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THE AROMATIC BOND AND SOME PROBLEMS OF THE STRUCTURE OF AROMATIC COMPOUNDS

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INTRODUCTION

The formula proposed by Kekulé[1,2] for benzene, with alternating double and single bonds, explained many but not all its properties. This formula made it difficult to understand, for example, the specific type of reactivity shown by benzene and the existence of one instead of two *ortho*-isomers[3,4].



For this reason Kekulé later suggested[5] that the double bonds in the benzene ring are not fixed but mobile, i.e. they oscillate rapidly, moving around the ring.

The concept of the oscillation of double bonds as an important distinguishing feature of aromatic compounds was accepted rapidly and held sway for a long time. In subsequent papers it was developed into an orderly system of ideas[6]. This concept explained in particular the identity of the two *ortho*-positions in monosubstituted benzenes. In polysubstituted benzenes and especially in di- and polycyclic aromatic compounds, however, the *ortho*-positions are not equivalent, one being more reactive than the other. This led to the suggestion that in these compounds the possible oscillatory forms possess different stabilities, and therefore, being in dynamic equilibrium, take part to different extents in reaction[7]. Thus the double bonds of such compounds are partly or even completely fixed[8-11].

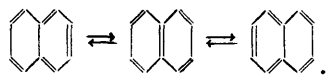
From the progress made in recent years in the study of the fine structure of aromatic compounds it may be concluded that there can be neither oscillation nor complete fixation of the bonds in aromatic molecules.

It has been established by numerous methods that the structure of the benzene molecule is a regular hexagon in which the six π electrons of the carbon atoms do not interact in pairs but as a single sextet. Therefore, all the C – C bonds of benzene are completely equivalent and differ in electron density both from single and from double bonds. From this point of view, Thiele's theory of partial valencies[12] represents the actual structure of aromatic substances better than Kekulé's concept of oscillating bonds. However, many experimental facts indicate that in aromatic compounds other than benzene the C – C bonds are not identical; some of them possess greater electron density, or have greater "double-bond character", than others.

The complete equivalence of the C – C bonds characteristic of the benzene molecule contrasts with the state of these bonds in its derivatives, e.g. di- and polycyclic aromatic compounds. Therefore, it is possible to consider that substituent groups or condensed rings upset to some extent the equivalence of the bonds.

PARTIAL BOND FIXATION

The non-equivalence of the bonds in aromatic compounds was first studied in the case of naphthalene. By analogy with the Kekulé dynamic structure for benzene, the naphthalene molecule can be represented by dynamic formulae[13,14], on the basis of which it might be supposed that the bonds in naphthalene would be equivalent:

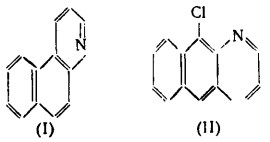


However, many observations indicate the great difference in properties between the 1 – 2 and 2 – 3 bonds. For the sake of clarity, these observations are classified below according to the types of reactions studied.

Cyclisation Reactions and Reactions Occurring via the Intermediate Formation of Rings

As early as 1893 Markwald[15-17] noted the considerable reactivity of one of the two *ortho*-positions in β-naphthol and β-naphthylamine. Thus, when the Skraup reaction is carried out with β-naphthylamine, only the angular benzoquinoline (I) is obtained. In a number of cases formation of I is accompanied by displacement of a substituent present in position 1 of the 2-naphthylamine molecule. According to

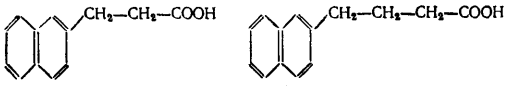
Markwald the reason for this phenomenon was that formation of the new ring occurs at the double bond, and hence that in naphthalene the 1–2 bond is double but the 2–3 bond is single, and this distribution of the bonds is fixed. However, as was shown subsequently[18-20], this course of the Skraup reaction with formation of the benzoquinoline (I) is not the only possible reaction. With certain derivatives of β-naphthylamine, products of linear structure also can be obtained, in moderate yield, e.g. II.



(I) (II)

In the Skraup reaction a certain similarity of behaviour is observed between derivatives of naphthalene and of its heterocyclic analogues, e.g. quinolines[21].

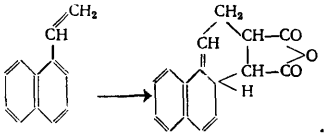
When β-2-naphthylpropionic (III) and γ-2-naphthylbutyric (IV) acids[22-25] are cyclised,



(III) (IV)

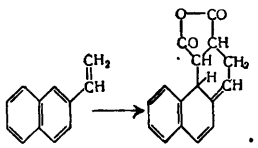
products of angular structure are formed exclusively, although here too, if position 1 is occupied, cyclisation can occur in position 3 [26].

Derivatives of naphthalene also behave peculiarly in diene synthesis reactions[27-30]. 1-Vinylnaphthalene (V) exhibits diene properties, giving with maleic anhydride the corresponding adduct (VI):



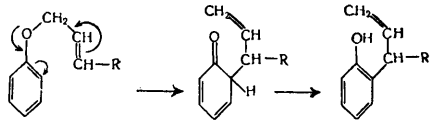
(V) (VI)

Thus the 1–2 bond in the naphthalene molecule behaves in this reaction as a double bond[31-33]. In the case of 2-vinylnaphthalene (VII), the reaction could involve either position 1 or 3. It was shown that the product is formed entirely by reaction at position 1 [34] (VIII):

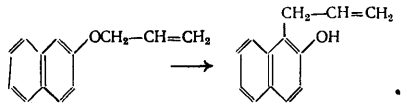


(VII) (VIII)

The non-equivalence of the bonds was also studied by means of the Claisen rearrangement[35,36], by which allyl ethers of phenols and enols are converted into the corresponding *C*-allyl derivatives. The reaction evidently occurs via the intermediate formation of cyclised products and dienes, and with isomerisation of the allyl radical[37,38]:



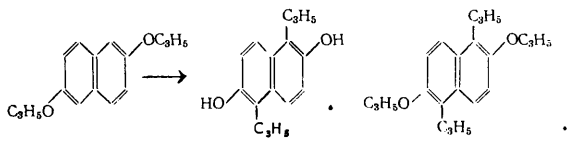
According to this mechanism two double bonds take part in the reaction, and on this basis it is suggested that the process entails fixation of the bonds of the aromatic nucleus. Rearrangement of 2-allyloxynaphthalene (IX) occurs solely at position 1, with formation of X:



(IX) (X)

1-Allyloxynaphthalene is similarly smoothly converted into 2-allyl-1-naphthol; this shows that the direction of the rearrangement IX → X cannot be explained by increased reactivity of the 1-position of naphthalene. If the 2-allyloxynaphthalene (IX) has a substituent in position 1, the Claisen rearrangement does not occur, although position 3 is free[35]. On this basis it can be concluded that the 2–3 bond of naphthalene, in contrast to the 1–2 bond, cannot function as a double bond.

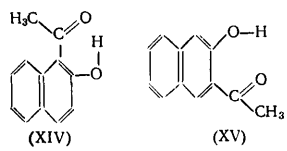
It is known also that, whereas 2,6-diallyloxynaphthalene (XI) rearranges smoothly to 1,5-diallyl-2,6-dihydroxynaphthalene (XII), 1,5-diallyl-2,6-diallyloxynaphthalene (XIII) is not capable of such a rearrangement. This confirms that the partial bond fixation in naphthalene is symmetrical. Naphthalene derivatives do not enter into reactions which require the presence of double bonds in the 2–3 and 6–7 positions[9]:



(XI) (XII) (XIII)

Further investigations of the Claisen rearrangement, pointing to the non-equivalence of the bonds, were carried out with derivatives of anthracene[40], phenanthrene[41], and certain heterocyclic aromatic compounds[42-45].

In 1934, Baker[46] noted that the ability of *o*-hydroxyacetophenone and similar compounds to form six-membered chelate rings containing a hydrogen bond depends on the presence of a double bond between the carbon atoms linked to the hydroxyl and acetyl groups. If it is assumed that only the 1–2 bond in the naphthalene nucleus can behave as a double bond, 1-hydroxy-2-acetylnaphthalene and 2-hydroxy--1-acetylnaphthalene (XIV) should be able, but 2-hydroxy--3-acetylnaphthalene (XV) should be unable, to form a hydrogen bond:



(XIV) (XV)

Actually, a hydrogen bond is present in all three compounds[47]. This could mean that the 2–3 bond can function as a double bond. However, as the authors remark, such a conclusion is not definitive, since the formation of the hydrogen bond itself may change the normal state of the bonds in the molecule[48-51].

Infra-red spectra of nitronaphthylamines show that the 1,2- and 2,1-isomers contain a stable hydrogen bond, whereas no such bond has been detected in the 2,3-isomer[52].

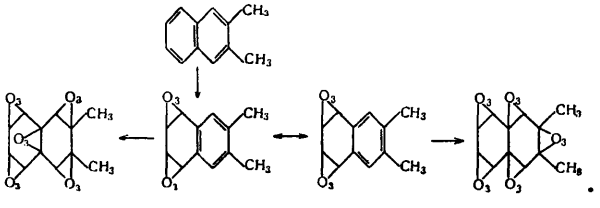
Substances which React with a Double Bond

Interesting and convincing results were obtained in the study of the structure of aromatic compounds by their reaction with substances which can add on to double bonds — ozone, osmium tetroxide, and aliphatic diazo compounds[53]. In the reaction of compounds containing double bonds with ozone, ozonides are obtained[54], the structure of which has not yet been finally elucidated[55].

With benzene, ozone forms a triozonide[56,57]. Levine and Cole studied the ozonisation of *o*-xylene and obtained a mixture of products[58]. Later Haaijman and Wibaut determined the quantitative composition of this mixture, which contained glyoxal, methylglyoxal, and diacetyl, and came to the conclusion that it corresponds strictly to an equilibrium mixture of two isomeric *o*-xylenes having fixed bonds[59,60]. Since such isomers do not exist, these results obviously indicate that all the bonds in *o*-xylene are equivalent. Thus, although the presence of methyl groups does accelerate the ozonisation of benzene derivatives[61], it does not have an appreciable effect on the comparative reactivity of its individual bonds.

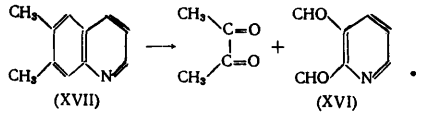
The ozonisation of 2,3-dimethylpyridine and 2,3,4-trimethylpyridine[62] yields a mixture of glyoxal, methylglyoxal, diacetyl, formic and oxalic acids, and ammonia. This also is explained by the pyridine reacting with ozone in the form of two Kekulé structures. From the present point of view this can be treated as proof of the equivalence of the double and single bonds in pyridine.

Ozonisation was also used to study the structure of naphthalene. In 1904 Harries and Weiss obtained phthalic dialdehyde by this reaction[63]. Considerably later, in 1946, Wibaut and Dijk studied the ozonisation of 2,3- and 1,4-dimethylnaphthalene[10]. The former yielded glyoxal, diacetyl, and, what was especially important, methylglyoxal. The ratio of methylglyoxal to diacetyl was 1 : 10. This result was at first treated as a proof that the 2–3 bond of naphthalene can react as a double bond. Then, an apparently more correct explanation was given by Kooyman[64], who considered that this reaction also initially involves the 1–2 and 3–4 bonds, but not the 2–3 bond. The formation of methylglyoxal takes place in the second stage, as a result of further reaction of an intermediate product, in which there is no longer the disruption of bond equivalence characteristic of naphthalene:



The formation of methylglyoxal from 1,4-dimethylnaphthalene can be explained in the same way.

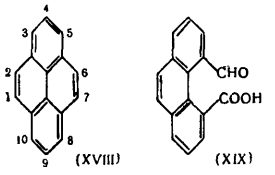
In the reaction of quinoline with ozone[65] a diozonide is formed at the expense of the bonds in the benzene nucleus, and it is only with difficulty that this reacts further with ozone. Decomposition of the diozonide yields glyoxal and pyridine-2,3-dialdehyde (XVI). The products of the ozonisation of 6,7-dimethylquinoline (XVII) are diacetyl and pyridine-2,3-dialdehyde; methylglyoxal and pyridone are not observed:



(XVII) (XVI)

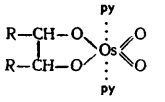
In the ozonisation of 5,8- and 2,3-dimethylquinolines reaction also occurs at the 5–6 and 7–8 bonds, but not at the 6–7 bond, which behaves as a single bond.

The ozonisation of several polycyclic aromatic compounds has also been studied. Anthracene forms only anthraquinone[66]. Pyrene (XVIII) adds on ozone successively at the 1–2 and 6–7 bonds[67,68]. On decomposition of the ozonides, 4-formylphenanthrene-5-carboxylic acid (XIX)[69,70] and the corresponding diphenyl derivative were obtained. It may be noted here that electrophilic reagents, in contrast to ozone, attack in the first instance the very unsaturated[67] positions 3, 5, 8, and 10 in pyrene.



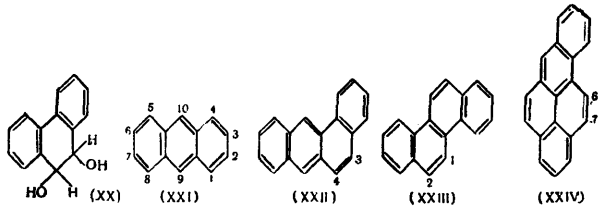
(XVIII) (XIX)

Osmium tetroxide is a considerably milder reagent than ozone. When it interacts in pyridine solution with compounds containing a double bond, crystalline products of the following structure generally separate in theoretical yield:



On careful hydrolysis, diols are obtained from them, and these are often the products required[71,72].

Osmium tetroxide reacts very slowly with aromatic compounds, and adds on only to the most reactive bonds[73]. Thus, with benzene reaction can occur only under extreme conditions[74], and usually it does not occur. Phenanthrene reacts with osmium tetroxide at the 9–10 bond, and after decomposition of the complex *cis*-9,10-dihydroxy-9,10-dihydrophenanthrene (XX) is obtained[71]. Anthracene (XXI) reacts at the 1–2 and 3–4 bonds, giving an addition product containing two molecules of OsO_4.[75] 1,2-Benzanthracene (XXII) adds on osmium tetroxide at the 3–4 bond[73,76], chrysene (XXIII) and pyrene (XVIII) at the 1–2 bonds, and 4,5-benzopyrene (XXIV) at the 6–7 bond[73].

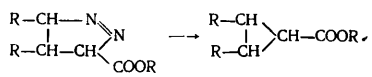


(XX) (XXI) (XXII) (XXIII) (XXIV)

The bonds in polycyclic aromatic compounds possess differing reactivity with respect to OsO_4. Quantitative investigations show, for example, that osmium tetroxide adds on to 1,2-benzanthracene (XXII) ten times as rapidly as to phenanthrene[77]. The presence in the 1,2-benzanthracene molecule of an electron-donor substituent (a methyl group) accelerates the addition of OsO_4, but an

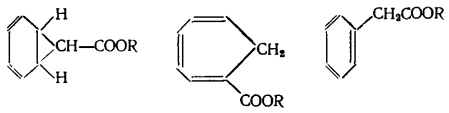
electron-acceptor substituent (a CN group) retards it[78,79].

To elucidate the nature of the aromatic bond, the action of aliphatic diazo compounds — diazoacetic ester and diazomethane — on various compounds was studied. Diazo compounds add on to a double bond, forming pyrazolines, which eliminate nitrogen on mild heating, passing into derivatives of cyclopropane[80-82]:



Diazoacetic ester and diazomethane react with aromatic compounds only with difficulty, and nitrogen is eliminated even before the addition. It has been suggested that the active agent in this reaction is the CH_2 radical[83]. The reaction can also be carried out without heating, using activation with ultra-violet radiation[84].

The reaction of diazoacetic ester with benzene derivatives was studied by Buchner[85-89], who established that the primary product of this reaction is norcaradienecarboxylic ester (XXV), which can undergo further rearrangement to cycloheptatrienecarboxylic (XXVI) and phenylacetic (XXVII) esters.



(XXV) (XXVI) (XXVII)

Reactions with methylated benzenes can also yield phenylpropionic acids. Diazomethane reacts in a similar way. Substituted benzenes always add on diazomethane at a bond between unsubstituted carbon atoms[90].

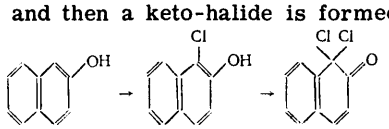
Naphthalene adds on diazoacetic ester at the 1–2 bond[91], phenanthrene at the 9–10 bond[92,93], anthracene at the 1–2 bond[94], benzanthracene (XXII) at the 3–4 bond, and pyrene (XVIII) at the 1–2 bond[95], the products obtained being unable to undergo rearrangement.

The cyclopropane ring is regarded as capable of conjugating with double bonds, and as a result the addition products obtained contain no isolated double bonds[96]. This evidently explains why reactions with diazo compounds terminate at the stage in which these products are obtained.

Substitution Reactions and Transmission of Conjugation Effect

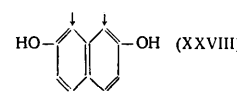
It is well known that the more unsaturated an aromatic bond, the more completely the conjugation transmitted by it. Hence by studying the direction of substitution reactions in aromatic compounds and the readiness with which they occur it can be judged whether and to what extent the equivalence of the bonds in a compound has broken down.

Markwald and then Fries and Fieser discovered a large degree of similarity in the halogenation and coupling of certain phenols and aliphatic enols. For example, in the halogenation of 2-naphthol the first halogen atom enters position 1[97], and then a keto-halide is formed[98-101]:



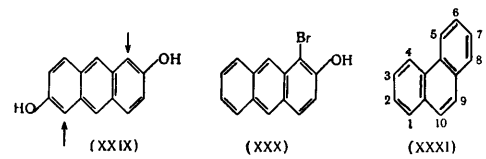
A halogen atom does not enter position 3.

Further, 2-naphthol and its derivatives undergo azo coupling solely in position 1. If this position contains chlorine, bromine, carboxyl, an aldehyde group, a carbinol residue, a sulphonic-acid group, or certain others[102], the coupling reaction involves elimination of these substituents. 1-Alkyl-2-naphthols, however, do not react. On the basis of these data it is suggested that in naphthalene the conjugating effect of a 2-hydroxyl group is readily transmitted to position 1, but not to position 3, since the 2–3 bond approximates to a single bond. Ruggli[103] showed that 2,7-dihydroxynaphthalene (XXVIII) couples with diazonium compounds in positions 1 and 8, which indicates the symmetrical nature of the partial bond fixation in the two rings of naphthalene. If positions 1 and 8 in 2,6-dihydroxynaphthalene are blocked by alkyl groups, azo coupling does not occur even with very reactive diazonium compounds[104].



(XXVIII)

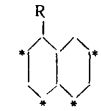
The same methods were used to study the properties of hydroxy derivatives of anthracene, phenanthrene, pyrene, and other compounds. For example, it was established that 2,6-dihydroxyanthracene (XXIX) is brominated in positions 1 and 5[105], 1-bromo-2-hydroxyanthracene (XXX) couples in position 1 with elimination of the bromine atom[106], and 1,5-dialkyl-2,6-dihydroxyanthracenes do not couple with diazonium compounds[40].



(XXIX) (XXX) (XXXI)

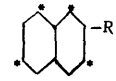
It follows from these observations that in anthracene the 1–2, 3–4, 5–6, and 7–8 bonds are close to double bonds in character, but the 2–3 and 6–7 bonds approximate to single bonds. Similarly, in phenanthrene (XXXI) the 1–2 and 3–4 bonds approximate to double bonds, but the 2–3 bond is close to a single bond[41].

Other experimental evidence exists showing that a substituent in position 2 in naphthalene and its analogues conjugates with position 1, but has hardly any effect on position 3. Substitution in the naphthalene rings to a certain extent obeys the rules formulated by the Czech scientists Vesely and Jakeš[107], according to which a substituent already in the naphthalene molecule exerts an effect at the "quinonogenic" positions, i.e. at positions corresponding to possible naphthaquinones. The effect of the substituent is strongest in the ring containing it. Thus in the case of a 1-substituted naphthalene the substituent will exert an effect at the positions denoted by asterisks:



The effect will be transmitted strongly to positions 2 and 4, and more weakly to positions 5 and 7.

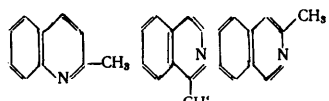
In a 2-substituted naphthalene, the effect of the substituent should also be transmitted to the "quinonogenic" positions:



It would appear that in this case positions 1 and 3 should be

most influenced by the substituent, and positions 6 and 8 to a less extent. In fact this rule breaks down for position 3. Thus in the sulphonation of 2-naphthol position 1 is the most active (according to the rate of entry of the sulphonic-acid group), then follow positions 8 and 6, and position 3 comes only after these[108]. It is known that in the benzene series a nitro group *ortho* or *para* to a halogen increases the lability of the latter. In the naphthalene series the bromine atoms in 1,2-, 2, 1-, and 1,4-bromonitronaphthalenes are labile, but not that in 2,3-bromonitronaphthalene[109]. It is also interesting to trace the effect of an *ortho* substituent on the basicity of amines. *o*-Nitroaniline is considerably less basic than aniline, and 1-nitro-2-naphthylamine than 2--naphthylamine, but the basicity of 3-nitro-2-naphthylamine is only slightly less than that of 2-naphthylamine[110].

Analogous rules can be traced also in the heterocyclic series. According to the Porai–Koshits rule[111,112], the hydrogen atoms of a methyl group are labile if the methyl group is conjugated with the hetero atom. Thus the hydrogen atoms of the CH_3 group in 2-methylquinoline (XXXII) are labile[113]. They are reactive also in 1-methylisoquinoline (XXXIII)[114], but not in 3-methylisoquinoline (XXXIV).



(XXXII) (XXXIII) (XXXIV)

This indicates that in the last compound there is no conjugation between the hetero atom and the methyl group. Thus the 2–3 bond in isoquinoline approaches a single bond in character, but the 1–2 bond is close to a double bond.

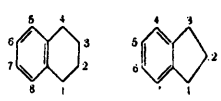
The experimental results given in this section demonstrate convincingly that the carbon–carbon bonds in aromatic systems containing condensed rings are not equivalent. Some of them are similar in character to aliphatic double bonds, and others resemble single bonds. Systems of this type clearly exhibit a phenomenon which can be described as partial bond fixation. The causes of this will be analysed below.

THE MILLS–NIXON EFFECT

In 1930 Mills and Nixon[115] published an investigation which for a long time attracted the constant attention of chemists and gave rise to a great controversy, which was settled only comparatively recently[116,117]. The basis for the theoretical ideas was the suggestion that in ethylene the angle between two single bonds α should be 109.5°, but the angle between a single bond and the double bond β should be 125.25°:

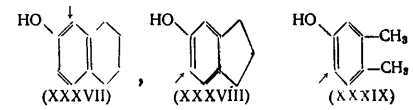


Since a regular hexagon has an angle of 120°, and a pentagon one of 108°, Mills and Nixon suggested that the bond common to the two rings of the tetralin molecule (XXXV) should be double, but the corresponding bond in indane (XXXVI) should be single.



(XXXV) (XXXVI)

In other words, the benzene ring should be fixed in one of its Kekulé forms in tetralin, and in the other Kekulé structure in indane. In fact, by studying the bromination and azo coupling of 6-hydroxytetralin (XXXVII) and 5--hydroxyindane (XXXVIII), Mills and Nixon were able to establish that these reactions occur at position 5 in the first case, and at position 6 in the second case, as would be expected from the formulae



(XXXVII) (XXXVIII) (XXXIX)

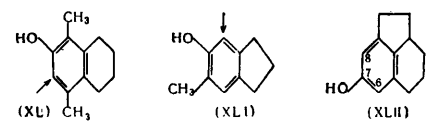
This phenomenon is now known as the Mills–Nixon effect.

On the basis of modern views of the structure of the benzene molecule the Mills–Nixon effect can be treated only as a more or less strong disturbance of the equivalence of the bonds in the benzene ring, occurring under the influence of distortion of the valency angles. In indane this disturbance of bond equivalence tends to give structure XXXVI, and in tetralin structure XXXV. However, on this basis, too, the existence of the Mills–Nixon effect was subject to serious doubts.

Thus it remained obscure why 4-hydroxy-*o*-xylene (XXXIX) couples in the same way as 5-hydroxyindane[118], although there would appear to be no reason for assuming non-equivalence of the bonds in XXXIX. If position 5 in 4-hydroxy-*o*-xylene is occupied by a methyl group, the resulting 2,4,5-trimethylphenol couples smoothly in the other, free *ortho*-position[119]. The comparative reactivity of the two *ortho*-positions in the 4-hydroxy-*o*-xylene molecule (XXXIX) was also determined, by substituting methyl groups in them in turn. The difference in reactivity between positions 3 and 5 proved to be comparatively small[120].

A more detailed investigation of the chemical properties of derivatives of indane and tetralin also showed lack of agreement with the hypothesis of Mills and Nixon. Thus, although 6-hydroxytetralin (XXXVII) couples and is brominated in position 5, it is nitrated in position 7.[121] If the Skraup reaction is carried out with 6-aminotetralin, ring closure also occurs in position 7 and a product of linear structure is formed[122]. 5-Aminoindane, however, undergoes ring closure in the Skraup reaction at position 6.[123]

Fieser and Lothrop discovered that 6-hydroxy-5,8-dimethyltetralin (XL) couples smoothly with diazonium compounds in position 7,[119,120] but 5-hydroxy-6-methylindane (XLI), in a moderately alkaline medium, couples in position 4,[125] which is evidence of the absence in these compounds of any non-equivalence of bonds similar to that observed in the naphthalene molecule.



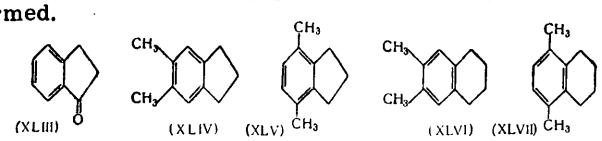
(XL) (XLI) (XLII)

In derivatives of tetrahydroacenaphthene (XLII), in which two saturated rings, one five-membered and the other six-membered, would be acting together, and therefore should influence the state of the bonds in the benzene nucleus more strongly, no naphthalene-like fixation is observed: 7-hydroxy-, 8-hydroxy-, and 7-hydroxy-6-methyl--tetrahydroacenaphthene couple equally smoothly with diazonium compounds[126]. Absence of bond fixation was established by an investigation of the Claisen rearrangement

of 5-allyloxy-6-methylindane and 5-allyloxy-4,7-dimethylindane. Both these compounds rearranged without any difficulty[125]. In the rearrangement of the allyl ether of 6-hydroxytetralin the allyl group rearranges to position 7, not to position 5, as would be expected according to Mills and Nixon. If position 7 is occupied, the allyl group goes into position 5.[127]

Other methods of investigation also show that there is no bond fixation in indane and tetralin. Thus 4- and 6-acetyl--5-hydroxyindane are intramolecularly hydrogen bonded[128]. The acid dissociation constants of 4- and 6-nitro-5-hydroxyindanes and 5-nitro-4-hydroxy-*o*-xylene are almost identical[129], and the heats of hydrogenation of alkylbenzenes and indane are very similar[130].

Important results were obtained in a study of the action of double-bond reagents on indane and tetralin. Arnold[131] established that diazoacetic ester adds to indane at the 4–5 bond, not the 5–6 bond, as would follow according to the theory of Mills and Nixon. The action of ozone on indane was first studied by Young and Fieser[132]. It was found that this reaction starts with the oxidation of indane to indanone (XLIII), and therefore the results obtained are unreliable. The work was then continued by de Jong[133], who studied the ozonisation of 5,6- and 4,7-dimethylindanes (XLIV and XLV) and also 6,7- and 5,8-dimethyltetralins (XLVI and XLVII), and determined quantitatively the proportions of glyoxal, methylglyoxal, and diacetyl thus formed.

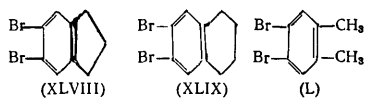


If the Mills–Nixon hypothesis is correct, one mole of compound XLIV should yield two moles of methyglyoxal, but if there is no bond fixation, the ratio of methylglyoxal to diacetyl should be 2 : 1. In fact, the ratio of products obtained is 17 : 6, which by the usual calculation shows a content of molecules having the Mills–Nixon bond fixation of only 15%. Similar treatment of 4,7-dimethylindane (XLV) leads to the conclusion that the proportion of such molecules here is 24%. Using the same method of calculation, it can be concluded from the results of these experiments that, on an average, every molecule of indane having the distribution of bonds indicated in XLIV is accompanied by four molecules with a different arrangement of bonds. This result is just the opposite of what should be observed according to the Mills–Nixon hypothesis. Moreover, these data are in good agreement with the results of theoretical calculations for the indane molecule carried out in 1949 by Longuet–Higgins and Coulson[134,135]. These calculations show that the benzene ring in indane is very slightly distorted in the opposite direction to that postulated by Mills and Nixon: the length of the contiguous 8–9 bond is shortened by 0.022 Å in comparison with that in benzene, and the 5–6 bond is 0.011 Å longer.

On ozonisation of the tetralin derivatives XLVI and XLVII, mixtures of products are obtained, indicating the absence of any bond fixation in their benzene rings. These results are in agreement with theoretical calculations for the tetralin molecule carried out by de Jong on the assumption that the C_2 and C_3 atoms in the alicyclic six-membered ring of this compound are in the *trans*-position with respect to the plane of the benzene ring. The Mills–Nixon effect was also studied in the benzene[136] and pyridine[137] series by means of the ultra-violet and infra-red spectra. The results show the absence of any bond fixation in both cases.

The same conclusion follows from a comparison of the oxidation–reduction potentials of the quinones of indane and tetralin[138]. Thus, all the experimental and theoretical data existing at the present time contradict the existence of the Mills–Nixon effect.

As has already been pointed out, the basis for the Mills–Nixon hypothesis was the assumption that the angles between the single bonds in the ethylene molecule are smaller than those formed between a single and the double bond. Data which have accumulated at the present time[139-142] show that in fact this is not so: all angles in ethylene are very close to 120°. Therefore, although the "linking" of the methyl groups of *o*-xylene by means of one or two methylene groups (formation of a five- or six-membered ring) can somewhat distort the direction of the bonds emerging from the benzene nucleus (especially in the case of indane), this distortion does not affect the state of the bonds in the benzene ring in the Mills–Nixon sense. For a discussion of this question in connection with measurement of the dipole moments of 4,5-dibromoindane (XLVIII, μ = 1.78 *D*), 5,6--dibromotetralin (XLIX, μ = 2.11 *D*), and 4,5-dibromo-*o*--xylene (L, μ = 2.13 *D*), see the papers cited at the end of this review[143-146].



Distortion of the valency angles diminishes the effect of the methylene groups, as electron-donor substituents, on the benzene ring, and therefore this is appreciably smaller with indane than with tetralin. Arnold and his coworkers[147-151] showed this by various experiments. Perhaps this distortion is the actual cause of the different behaviour of 5--hydroxyindane (XXXVIII) and 6-hydroxytetralin (XXXVII) toward coupling with diazonium compounds[133,152-155].

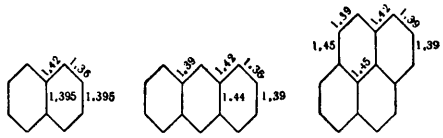
CARBON–CARBON BOND LENGTHS

The above chemical and physicochemical data relating to the difference in the properties of the carbon–carbon bonds in aromatic molecules containing condensed rings have received important confirmation during the past decade from direct determination of C–C bond lengths in such substances.

Several methods exist for the experimental determination of interatomic distances; the most important for organic molecules are those based on the diffraction of X-rays by crystals or the diffraction of electrons by gases. The best results are given by Fourier analysis of the X-ray diffraction patterns, which previously was used comparatively rarely owing to the labour involved in the calculations, but now, with the development of computer techniques, is employed much more widely.

As is known, the length of the single C–C bond is 1.54 Å, that of the double bond in ethylene is 1.34 Å, and that of the triple bond in acetylene 1.2 Å. The C–C bonds of benzene occupy an intermediate position between a single and a double bond, all being alike and 1.39 Å in length. In molecules of polycyclic aromatic hydrocarbons and heterocycles of aromatic character, however, the lengths of all the bonds are not the same[156]. As an illustration, the accompanying formulae show the experimental

interatomic distances for naphthalene[157,158], anthracene[159], and pyrene[160].

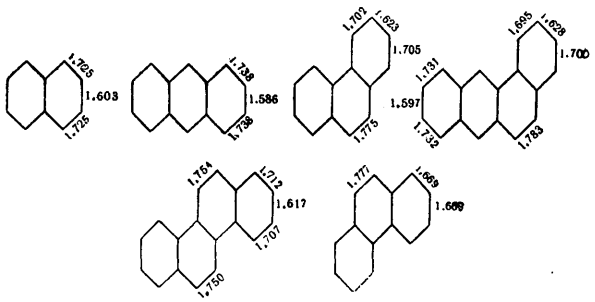


Analogous results have been obtained for the interatomic distances in coronene[161], ovalene[162,163], 1,12-benzoperylene[164], 1,2,5,6-dibenzanthracene[165], triphenylene[166], and a number of other compounds.

These results show that single and double bonds do not exist in polycyclic aromatic hydrocarbons any more than they do in benzene. From the interatomic distances, all bonds are intermediate between single and double bonds. However, some of them, those which in the preceding treatment were regarded as fixed double bonds, are somewhat shorter and therefore closer to double bonds; whereas others, previously regarded as fixed single bonds, are rather longer, and are obviously closer in character to single bonds.

THE ORDER OF AN AROMATIC BOND AND ITS REACTIVITY

The intermediate, non-integral character of the aromatic bond can be established by quantum-mechanical calculations on organic molecules. In the molecular-orbital method, it is assumed that the order of the C–C bonds in ethane is 1, that in ethylene is 2, and that in acetylene 3[142,167,168]. The C–C bonds in aromatic systems are then characterised by fractional orders. Thus the order of all the C–C bonds in benzene is calculated as equal to 1.667, and that in graphite as 1.530. Some results for the calculated order of C–C bonds in aromatic hydrocarbons with condensed rings, calculated by the molecular-orbital method, are shown in the formulae below[169-171].



Analogous results were obtained also in the calculation of the C–C bond orders for anthra-anthracene, dibenzopyrene[172], tetrabenzonaphthalene, tetrabenzanthracene[173], dibenzophenanthrene[174], coronene, ovalene, circumanthracene[175], and a number of other hydrocarbons, as well as heterocyclic compounds[176].

Without attempting in this paper to give a summary of work on the quantum-mechanical calculations on organic molecules, it is pointed out that apparently completely satisfactory results are given by the tabular method, based on an examination of the purely geometrical properties of the molecules, which enables the order of the C–C bonds in aromatic molecules to be found without complicated calculations[177-179].

Application of the linear combination of atomic orbitals (L. C. A. O.) with self-consistent field treatment to the calculation of the naphthalene molecule gives bond orders differing appreciably in magnitude from those given above[180]. This method generally gives too high values for the highest bond orders, and too low values for the lowest bond orders[179].

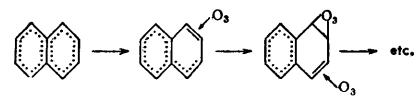
The work of Bykov is worthy of attention, as he proposed the use of electron densities instead of conventional bond orders to characterise chemical bonds. He gave semi-empirical formulae which enabled the latter to be readily calculated from the interatomic distances[181-183]. The electron density of a bond and its order should, of course, be related in a simple manner.

Thus all results show that the various C–C bonds in aromatic compounds differ from one another in their order and electron density. Bonds having a higher order are the most reactive chemically. They add ozone, osmium tetroxide, and diazoacetic ester more readily than do the remaining bonds. In older work they were taken to be fixed double bonds, since in many reactions they behave like actual double bonds. The higher the order of a bond the more reactive it is, and the more it resembles a double bond. An example is the reaction of osmium tetroxide with phenanthrene and 1,2-benzanthracene, already mentioned, which is ten times slower with the former hydrocarbon than with the latter. Correspondingly, the order of the 9–10 bond in phenanthrene is 1.775, and that of the 3–4 bond in 1,2-benzanthracene is 1.783.

1-Nitro-2-naphthylamine is far less basic than 3-nitro-2-naphthylamine, because the effect of the conjugation of the nitro groups is transmitted more completely through the 1–2 bond, which has an order of 1.725, than through the 2–3 bond, the order of which is 1.603. For the same reason, the Claisen rearrangement of the allyl ether of 2-naphthol and the azo coupling of 2-naphthol occur in position 1, and not in position 3, etc.

To show the physical reality of these bond orders, it should be mentioned that they are related to the interatomic distances by a smooth curve[169,184], as shown in Fig. 1[184]. Conversion from bond orders to bond lengths is also easily accomplished by means of the Deas relationship[185,186].

The relationship between the order of a bond and its reactivity is of the greatest importance for chemistry and should therefore be examined more fully. Evidently the start of the process of addition of reagents to an aromatic bond is the conversion of the latter into an actual double bond[187]. This means that two π electrons must be removed from the general π-electron system of an aromatic compound and localised, and the remaining electrons should regroup to form a system with minimum energy. For example, the addition of ozone to naphthalene can be illustrated by the scheme



The energy required to achieve such localisation, termed the localisation energy of the bond, can be easily calculated by the methods of quantum mechanics. Thus by the molecular-orbital method the localisation energy has been calculated[188] as 30 kcal for a bond in benzene, 22 kcal for the 1–2 bond in naphthalene, and 37 kcal for the 2–3 bond. The considerably lower localisation energy explains why naphthalene reacts at the 1–2 bond. The localisation

energy of the 9–10 bond in the phenanthrene molecule is still lower, amounting to only 16 kcal, etc. There is no doubt that the magnitude of the localisation energy is one of the most important factors governing the reactivity of an aromatic bond. In a study of the ozonisation reaction, for example, it was established that, if the difference in localisation energy of two bonds is taken as equivalent to the difference in activation energy, the calculated difference in reaction velocity is in good agreement with the experimental value. At the same time, as Brown[188] has shown, the localisation energy of a bond is very clearly connected with the bond order (see Fig. 2. in Brown[188]). The relationship between the energy and the length of a bond has also been discussed by Pauling[189].

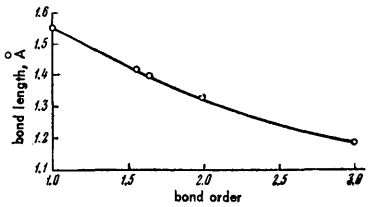


Fig. 1.

The order and the localisation energy of a bond are also closely related to the oxidation–reduction potential of the corresponding *o*-quinone. This fact was first noted as early as 1940 by Clar[190], who pointed out that the more active a hydrocarbon the less reactive is the quinone obtained from it. This question was subsequently discussed in a number of papers[191-193]. The relationship between the order of a bond and the oxidation–reduction potential of the corresponding *o*-quinone is shown by the graph in Fig. 3 [78].

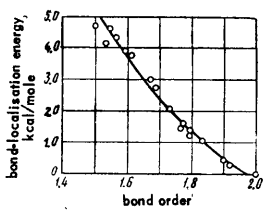


Fig. 2.

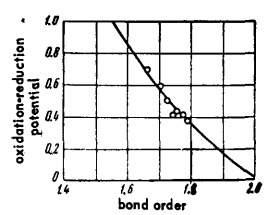
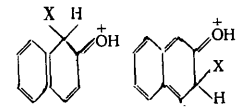


Fig. 3.

This relationship enables the order of the C–C bond of a compound to be found when the oxidation–reduction potential of the corresponding *o*-quinone has been determined. On the other hand, it explains why 2,3-naphthaquinone is so difficult to obtain, and so far has still not been prepared: this quinone should be very unstable, since its oxidation–reduction potential should be considerably higher than the potential of the not very stable *o*-benzoquinone. Finally, the same relationship sheds additional light on the cause of the selective substitution of 2-naphthol at position 1. The formation of an intermediate product of quinonoid structure is obviously of great significance here.



It can be seen that the addition of a cation to position 1 should give a far more stable intermediate than addition to position 3. Thus, for this reason too, when there are two possible *ortho*-positions, attack occurs where the bond order is high.

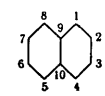
THE EFFECT OF A FUSED RING ON THE BENZENE RING IN CONDENSED SYSTEMS

The chemical and physical data given above and the results of quantum-mechanical calculations show that in the benzene molecule all the bonds are completely equivalent, and the electrons forming them are delocalised, but that in aromatic compounds having condensed rings the C–C bonds are not the same, some of them being more unsaturated and having a higher order (being more "double-bonded") than others. In these cases partial localisation of the double and single bonds is said to occur. As is clear from the above, this partial localisation of bonds has a very great influence, in many cases even a decisive effect, on the chemical behaviour of aromatic compounds, and is therefore of particular interest.

From a comparison of unsubstituted benzene with compounds in which the benzene ring forms part of a fused-ring system, it can be concluded that the partial localisation of the double bonds in the benzene ring of such compounds is due to the influence of the adjacent ring. Such a treatment enables the causes of this influence and the opportunities for exercising it to be examined in an approximate, qualitative fashion.

Examination of the literature shows that only a fused ring of aromatic character has such an effect, independently of whether it is carbocyclic or heterocyclic. The saturated five- and six-membered rings in the indane and tetralin molecules hardly produce any bond fixation in the benzene rings: the Mills–Nixon effect does not exist.

As has been said above, the simplest molecule in which the partial localisation of double bonds can be clearly detected is naphthalene. In this compound the phenomenon is caused by the mutual influence of two condensed benzene rings, each of which requires the π electrons of the adjacent atoms 9 and 10 to form a stable π-electron sextet[194].



A simple explanation of the mechanism of this phenomenon was put forward a few years ago by Shigorin[195]. It is based on the following elementary but completely logical postulates:

1) In a molecule having conjugated bonds (under appropriate conditions) any π electron simultaneously interacts (forms bonds) with all its closest neighbours having π electrons with antiparallel spins.

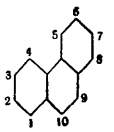
2) The nature of the interaction of π electrons having anti-parallel spins is such that a strengthening (or a weakening) of their interaction with some of their neighbours leads to a weakening (or a strengthening) of their interaction with the others.

3) In the systems under consideration the characteristics of the bonds and the atoms vary linearly with change in the number of neighbours and their electronegativity.

Using these postulates Shigorin[196,197] recently deduced simple equations providing a very easy method of calculating values of the unsaturation, bond orders, interatomic distances, and bond energies which are in very good agreement with those found experimentally or calculated by the molecular-orbital method. A special merit of Shigorin's work in this field is that his equations and the deduction of them follow directly from the peculiarities of the chemical structure of the molecules, and are therefore comprehensible and accessible to the organic chemist.

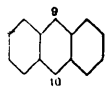
According to Shigorin the breakdown of bond equivalence in the naphthalene molecule is explained by the π electrons of atoms 9 and 10 (common to the two rings), unlike the remaining ones, interacting with three neighbouring π electrons. Because of this, the 9–10, 1–9, 8–9, 4–10, and 5–10 bonds should have a diminished order. The order of the 1–2, 3–4, 5–6, and 7–8 bonds should be correspondingly greater, and that of the 2–3 and 6–7 bonds lower.

These arguments are applicable also to more complicated compounds. Thus examination of the phenanthrene molecule shows that in its outer rings there should be a partial localisation of butadiene groupings, as in the naphthalene rings.



The order of the 1–2, 3–4, 5–6, and 7–8 bonds is increased. In the central ring the ethylene link is partially localised in the 9–10 position. Since this localisation occurs under the simultaneous influence of two benzene rings, the resulting bond order should be considerably greater than that of the 1–2 and 3–4 bonds in the outer rings.

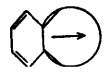
In the molecule of anthracene the state of the bonds in the outer rings is practically the same as in naphthalene and phenanthrene. In the central ring, however, the influence of the two adjacent benzene rings should lead to a partial localisation in positions 9 and 10 of single unpaired π electrons. This leads also to the appearance in the anthracene molecule of the specific high reactivity of the *meso*-positions[198]. Quantum-mechanical calculation, in its turn, confirms this conclusion, indicating the increased free-valency index of the *meso*-positions in anthracene.



These arguments can also be readily used to characterise the state of the bonds of more complex hydrocarbons. The conclusions which are reached are in good qualitative agreement both with the results of calculation and direct determination of interatomic distances and with data from chemical investigations.

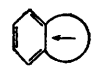
There arises, however, the more general question of the nature of the effect of the heterocyclic or non-benzenoid aromatic ring on the state of the bonds in the condensed benzene ring[198]. In the above cases it was assumed that the π electrons of the shared carbon atoms were equally necessary for the completion of the aromatic sextets of the two condensed rings. In the case of heterocyclic and non-benzenoid aromatic rings this may still be the case, and then the partial localisation of the double and single bonds in the condensed benzene ring should not differ substantially from the localisation occurring in naphthalene. However, if the added ring possesses a considerably greater or considerably smaller affinity for π electrons than that of the benzene ring, there is theoretically the possibility of the existence of two types of partial localisation of double and single bonds in the benzene ring[199].

In the first case it may be expected that the fused ring will "pull" the π electrons of the common carbon atoms out of the benzene ring, leaving in it only a partly localised butadiene grouping similar to that existing in *o*-quinones:



Such a transfer of electrons can obviously be regarded as an intramolecular oxidation–reduction process, in which the benzene ring of the molecule is oxidised with simultaneous reduction of the fused ring[200].

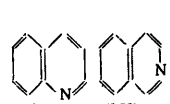
In the second case the fused ring does not require the π electrons of the common atoms for its energetic stability. It either exerts no effect on the state of the bonds in the benzene ring* or, possessing an excess of π electrons, it will "push" the π electrons of the common atoms into the benzene ring, causing a partial localisation of the double and single bonds, similar to that erroneously proposed for indane:



Below we shall examine some experimental results relevant to the existence of these three types of interaction between the benzene and the fused rings in condensed-ring molecules.

Two Condensed Rings Possessing Approximately Equal Affinity for π Electrons

Partial localisation of double and single bonds has been observed in the benzene ring of quinoline (LI) and isoquinoline (LII). This localisation is similar to that occurring in the naphthalene molecule.

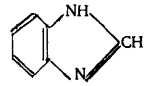


(LI) (LII)

* We have already met such cases in tetralin and indane.

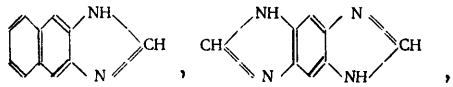
Results have already been given above for ozonisation, transmission of conjugation effect, substitution reactions, and certain other data[201] which confirm such localisation.

Localisation of this type is apparently encountered quite often, being produced under the influence not only of six-membered but also of five-membered heterocyclic rings of aromatic character. A study of such systems was described by Fries and his coworkers[98]. The methods of investigation adopted in their work are identical with those employed for the study of naphthalene. However, the discussion of the results of chemical experiments is complicated in these cases by the necessity for taking account of the influence of the polarity of the hetero atoms on the chemical properties. In the case of benzimidazole (LIII), for example, this leads to the β-position being, in contrast to naphthalene, more reactive than the α-position[202,203].



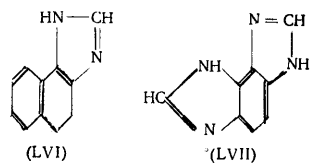
(LIII)

With such heterocyclic compounds, therefore, a valuable method for ascertaining the nature of the mutual influence of the rings is to study the chemical properties of the linear and angular tricyclic molecules. With approximately the same affinity for π electrons in all the rings, the reactivity of the central benzene ring of the compound of linear structure should be similar to the reactivity of anthracene described already, and that for the angular molecule should correspond to phenanthrene. Thus the properties of 2,3-naphthimidazole[105] (LIV) and 1,2:4,5-bisimidazolobenzene (LV)[204],



(LIV) (LV)

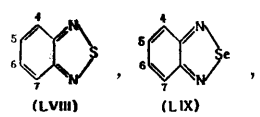
are very like those of anthracene, but the behaviour of 1,2-naphthimidazole (LVI)[205-207] and 1,2:3,4-bisimidazolobenzene (LVII)[194,208] resemble that of phenanthrene.



(LVI) (LVII)

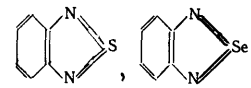
Molecules with a Fused Ring Possessing Considerably Greater Affinity for π Electrons than the Benzene Ring

Benzothiadiazole (LVIII) and benzoselenadiazole (LIX)[199],



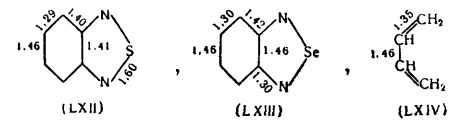
(LVIII) (LIX)

are examples of compounds in which a strongly electrophilic heterocyclic ring causes a marked disturbance to the bond equivalence with formation of a quinonoid structure in a condensed benzene ring. These compounds are obtained by condensation of *o*-phenylenediamine with sulphur dioxide[209,210] (and also thionyl chloride)[211] and with selenium dioxide[209] respectively; from their methods of preparation their structures can be represented as



(LX) (LXI)

However, the presence of cumulative bonds in the ring made the validity of the last two structures doubtful. In 1951 Luzzati[212] determined the interatomic distances in these substances, as shown in LXII and LXIII:

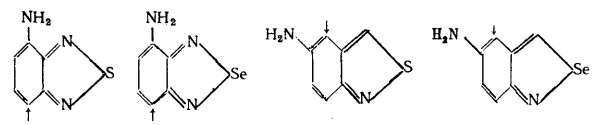


(LXII) (LXIII) (LXIV)

These interatomic distances indicate clearly that the benzene ring has a quinonoid structure. Thus closure of the heterocyclic rings produces in this case a considerable rearrangement of the π electron cloud of the whole molecule: to achieve stability the heterocyclic ring has "extracted" two π electrons from the benzene ring, and has partially localised the butadiene grouping in it. It is also noteworthy that in these molecules the localisation of the bonds in the benzene ring is considerably more marked than in the preceding case: the interatomic distances of the butadiene grouping localised in the benzene ring differ little from those in butadiene itself (LXIV).

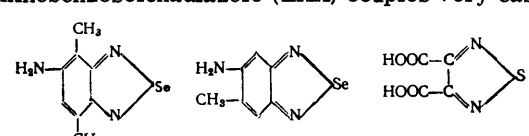
The question arises as to how this affects the chemical properties of these substances. Investigation shows that, as for other aromatic compounds, their most characteristic reactions are of substitution, occurring primarily at the α-positions (positions 4 and 7): nitration[199,200,213,214], sulphonation, and chlorination in the presence of a catalyst[215]. During chlorination and bromination in the absence of a catalyst, as Khaletskii and his coworkers have shown[216,217], benzothiadiazole (LVIII) can add on four atoms of halogen at the butadiene grouping with formation of unsaturated ring products.

The isomeric 4- and 5-amino derivatives of benzothiadiazole and benzoselenadiazole are intensely coloured, possess low basicity ($pK_B \cong 11.3$), and do not differ in chemical properties from ordinary aromatic amines. They give acyl derivatives, are readily diazotised, and undergo the Sandmeyer reaction. These amines readily couple with diazonium compounds, the 4-amino derivatives LXV and LXVI coupling in position 7, but the 5-amino derivatives LXVII and LXVIII solely in position 4.[200,215,218]



(LXV) (LXVI) (LXVII) (LXVIII)

If position 4 is blocked by a methyl group, the resulting substances are no longer able to couple. Thus 4,7-dimethyl-5-aminobenzoselenadiazole (LXIX) does not couple even with very active diazo compounds, whereas 6-methyl-5-aminobenzoselenadiazole (LXX) couples very easily[219].

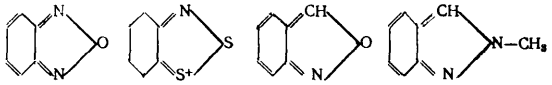


(LXIX) (LXX) (LXXI)

Ozonisation of benzothiadiazole and also oxidation with permanganate occur in the first place at the 4–5 and 6–7 bonds, yielding thiadiazole dicarboxylic acid (LXXI).[220] However, in spite of the large degree of bond fixation, these compounds do not undergo diene-synthesis reactions[200].

The quinonoid character of the benzene rings is shown in the intense colour, the absorption spectra, the addition of halogens already mentioned, and also in the ease with which the heterocyclic rings are opened by reduction in an acid medium[215,218,221].

A number of substances are already known which exhibit an analogous type of dissymmetry of the benzene ring. Among them may be mentioned in particular benzoxadiazole (LXXII)[212], the benzothiazothiolium cation (LXXIII) obtained by the Hertz reaction, and also, judging from spectroscopic data[222], anthranil (LXXIV) and 2-methylindazole (LXXV).

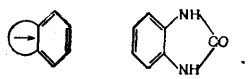


(LXXII) (LXXIII) (LXXIV) (LXXV)

However, the chemical properties of these products have not yet been extensively studied.

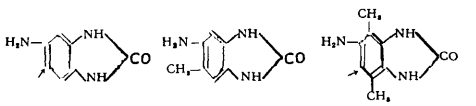
Compounds with a Fused Ring Possessing an Excess of Electrons, which "Expels" the π Electrons of the Common Atoms into the Benzene Ring

As has already been pointed out, an enrichment of the benzene ring with π electrons should theoretically lead to the partial localisation of double bonds shown in LXXVI:

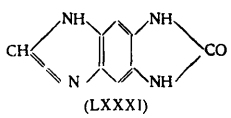


(LXXVI) (LXXVII)

Unfortunately there exist at present only a limited number of chemical data which might be regarded as providing experimental confirmation of the existence of this type of phenomenon. These concern the chemical properties of benzimidazolone (LXXVII) and have been obtained only very recently[223]. In accordance with the partial bond fixation in the benzene ring, 5-aminobenzimidazolone (LXXVIII) very readily undergoes azo coupling, which occurs exclusively at position 6.[224] Blocking of this position with a methyl group leads to 5-amino-6-methylbenzimidazolone (LXXIX), which does not couple, whereas 5-amino-4,7-dimethylbenzimidazolone (LXXX) couples readily with diazonium compounds[225].



(LXXVIII) (LXXIX) (LXXX)



(LXXXI)

Some confirmation of the influence of the imidazolone ring on the benzene ring may be provided also by the fact that 2'-oxo-1,2 : 4,5-bisimidazolobenzene (LXXXI) is not at all like 1,2 : 4,5-bisimidazolobenzene (LV) (already mentioned) or anthracene in chemical properties. The reason for this difference becomes clear if it is accepted that in this case the two heterocyclic rings simultaneously produce in the benzene ring bond fixation as shown in LXXXI, instead of the partial localisation of single π electrons in the *meso*-positions characteristic of anthracene[226].

Such are the experimental data at present available concerning the three possible types of partial localisation of double and single bonds in the benzene ring produced under the influence of a condensed ring. The review shows that the first two types definitely exist, but the existence of the third has not yet been demonstrated beyond doubt.

Further investigations of the mutual influence of cyclic groups in fused-ring molecules and clarification of the nature of the accompanying partial localisation of double and single bonds will enable a fresh approach to be made to the solution of many complicated questions of the chemistry of carbocyclic and heterocyclic aromatic compounds.

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