similar, for the product was found to have properties which indicate that it can be represented equally well by structure (XLVII; R = H) or (XLVIII; R = H).[60]



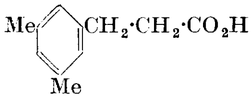
(XLVII.)



(XLVIII.)

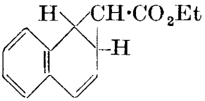


(XLIX.)

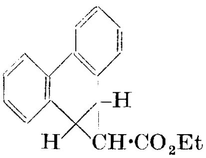


(L.)

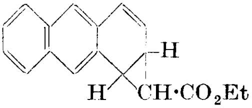
With substituted benzenes, steric hindrance seems to play an important part in deciding the actual bond to be affected. The addition always involves only unsubstituted carbon atoms, and a norcaradienecarboxylic acid with a quaternary carbon atom has never been obtained from a benzene derivative.[61, 62] With certain polyalkylbenzenes, however, an unsubstituted bond is not always available, and in such cases *cyclo*heptatriene derivatives seem to be formed directly. For example, hydrolysis of the reaction product from mesitylene and diazoacetic ester gave trimethyl*cyclo*heptatrienecarboxylic acid (XLIX), together with smaller amounts of 3 : 5-dimethylphenylpropionic acid (L) and mesitylacetic acid. No bicyclic compound could be detected.[62]



(LI.)



(LII.)



(LIII.)

Diazoacetic ester reacts with naphthalene to give ethyl 1 : 2-dihydro-1 : 2-naphthyleneacetate (LI), the structure of which has also been estab-

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[60] Doering and Knox, *J. Amer. Chem. Soc.*, 1950, **72**, 2305.

[61] Buchner and Curtius, *Ber.*, 1885, **18**, 2377; Braren and Buchner, *Ber.*, 1901, **34**, 982; Buchner and Feldmann, *Ber.*, 1903, **36**, 3509; Buchner and Delbrück, *Annalen*, 1908, **358**, 1; Buchner and Schulze, *ibid.*, 1910, **377**, 259.

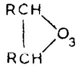
[62] Buchner and Schottenhammer, *Ber.*, 1920, **53**, 865.

lished by a series of degradations leading finally to the isolation of *cyclo*propanetricarboxylic acid. Unlike the product from benzene, however, this compound could not be induced to rearrange.[59] Similarly, phenanthrene is attacked at the 9 : 10-bond, to give ethyl 9 : 10-dihydro-9 : 10-phenanthryleneacetate (LII), which is also resistant to ring enlargement.[63] The structure of this product has been rigidly proved. Anthracene is also attacked by diazoacetic ester, and the product is almost certainly that obtained by addition of the acetic ester radical to the 1 : 2-bond (*i.e.*, LIII).[64, 65] *

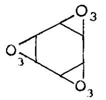
Monoaddition products have also been obtained recently from pyrene and from 1 : 2-benzanthracene.[65]

Reactions with Ozone. Ozone adds very readily to ethylenic double bonds, with the formation of so-called ozonides.[66] The structure of these compounds has not yet been completely elucidated, but they may be represented approximately as in (LIV).[67] The decomposition of such ozonides, either by treatment with water or by hydrogenation, usually results in the cleavage of the carbon–carbon bond, and the formation of carbonyl compounds, and it is this circumstance which makes the ozonolysis reaction so useful in determining the positions of unsaturated linkages in organic molecules.

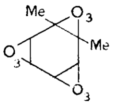
With benzene, ozone slowly forms a triozonide (LV) which gives glyoxal on decomposition.[68] This appears to support the Kekulé formula for benzene. Levine and Cole [69] attempted to settle the question of the existence



(LIV.)



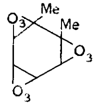
(LV.)



(LVI.)

$\downarrow$

CHO·CHO
+
2MeCO·CHO



(LVII.)

$\downarrow$

2CHO·CHO
+
MeCO·COMe

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[63] Drake and Sweeney, *J. Org. Chem.*, 1946, **11**, 67 ; Cook, Dickson, and Loudon, *J.*, 1947, 746.

[64] Clar, *Reichsamt Wirtschaftsausbau, Chem. Ber.* Prüf—Nr 015 (PB 52017) 859—878 (1942) ; *Chem. Abs.*, 1947, **41**, 6553.

[65] Badger, Cook, and Gibb, unpublished.

[66] Long, *Chem. Reviews*, 1940, **27**, 437.

[67] Cf. Allen and Sutton, *Acta Cryst.*, 1950, **3**, 52.

[68] Harries, *Annalen*, 1905, **343**, 311 ; Harries and Weiss, *Ber.*, 1904, **37**, 3431.

[69] *J. Amer. Chem. Soc.*, 1932, **54**, 338.

* At first sight it may be somewhat surprising that this reagent adds only *once* to benzene, naphthalene, and anthracene, for it seems that this gives a molecule having one, or more, *ethylenic* double bonds, which are unaffected by the reagent. The explanation is probably to be found in the fact that a *cyclo*propane ring can conjugate with double bonds. The apparently ethylenic double bonds, in fact, therefore have very greatly reduced reactivity. For references, see Volkenburgh, Greenlee, Derfer, and Boord, *J. Amer. Chem. Soc.*, 1949, **71**, 3593.

or otherwise of two isomeric *o*-disubstituted derivatives of benzene: they reasoned that if *o*-xylene exists in two isomeric configurations which depend on the position of the double bonds with reference to the methyl groups, or even if these two structures merely represent phases of a complex dynamic structure, then two ozonides (LVI and LVII) should be formed. Decomposition of (LVI) would be expected to yield glyoxal and two molecules of methylglyoxal, but (LVII) would give diacetyl and two molecules of glyoxal. All three decomposition products were successfully identified, and there can be no doubt therefore that *o*-xylene gives the two ozonides (LVI and LVII). These results have recently been confirmed by Haaijman and Wibaut,[70] who have also determined that the decomposition products, diacetyl, methylglyoxal, and glyoxal, are formed in the molecular ratios of 1 : 2 : 3 as expected if the two ozonides are formed in equal amount. The interpretation of the results is, of course, difficult. Levine and Cole maintained that *o*-xylene does exist in two isomeric configurations, although they recognised that a dynamic structure might lead to the same results.[71]

In the case of pyridine the situation is evidently very similar. Ozonolysis of 2 : 3-dimethylpyridine and of 2 : 3 : 4-trimethylpyridine,[72] followed by scission of the resulting ozonides, gave glyoxal, methylglyoxal, diacetyl, formic acid, oxalic acid, and ammonia. This may be taken as evidence that pyridine, like benzene, reacts according to both Kekulé-type structures.

The same method has also been applied to the study of the bond structure of naphthalene. In early experiments Harries and Weiss [68] found that naphthalene forms a diozonide, and as *o*-phthalaldehyde was obtained on decomposition, the 1 : 2- and 3 : 4-bonds must be involved. More recently, Wibaut and van Dijk [73] have studied the ozonisation of 2 : 3- and 1 : 4-dimethylnaphthalene. The former gave glyoxal, methylglyoxal, and diacetyl, the molecular ratio of diacetyl to methylglyoxal being 10 : 1. The presence of methylglyoxal among the products of decomposition clearly indicates that one of the ozonides obtained from 2 : 3-dimethylnaphthalene must have the structure (LVIII). This was first interpreted [73] as showing that the 2 : 3-bond in naphthalene sometimes reacts as a double bond, but an alternative explanation was given by Kooyman.[74] If the initial attack of ozone happens to be on either the 5 : 6- or the 7 : 8-bond of 2 : 3-dimethylnaphthalene, the resulting intermediates would very rapidly form a diozonide involving both the 5 : 6- and the 7 : 8-bond. Such a diozonide would simulate *o*-xylene, and might be expected to react according to either Kekulé structure (LIX) or (LX). The former (LIX) would give the pentozonide (LVIII) on further ozonisation. This explanation, which involves primary addition only to $\alpha\beta$-bonds, is therefore in harmony with other evidence regarding the structure of naphthalene, and a primary addition to a $\beta\beta$-bond need not be postulated. The further explanation of the ozonisation of 2 : 3-dimethylnaphthalene follows directly. Thus the diozonide (LX) would

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[70] *Rec. Trav. chim.*, 1941, **60**, 842.

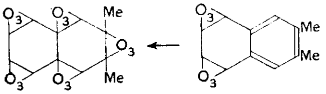
[71] Cf. Campbell, *Ann. Reports*, 1947, **44**, 127.

[72] Wibaut and Kooyman, *Rec. Trav. chim.*, 1946, **65**, 141.

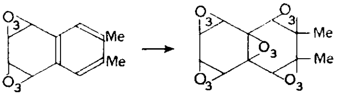
[73] *Ibid.*, p. 413.

[74] *Ibid.*, 1947, **66**, 201.

be expected to give the pentozonide (LXI) on further ozonisation, and this would give diacetyl and glyoxal on decomposition. The same pentozonide (LXI), together with an isomeric pentozonide (which would also yield diacetyl and glyoxal on scission), would be expected if the initial attack of ozone occurs at the 1 : 2- or 3 : 4-bond.



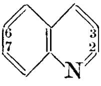
(LVIII.) (LIX.)



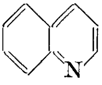
(LX.) (LXI.)

The formation of methylglyoxal following scission of the ozonides from 1 : 4-dimethylnaphthalene [73] may be explained similarly.

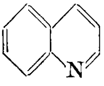
Quinoline might also be expected to react with ozone in the same manner as naphthalene, and the indications are that this is the case.[75] Velocity measurements have shown that the addition occurs fairly rapidly until two molecules of ozone have been taken up, after which the reaction becomes very slow. It seems therefore that the primary product is probably a diozonide, and this is confirmed by the identification of glyoxal and pyridine-2 : 3-dialdehyde among the products of decomposition. The identification of the latter product also indicates that the initial attack is on the hydrocarbon ring rather than on the heterocyclic ring, and that the attack is on the $\alpha\beta$-bonds. The ozonolysis of 6 : 7-, 5 : 8-, and 2 : 3-dimethylquinoline shows that quinoline and its derivatives react according to structure (LXII) or (LXIII), but *not* according to structure (LXIV). Decomposition of the ozonides from 6 : 7-dimethylquinoline, for example, gave diacetyl and pyridinedialdehyde ; but neither methylglyoxal nor pyridione was detected, although both would be expected if the initial attack occurs at the 6 : 7-bond.



(LXII.)



(LXIII.)



(LXIV.)

There can be little doubt therefore that in the ozonisation of both naphthalene and quinoline derivatives, the *initial* attack is always at an $\alpha\beta$-bond, and never at a $\beta\beta$-bond.

Relatively little work has been carried out on the ozonisation of polycyclic aromatic compounds. Attempts to ozonise anthracene have given only anthraquinone,[76] possibly by direct oxidation. On the other hand, in the ozonisation of pyrene (LXV) the 1 : 2-bond is first attacked, and then the 6 : 7-bond.[77] This has been clearly demonstrated by the isolation of 4-formylphenanthrene-5-carboxylic acid, and of the corresponding derivative of diphenyl, from the products of scission, and the method has

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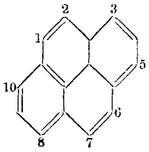
[75] Wibaut and Boer, *Proc. K. Ned. Akad. Wet.*, 1950, **53,** 19.

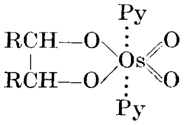
[76] Roitt and Waters, *J.*, 1949, 3060.

[77] Vollmann, Becker, Corell, and Streeck, *Annalen*, 1937, **531,** 1 ; Fieser and Novello, *J. Amer. Chem. Soc.*, 1940, **62,** 1855.

been applied to the synthesis of the difficultly accessible 4 : 5-dimethylphenanthrene.[78] This is a remarkable result, because the usual ionic electrophilic reagents (Br^+, etc.) attack pyrene at the 3-, 5-, 8-, and 10-positions. It seems that the 3-, 5-, 8-, and 10-positions are the most reactive *centres*, and the 1 : 2- and 6 : 7-bonds are the most reactive *bonds*.[57]



(LXV.)

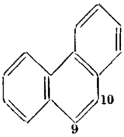


(LXVI.)

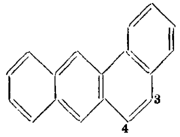
Reactions with Osmium Tetroxide. The third " double-bond reagent " is osmium tetroxide, which also adds very readily to ethylenic double bonds. If the reaction is carried out in the presence of pyridine, nicely crystalline addition compounds having cyclic structures of type (LXVI) are obtained, usually in theoretical yield.[79] These complexes give diols on mild hydrolysis, and the reaction is normally used synthetically for that purpose.

The addition of osmium tetroxide to aromatic double bonds takes place very slowly, only the most reactive bonds being attacked.[80] Thus osmium tetroxide does not attack benzene under the usual conditions, although there is evidence [81] that reaction by addition does occur in certain circumstances. It is in connection with the structure of the polycyclic aromatic compounds that osmium tetroxide provides information of unique value, for the reagent always seems to attack the most reactive *bond*, even when particularly reactive *centres* are available.

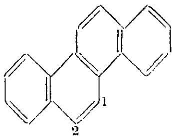
With phenanthrene (LXVII), osmium tetroxide adds to the 9 : 10-bond, and the complex gives *cis*-9 : 10-dihydroxy-9 : 10-dihydrophenanthrene on hydrolysis.[79] With 1 : 2-benzanthracene (LXVIII) and its derivatives, it adds exclusively to the 3 : 4-bond,[80, 82] although the 9 : 10-positions are the ones normally attacked by other reagents. With chrysene (LXIX), addition is to the 1 : 2-bond ; [80] and with pyrene (LXV) to the 1 : 2-bond,[80] in spite of the fact that the usual ionic reagents attack this hydrocarbon at the 3-, 5-, 8-, and 10-positions. Osmium tetroxide therefore resembles ozone in attacking the 1 : 2-bond. Similarly, osmium tetroxide attacks the 6 : 7-bond of 3 : 4-benzpyrene (LXX).[80]



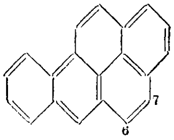
(LXVII.)



(LXVIII.)



(LXIX.)



(LXX.)

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[78] Newman and Whitehouse, *J. Amer. Chem. Soc.*, 1949, **71**, 3664 ; Badger, Campbell, Cook, Raphael, and Scott, *J.*, 1950, 2326.

[79] Criegee, *Annalen*, 1936, **522**, 75 ; Criegee, Marchand, and Wannowius, *ibid.*, 1942, **550**, 99.

[80] Cook and Schoental, *J.*, 1948, 170.

[81] *Idem*, *J.*, 1950, 47.

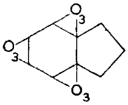
[82] Badger, *J.*, 1949, 2497.

With anthracene, osmium tetroxide adds to the 1 : 2- and the 3 : 4-bond.[83] The addition of *two* molecules of osmium tetroxide in this case is readily explained. The initial product, formed by the addition of one molecule of osmium tetroxide to the 1 : 2-bond, must contain a true ethylenic double bond (3 : 4), and this would be expected to react very rapidly with a second molecule of osmium tetroxide, to give the complex actually isolated.

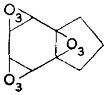
All these experiments with double-bond reagents indicate that aromatic bonds are not all identical, but that some are more " reactive " than others. With osmium tetroxide, and with ozone, these differences in relative reactivity can sometimes be measured quantitatively by measurement of the rate of addition. For example, it has been shown that the addition of osmium tetroxide to the 3 : 4-bond of 1 : 2-benzanthracene (LXVIII) proceeds about ten times faster than the addition to the 9 : 10-bond of phenanthrene (LXVII) under the same conditions.[84] In the same way it has been demonstrated that the presence of substituents in the benzanthracene ring system profoundly affects the rate of addition to the 3 : 4-bond. Methyl groups accelerate the addition, and deactivating substituents, such as the cyano-group, retard it.[57, 85] Similarly, it has been shown that alkyl substituents in benzene accelerate the addition of ozone.[86]

Double-bond Reagents and the Mills–Nixon Effect. Attempts have been made to use the double-bond reagents in the study of the Mills–Nixon effect.

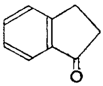
If indane has the structure required by Mills and Nixon [36] then the resulting triozonide (LXXI) should give *cyclo*pentane-1 : 2-dione, and two molecules of glyoxal, on decomposition. On the other hand, if it has the alternative Kekulé structure, the triozonide (LXXII) should give glyoxal and αα′-diketopimelic dialdehyde. The only scission products detected by Long and Fieser [87] after ozonolysis of indane were glyoxal and succinic acid, and some evidence was presented that the latter substance arises from *cyclo*pentane-1 : 2-dione. It was therefore concluded that indane reacts only in the form required by Mills and Nixon. The validity of this interpretation is, however, extremely doubtful, for it was also found that ozone oxidises a considerable proportion of the hydrocarbon to indan-1-one (LXXIII), and further ozonolysis of this product might also be expected to give succinic acid. The results are therefore inconclusive.



(LXXI)



(LXXII)



(LXXIII)

The use of diazoacetic ester in the study of the Mills–Nixon effect is complicated by the fact that, whenever possible, this reagent adds to

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[83] Cook and Schoental, *Nature*, 1948, **161**, 237.
[84] Badger and Reed, *ibid.*, p. 238.
[85] Badger, *J.*, 1950, 1809 ; Badger and Lynn, *J.*, 1950, 1726.
[86] van Dijk, *Rec. Trav. chim.*, 1948, **67**, 945.
[87] *J. Amer. Chem. Soc.*, 1940, **62**, 2670.

unsubstituted double bonds, and norcaradiene derivatives with a quaternary carbon atom are never obtained.[61, 62] Such compounds may not even be formed as intermediates, for compounds having no unsubstituted bond always give *cyclo*heptatriene derivatives, or substances formed by interaction of the diazoacetic ester with an alkyl group. In substituted aromatic compounds, therefore, the results are always consistent with the view that the addition takes place almost entirely at an unsubstituted bond if one is available, so that complex discussions on the many possible routes of addition, such as have sometimes been published by chemists interested in the preparation of azulenes, are usually unnecessary.[88]

In view of these steric factors it seems that only three bonds in indane are likely to be attacked by diazoacetic ester, namely the 4 : 5-, 5 : 6-, and 6 : 7-bonds. If indane has the structure attributed to it by Mills and Nixon, then there should be a double bond in the 5 : 6-position, so that addition of diazoacetic ester should occur there. On the other hand, if indane has the alternative structure, it should undergo addition at either the 4 : 5- or the 6 : 7-bonds. Arnold [89] has produced evidence that the addition occurs at the 4 : 5-bond, and *not* at the 5 : 6-bond as required by Mills and Nixon. Here again, however, the results are inconclusive, for, as the 4 : 5- and 6 : 7-bonds are identical, there is, on a simple statistical basis, twice the chance that addition will occur there rather than at the 5 : 6-bond. Moreover, the crude product obtained in this reaction was clearly a mixture, so that this work does not differentiate between the two bond structures.

Carbon–carbon Bond Lengths.—The application of *X*-ray and electron-diffraction techniques to the study of organic molecules has shown that the nature of chemical bonds is intimately connected with their length. The length of a carbon–carbon single bond, such as occurs in diamond and in the paraffins, is 1·54 A. The length of a carbon–carbon double bond, as in ethylene, is about 1·34 A., and that of a triple bond, as in acetylene, is 1·20 A. In all non-conjugated molecules these bond lengths apply very accurately, but experiment has shown that in *conjugated* compounds, there are considerable deviations from the normal. In all such conjugated compounds the bonds which are classically represented as single are found to be significantly *shorter* than 1·54 A., and those bonds which are classically represented as double are *longer* than 1·34 A. It seems reasonable to suppose, therefore, that conjugated bonds are neither pure double nor pure single bonds, but that they have intermediate " character ".[90]

Benzene is, of course, a conjugated molecule *par excellence*, and conclusive experimental evidence has been obtained that all the carbon–carbon bonds are of the same length, namely 1·39 A. They are therefore intermediate in " character " between single and double bonds. The electron-diffraction and *X*-ray data for benzene and its derivatives are consistent

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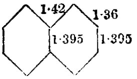
[88] Cf. Plattner and Roniger, *Helv. Chim. Acta*, 1942, **25**, 590.

[89] *Chem. Ber.*, 1947, **80**, 123.

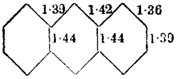
[90] Pauling, " The Nature of the Chemical Bond ", Cornell U.P., 2nd edn., 1940; Wheland, " The Theory of Resonance ", John Wiley, New York, 1944.

with this view,[91] but the most satisfactory evidence for the plane regular hexagonal model for benzene is that obtained by a study of the atomic vibrations of benzene and its deuterated analogues which are recorded in the infra-red and Raman spectra.[92]

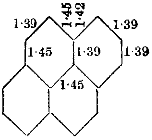
Although all the carbon–carbon bonds in benzene are identical in length, this is not the case with polycyclic aromatic hydrocarbons,[93] nor with the heterocyclic analogues of benzene. *X*-Ray crystallographic analysis has shown that in naphthalene (LXXIV) the $\alpha\beta$-bonds are significantly shorter (*i.e.*, nearer a double bond) than the $\beta\beta$-bonds, and also significantly shorter than the carbon–carbon bonds in benzene.[94] Similarly, in anthracene (LXXV) the $\alpha\beta$-bonds are also found to be significantly shorter (and nearer a double bond) than the $\beta\beta$-bonds, and the bonds common to two rings are significantly longer than benzene bonds.[95] Considerable bond-length variations have also been determined for pyrene (LXXVI).[96] In this molecule all the "external" bonds appear to be significantly shorter than the remainder.



(LXXIV.)



(LXXV.)



(LXXVI.)

These are not isolated examples. Bond-length variations have now been observed in a large number of polycyclic aromatic hydrocarbons, including coronene,[97] 1 : 12-benzperylene,[98] ovalene,[99] 1 : 2 : 5 : 6-dibenzanthracene,[100] and triphenylene.[101] The reactions of some of these, especially naphthalene, anthracene, 1 : 2-5 : 6-dibenzanthracene, and pyrene, have been investigated, and it is noteworthy that it is the *shortest* bonds which are preferentially attacked by double-bond reagents, and it is precisely these bonds which appear to function most readily as double bonds in other reactions.

The Nature of Aromatic Bonds.—There are thirty valency electrons in benzene. Twelve are allocated to the six carbon–carbon bonds, and twelve to the six carbon–hydrogen bonds. The remaining six form the "aromatic sextet" of unsaturation electrons (π-electrons, or mobile electrons), upon

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[91] Pauling and Brockway, *J. Chem. Physics*, 1934, **2,** 867; Schomaker and Pauling, *J. Amer. Chem. Soc.*, 1939, **61,** 1769; Brockway and Robertson, *J.*, 1939, 1324.

[92] Ingold, *Proc. Roy. Soc.*, 1938, *A*, **169,** 149; see also Ingold *et al.*, *J.*, 1936, 912—987, 1210; 1946, 222—333.

[93] For a review see Robertson, *Acta Cryst.*, 1948, **1,** 101.

[94] Abrahams, Robertson, and White, *ibid.*, 1949, **2,** 233, 238.

[95] Sinclair, Robertson, and Mathieson, *ibid.*, 1950, **3,** 251.

[96] Robertson and White, *J.*, 1947, 358.

[97] *Idem*, *J.*, 1945, 607.

[98] White, *J.*, 1948, 1398.

[99] Donaldson and Robertson, *Nature*, 1949, **164,** 1002; Buzeman, *Proc. Phys. Soc.*, 1950, **63,** 827.

[100] Robertson and White, *J.*, 1947, 1001.

[101] Klug, *Acta Cryst.*, 1950, **3,** 165.

which the peculiar properties of benzene and other aromatic compounds chiefly depend. Kekulé allocated these six electrons to the three double bonds in his *cyclo*hexatriene formula, but Dewar favoured a formula having two double bonds and one *para*-bond ; and others, particularly Claus, Armstrong, and Baeyer, have favoured different distributions. The experimental evidence, however, clearly indicates that the carbon–carbon bonds in aromatic and other conjugated compounds are neither pure single nor pure double bonds, but are of intermediate " character ". The π-electrons are therefore " delocalised ", and no satisfactory single valence-bond structure can be written for benzene, or indeed for any conjugated molecule.[90]

According to the theory of resonance, however, although no single adequate structure can be written, benzene can be represented as a resonance *hybrid* of all the possible valence-bond structures.[90] There are five such structures for benzene,[102] two of the Kekulé type, and three of the Dewar type, but in a very simple analysis the contributions of the Dewar structures to the hybrid can be neglected, and benzene may be considered simply as a hybrid of the two Kekulé structures. In these circumstances all the carbon–carbon bonds would be identical, and have 50% double-bond character.[90] In the same way, naphthalene may be considered as a hybrid of the three Kekulé-type structures (III—V). In two of these structures (III and IV) the 1 : 2-bond is " double ", but in the other (V) it is " single ". In the naphthalene hybrid, therefore, the 1 : 2-bond may be said to have $66\frac{2}{3}$% double-bond character. On the other hand, the 2 : 3-bond is double in only one (V) of the contributing structures, so that in the naphthalene hybrid the 2 : 3-bond must have $33\frac{1}{3}$% double-bond character. Estimates of the double-bond characters of all the bonds in naphthalene, in anthracene, in phenanthrene, and in other compounds can be made in exactly the same way, and it is significant that there is a smooth-curve relationship between percentage of double-bond character as evaluated in this way, and experimentally determined bond lengths.[90]

This method is somewhat oversimplified, especially as it neglects all the Dewar-type structures which are of increasing importance in larger molecules. Other more comprehensive methods of assigning numerical values to the characters of bonds have been developed, especially by Penney [103] and by Daudel ; [104] they are all based on the theory of resonance, and suffer from the disadvantage that the solution of the problem becomes increasingly tedious as the size of the molecule is increased. A more satisfactory method, based on the theory of molecular orbitals, has been introduced by Coulson.[105]

Coulson defines the *order* of a bond as the sum of two parts : (i) that due to the carbon–carbon single bonds (σ-bonds) which is assumed to have a value of unity in each case, and (ii) that due to the π-electrons. The

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[102] Pauling and Wheland, *J. Chem. Physics,* 1933, **1,** 362.

[103] *Proc. Roy. Soc.,* 1937, *A,* **158,** 306.

[104] Daudel and Daudel, *J. Chem. Physics,* 1948, **16,** 639 ; Pullman, *Ann. Chim.,* 1947, **2,** 5.

[105] *Proc. Roy. Soc.,* 1939, *A,* **169,** 413.

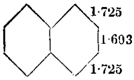
latter, the contribution of the mobile electrons, is called the *mobile bond order* (p). Each of the six π-electrons must contribute in some measure to the mobile bond order, and the problem resolves itself into one of calculating the contribution which each electron makes.

The six π-electrons in benzene are supposed to " occupy " three molecular orbitals in pairs.[106] * Each molecular orbital can be represented approximately by an equation of the form :

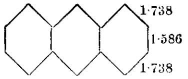
$$\Psi = a_1\psi_1 + a_2\psi_2 + a_3\psi_3 + a_4\psi_4 + a_5\psi_5 + a_6\psi_6$$

where ψ_1 is the wave function which the electron would have if confined to nucleus 1 ; ψ_2 is the wave function which it would have if confined to nucleus 2, and so on ; and where Ψ is the wave function of the molecular orbital. The coefficients, a_1, a_2, etc., are constants for a particular molecular orbital. The contribution of each electron to the mobile bond order between carbon atoms 1 and 2 is given by a_1a_2, so that the total mobile bond order of the bond between atoms 1 and 2 will be the sum of the contributions a_1a_2 from each of the six mobile electrons. The constants have different values for each occupied molecular orbital, and it is a relatively simple mathematical problem to evaluate them.[105]

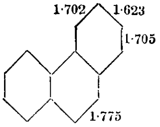
According to this definition, ethane has a mobile bond order of 0, ethylene of 1, and acetylene of 2. The total bond orders are, therefore, 1, 2, and 3 respectively. The carbon–carbon bonds in benzene are calculated as above to have a total bond order of 1·667, and those in graphite to have a bond order of 1·530. In the same way, bond orders for the bonds in a large number of polycyclic compounds have been calculated,[107] and the values are appended to the formulæ (LXXVII—LXXXII).



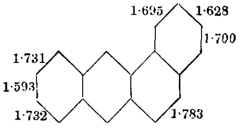
(LXXVII.)



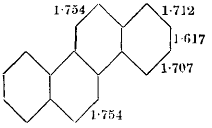
(LXXVIII.)



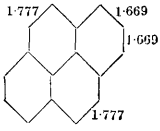
(LXXIX.)



(LXXX.)



(LXXXI.)



(LXXXII.)

The different carbon–carbon bonds in these aromatic compounds do not all have the same order. The 1 : 2-bond in naphthalene, for example, has a much higher bond order (and is therefore nearer a double bond) than the 2 : 3-bond ; and the same relationship holds in anthracene. In phenan-

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[106] Coulson, *Quart. Reviews*, 1947, **1,** 144 ; *Proc. Roy. Soc. Edin.*, 1941, **61,** 115.

[107] Coulson and Longuet-Higgins, *Rev. Sci.*, 1947, **85,** 929 ; Berthier, Coulson, Greenwood, and Pullman, *Compt. rend.*, 1948, **226,** 1906 ; Baldock, Berthier, and Pullman, *ibid.*, 1949, **228,** 931.

* This refers to the ground state of the molecule. If light is absorbed, one or more electrons may be promoted to an orbital of higher energy content.

threne the 9 : 10-bond has the highest order; in 1 : 2-benzanthracene it is the 3 : 4-, in chrysene the 1 : 2-, and in pyrene the 1 : 2-bond.

In every case which has been studied it has been found that the double-bond reagents add preferentially to those bonds having the highest orders. Thus osmium tetroxide adds to the 9 : 10-bond of phenanthrene, to the 3 : 4-bond of 1 : 2-benzanthracene, to the 1 : 2-bond of chrysene, and to the 1 : 2-bond of pyrene.[79, 80] Similarly, diazoacetic ester adds to the 9 : 10-bond of phenanthrene,[63] and ozone adds to the 1 : 2-bond of pyrene.[77] Furthermore, the bonds with the highest orders (*e.g.*, in naphthalene and in anthracene) are precisely those which were supposed, by earlier workers, to be " fixed " double bonds, and it therefore seems reasonable to conclude that only those bonds which have high orders can function as double bonds. It is the 1 : 2-bond, but not the 2 : 3-bond, of 2-vinylnaphthalene which is involved in the Diels–Alder addition of maleic anhydride,[24] because only the former is a bond of high order. Similarly, 1-nitro-2-naphthylamine is a much weaker base than 3-nitro-2-naphthylamine [34] because the tautomeric effect of the nitro-group can be exerted much more strongly through a bond of high order. Again, in the Claisen rearrangement, 2-allyloxynaphthalene rearranges to give 1-allyl-2-hydroxynaphthalene [25] because a bond of high order is necessary to enable the required polarisations to occur . . . and so on.

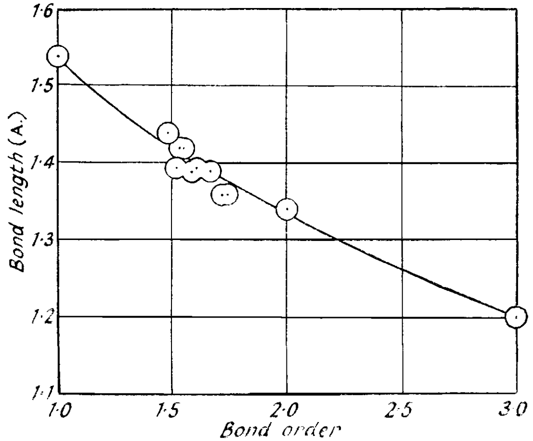
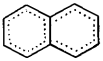


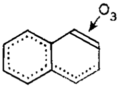
FIG. 1

The relation between calculated bond orders and observed bond lengths (Cf. Coulson [107]).

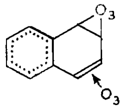
As a confirmation of the physical reality of bond orders, it may be mentioned that there is a very smooth relationship between the calculated bond orders and the experimentally determined bond lengths.[105] This is shown in Fig. 1, the points recorded being those for ethane, ethylene, acetylene, graphite, benzene, and all the carbon–carbon bonds in naphthalene and anthracene. This curve may also be expressed mathematically, and may be used in other cases either (i) to calculate bond lengths from bond orders, or (ii) to derive bond orders from experimentally determined bond lengths. In this way many useful comparisons between the calculated and experimental values have been made, and the agreement is surprisingly good.

The relation between bond order and bond " reactivity " is of fundamental importance, and may therefore be considered more fully. As Kooyman and Ketelaar [108] have suggested, the initial process in the addition of a double-bond reagent to an aromatic compound is the conversion of an *aromatic* bond into a pure *double* bond. That is, two π-electrons must be " localised " by the approach of the reagent, and the remaining disturbed system of π-electrons rearranges to form a structure of minimum energy. The addition of ozone to naphthalene may therefore be illustrated by the structures (LXXXIII—LXXXV).


(LXXXIII.)



(LXXXIV.)



(LXXXV.)

The energy required to effect this localisation, the *bond localisation energy*, can be determined without difficulty. In the simple treatment by Kooyman and Ketelaar,[108] who introduced the quantity, the localisation energy is estimated by subtracting the resonance (delocalisation) energy of the " residual " molecule from that of the " original " molecule. The " residual " molecule formed when one double bond is localised in benzene, simulates butadiene. Taking the resonance energy of benzene to be 39 kcals./mole, and that of butadiene to be 3·5 kcals./mole, the bond localisation energy in this case is therefore 39 — 3·5 = 35·5 kcals./mole. Similarly, the energy required to localise a double bond in the 1 : 2-position of naphthalene (as in LXXXIV), is 29 kcals./mole. This is the difference between the resonance energies of naphthalene (75 kcals./mole) and styrene (46 kcals./mole).

This treatment suffers from the disadvantage that very few experimentally determined resonance-energy values are known. For this reason, Ketelaar and van Dranen,[109] and Brown,[110] have determined the bond localisation energies for a number of bonds in different aromatic hydrocarbons using resonance-energy values calculated by the method of molecular orbitals.

According to this method, the bond localisation energy for benzene is 30 kcals./mole ; that for the 1 : 2-bond of naphthalene is only 22 kcals./mole, but that for the 2 : 3-bond is 37 kcals./mole. The much smaller energy required to localise a double bond in the 1 : 2-position is clearly the reason why naphthalene always reacts as if double bonds are " available " only at that position. The bond localisation energy for the 9 : 10-bond in

[108] *Rec. Trav. chim.*, 1946, **65**, 859.

[109] *Ibid.*, 1950, **69**, 477.

[110] *Australian J. Sci. Res.*, 1949, **2**, *A*, 564.

phenanthrene is only 16 kcals./mole, and similar small values are calculated for the 3 : 4-bond of 1 : 2-benzanthracene, and for other very reactive bonds.[110]

There can be little doubt that the bond localisation energy is the most important single factor governing the rate of addition of a double-bond reagent to an aromatic bond. Ketelaar and van Dranen [109] have shown that if the difference in the bond localisation energies for two bonds is taken to be equivalent to the difference in the energies of activation, the calculated difference in the reaction rate agrees remarkably well with the observed value. Furthermore, if the bond localisation energies are plotted against the bond orders of the same bonds, as in Fig. 2, an excellent correlation is obtained.[110] There seems no reason to doubt, therefore, that bond "reactivity" is directly related not only to bond localisation energy, but also to bond order.

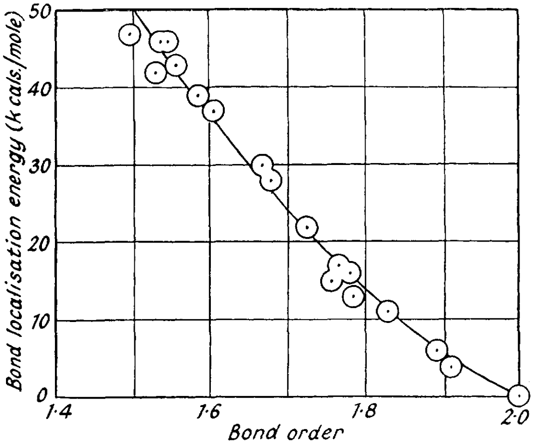


FIG. 2

The relation between bond localisation energies and bond orders. Mainly after Brown.[110]

Bond localisation energies are also very closely related to the oxidation–reduction potentials of the corresponding *o*-quinones, for such potentials are simply measures of the energy required to convert the quinols into the quinones. Indeed, a linear relation may be demonstrated between the bond localisation energies of a series of bonds, and the "corrected" oxidation–reduction potentials of the corresponding series of *o*-quinones.[111, 112]

The relation between bond order and bond localisation energy on the one hand, and the linear relation between bond localisation energy and oxidation–reduction potentials on the other, implies that there must also be a relationship between bond order and oxidation–reduction potentials

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[111] Branch and Calvin, "The Theory of Organic Chemistry", Prentice-Hall Inc., New York, 1941, pp. 303 *et seq.*

[112] Evans, Gergely, and De Heer, *Trans. Faraday Soc.*, 1949, **45**, 312 ; Evans and De Heer, *Quart. Reviews*, 1950, **4**, 94.

of the corresponding *o*-quinone.* It is possible to obtain a " theoretical " curve of this nature, as in Fig. 3, and the experimental points are in good agreement, as has already been observed by Badger.[85]

The relation is of some practical significance, for it means that experimentally determined oxidation–reduction potentials can be used to evaluate the bond orders of the corresponding bonds in heterocyclic, and possibly also in substituted aromatic, compounds.[113] The parameters required to carry out the necessary calculations with such compounds are not known with certainty, and it is possible that " experimentally " evaluated bond orders will be of value in this connection.

Finally, this relation makes it possible to re-examine the early use of substitutive reagents in attempts to demonstrate bond fixation in aromatic compounds. It seems to be generally accepted that the approach of a substituting reagent produces a transition state of quasi-quinonoid character, which then ejects a proton and forms the substitution product. In the case of 2-naphthol, the transition state (LXXXVI) corresponds to 1 : 2-naphthaquinone, and the state (LXXXVII) corresponds to 2 : 3-naphthaquinone, which is so unstable that it has never been prepared. From

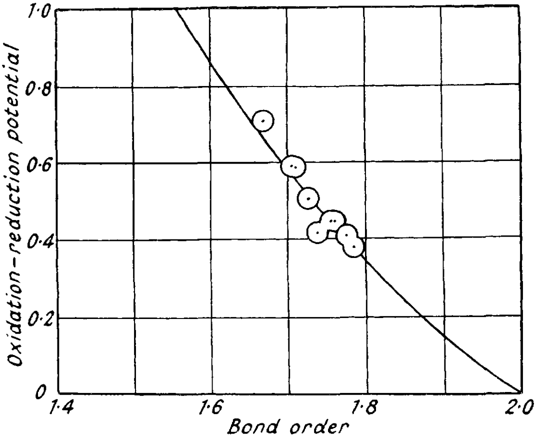
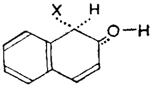
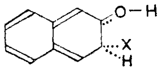


FIG. 3

The relation between bond order and the oxidation–reduction potential of the corresponding o-*quinones. Cf. Badger.*[85]



(LXXXVI.)



(LXXXVII.)

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[113] Badger, unpublished.

* This is evidently the explanation of the fact, first observed by Clar (*Ber.*, 1940, **73,** 104 ; " Aromatische Kohlenwasserstoffe ", Berlin, 1941), that the most reactive quinones correspond to the least reactive hydrocarbons, and *vice versa.*

the foregoing relationships between bond order and oxidation–reduction potential, there is no doubt that the formation of a transition state which corresponds to 2 : 3-naphthaquinone would involve such a high energy of activation that it never, or hardly ever, occurs.[55] It may be concluded, therefore, that these reagents do differentiate between bonds of different orders. Of the two possible *ortho*-positions, that which is linked to the carbon atom bearing the hydroxyl group by a bond of greater order is always attacked. On the other hand, with polysubstituted aromatic compounds (such as hydroxyindane, and hydroxytetralin) the situation is more complex, and the use of substitutive reagents is not without objection.