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CONJUGATION AND THE STRUCTURE OF BENZENE¹

BY MAURICE L. HUGGINS

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In another paper² the writer shows that pairing and, in the heavier elements, triplet formation of electrons in atomic shells and the formation of electron bonds may be explained very simply by assuming that the repulsion between electrons obeys a law of force of the type represented by Fig. 1. In the present paper this assumption will be applied to a number of the problems of organic chemistry.

Reaction Mechanisms.—Let us first consider the mechanisms of the simplest types of organic reactions, not discussing in what cases a certain reaction will take place, but concerning ourselves only with the process which occurs when it does take place.

Suppose that two atomic kernels A and A (constituting a molecule or

¹ This article is a revision and abridgment of the author's thesis presented in partial fulfillment of the requirements for the degree of Master of Science at the University of California 1920.

² Huggins, *J. Phys. Chem.*, soon to be published.

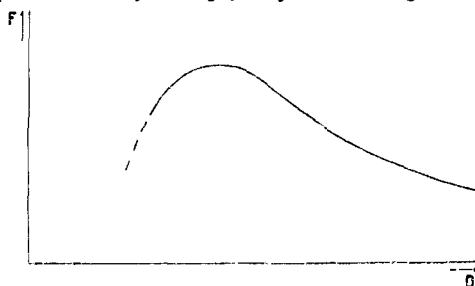


Fig. 1.—Illustrating the type of law of force between electrons which will result in the formation of pairs and triplets.

part of a molecule) are joined by a single bond, and a third atom B, containing an unpaired electron in its valence shell, approaches close to AA as shown in Fig. 2A. Then, if the distance between the electron pair and the unpaired electron is less than the distance of maximum re-

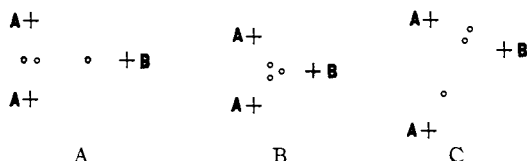


Fig. 2.—Mechanism of a simple replacement reaction.

pulsion (Fig. 1), the attraction of the kernels A and A for the single electron and of B for the pair more than overcomes the repulsion between the electrons, a structure such as is shown in Fig. 2B³ is formed, and this structure then breaks as shown in Fig. 2C.

A more common type of reaction is that depicted by Fig. 3. Two molecules, AA and BB, approach each other until the distance between

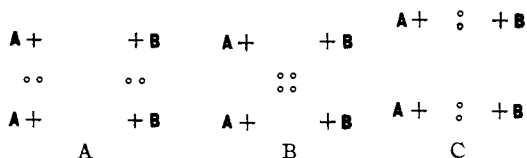


Fig. 3.—Mechanism of a simple metathetical reaction.

electron pairs is less than the distance of maximum repulsion. A 4-electron bond between the 4 kernels (Fig. 3B) is momentarily formed, this then breaking up as shown (Fig. 3C).

Electron pairs in double or triple bonds (or any electron pairs displaced from the straight line joining two atomic nuclei⁴) are especially exposed to the attractions of other molecules, since it is easier for electrons in other bonds to approach within the distance of maximum repulsion, and they form multiple-electron bonds much more readily than do pairs in ordinary single bonds. This explains the greater reactivity characteristic of compounds containing double or triple bonds.

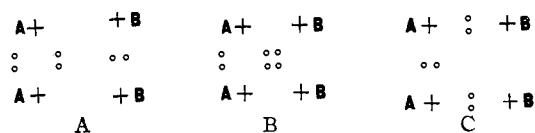


Fig. 4.—Addition onto a double bond.

³ The H₃ molecule [Wendt and Landauer, *THIS JOURNAL*, **42**, 920 (1920); **44**, 510 (1922)] probably has a structure of this type.

⁴ For instance, the pairs connecting ring atoms in 3- and 4-membered rings. Nef, *THIS JOURNAL*, **26**, 1549 (1904). Kohler and Conant, *ibid.*, **39**, 1404, 1699 (1917).

The mechanism of a simple addition reaction is illustrated in Fig. 4. The process is entirely analogous to those already discussed.

Two molecules containing double or triple bonds sometimes combine to form a 4-membered ring compound (Fig. 5), due to the *apparent* attraction between the electron pairs of the double or triple bonds.⁵

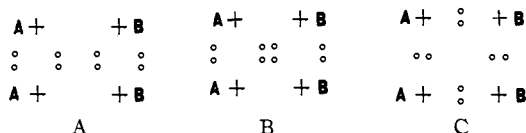


Fig. 5.—Reaction between two compounds containing double bonds.

Conjugation.—Under some circumstances multiple-electron bonds may have more than a transitory existence. For example, the double bond electron pairs *a* and *d* in a "conjugated" system, represented by the general formula $\text{A}=\text{B}-\text{C}=\text{D}$ (Fig. 6A) will be attracted to each other, producing the structure illustrated in Fig. 6B. Erlenmeyer, Jr.,⁷ has shown that the peculiar addition reactions of conjugated systems may be simply explained by assuming that they possess structures of this type. Bromine, for instance, will add to such a system to give the arrangement

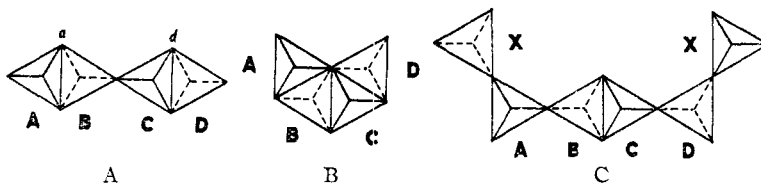


Fig. 6.—Conjugation.⁶

$\text{Br}-\text{A}-\text{B}=\text{C}-\text{D}-\text{Br}$. Looking at this reaction from the present viewpoint, the bond electron pair in a bromine molecule will be attracted to the center of the structure (of Fig. 6B) forming, temporarily, a 6-electron bond surrounded by 6 atoms. This structure at once breaks up, one bromine atom going to A, the other to D, leaving a double bond between B and C, as shown in Fig. 6C.

⁵ Lebedev, *J. Soc. Chem. Ind.*, **33**, 1223 (1913). Lebedev and Merezhkovskii, *J. Russ. Phys. Chem. Soc.*, **45**, 1249 (1913). Hale, *THIS JOURNAL*, **41**, 370 (1919). Hale and Lange, *ibid.*, **41**, 379 (1919).

⁶ In these and the following illustrations, the atoms, except hydrogen, are usually represented by tetrahedra. Unlettered tetrahedra denote carbon atoms. When two or more tetrahedron corners are shown in contact, each represents a single electron; each tetrahedron corner not in contact with another stands for a pair of electrons. Where no other atom is shown attached to a tetrahedron corner of a *carbon* atom, a hydrogen atom is understood to be bonded. For simplicity the atoms are represented (with one or two exceptions) by *regular* tetrahedra all of the same size.

⁷ Erlenmeyer, Jr., *Ann.*, **316**, 71 (1901).

What may be called "double conjugation" (general formula $A=B-C=D-E=F$) occurs in such compounds as hexatriene $H_2C=CH-CH=CH-CH=CH_2$, fumaric acid $\begin{array}{c} HC-CO_2H \\ || \\ HO_2C-CH \end{array}$, and maleic acid $\begin{array}{c} HC-CO_2H \\ || \\ HC-CO_2H \end{array}$ (Figs. 7, 8 and 9). It is evident from the illustrations that

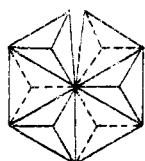


Fig. 7.
Hexatriene.

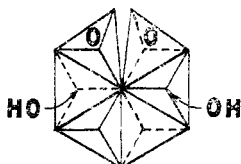


Fig. 8.
Fumaric acid.

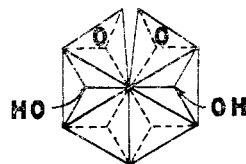


Fig. 9.
Maleic acid.

the fumaric acid configuration is more stable than that of maleic acid, and that only the latter can give an anhydride.⁸

Substances of the general formula, $A=B-CH_2-D=E$, can also be conjugated, but the effect of the conjugation on the chemical properties of the substances is quite different from what it is in the other case. Malonic ester, aceto-acetic and other ketonic esters, 1-3 diketones, esters of 2-3 unsaturated acids, cyano-acetic ester, etc., are included in this category. Two of the most unusual characteristics of these compounds are the reactivity of the hydrogen atoms between the 2 negative groups and the tautomerism existing in many cases between what are termed the keto and enol forms, which might be represented by the general formulas $A=B-CH_2-D=E$ and $HA-B=CH-D=E$, respectively.

The mechanism of this tautomeric change is shown in Fig. 10 for aceto-acetic ester, $CH_3-CO-CH_2-CO_2H$. Every step of the change is abso-

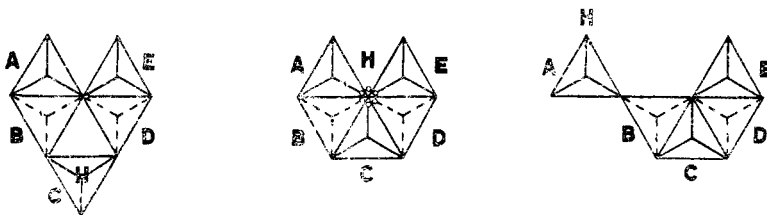


Fig. 10.—Aceto-acetic ester.

lutely in accord with this theory. The hydrogen is probably most reactive (being easily replaced by a sodium kernel, for instance) when the molecule is in the intermediate form of Fig. 10B.

⁸ A full discussion of the transformations and other reactions of these substances would necessarily be lengthy, and therefore will not be attempted at this time.

Benzene.—The structure represented by Kekulé's formula for benzene may be either that shown in Fig. 11, in which the hydrogens connected to the carbon atoms on each side of each double bond are *cis* with respect to each other, or a similar structure in which each is *trans* with respect to the neighboring ones. Let us assume for the moment that each of these two structures actually exists. According to the present theory, the

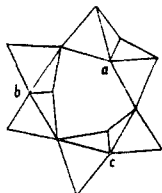


Fig. 11.
Kekulé's benzene model.

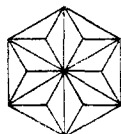


Fig. 12.
Baeyer's benzene model.

electron pairs, *a*, *b* and *c*, of the double bonds will be drawn toward each other forming, in either case, a centric bond of 6 electrons surrounded by 6 atomic kernels (Figs. 12 and 13).

The first of these is the benzene structure proposed by Baeyer.⁹ The second was first proposed by Körner,¹⁰ and was later championed by Vaubel¹¹ and others. Baeyer's model is less symmetrical than the other, especially as regards the positions of the atomic kernels with respect to the electron bonds between them; also, the structures of derivatives of benzene (naphthalene, anthracene, etc.) based on this model appear very improbable. Chiefly for these reasons, this type of structure must be eliminated from consideration. The *centroid* structure of Fig. 13, however, represents in a very satisfactory way the known properties of benzene and its derivatives, especially when taken in conjunction with the theory presented in this paper.

Although this structure has been discussed *pro* and *con* to a considerable extent by others, a resumé of some of the most important evidence may not be out of place here.

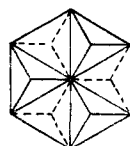


Fig. 13.—Körner's centroid model of benzene.

Little comment need be made with reference to the stability and saturation of this arrangement; it is evident that in order to break it up, not one but several very tight bonds must be broken. The residual affinities of the outer electron pairs are not strong enough, by themselves, to hold other molecules, forming addition products, but they are strong enough

⁹ Baeyer, *Ann.*, **245**, 103 (1888).

¹⁰ Körner, *Gaz. chim. ital.*, **4**, 444 (1874).

¹¹ Vaubel, *J. prakt. Chem.*, [2] **44**, 137 (1891); **49**, 308 (1894); **50**, 58 (1894). Cohen, "Lehrbuch der theoretischen Chemie," Springer, Berlin, 1903, vol. I, p. 468.

to play a very important part in the orientation of substituting and substituted groups, as we shall soon see.

Although benzene does not show the unsaturated properties common to ethylenic aliphatic compounds, there is plenty of evidence¹² that ethenoid linkages are actually present in the molecule. The formation of a tri-ozonide, the Buchner-Curtius reaction with diazo-acetic ester, and the exaltation of refractivity and magnetic rotation produced when an unsaturated side chain is conjugated with the ring,¹³ all favor this idea.

The original idea of conjugation¹⁴ is by no means sufficient to account for the saturated nature of benzene, for cyclo-octatetrene, $\begin{array}{c} \text{CH}=\text{CH}-\text{CH}=\text{CH} \\ | \qquad \qquad \qquad | \\ \text{CH}=\text{CH}-\text{CH}=\text{CH} \end{array}$, which, according to Thiele's ideas, should be just as saturated, stable and unreactive as benzene, behaves as a truly unsaturated compound.¹⁵ The reason for this is evident from Fig. 14.

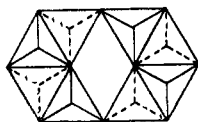


Fig. 14.
Cyclo-octatetrene.

A comprehensive discussion of the many peculiar facts connected with the reduction of the dicarboxylic acids of benzene and the reverse process, oxidation of the reduced acids, which have been carefully studied by Baeyer,¹⁶ is impossible here, but after a careful study of this evidence, the author finds none against the centroid structure of Fig. 13, and considerable in its favor.

The writer has shown elsewhere¹⁷ that the X-ray data obtained by Hull¹⁸ and by Debye and Scherrer¹⁹ indicate that graphite consists of layers which are exactly the same, both as regards the position of the carbon nuclei and of electrons, as would be obtained by "close-packing" benzene nuclei (of the centroid type), as in Fig. 15. Furthermore, the mole-

¹² For a discussion of this evidence as well as of much other evidence concerning the benzene nucleus, see Cohen, "Organic Chemistry for Advanced Students," Longmans, Green and Company, 1919, Vol. 2.

¹³ This term is explained a little further on in this paper.

¹⁴ Thiele, *Ann.*, **306**, 125 (1899).

¹⁵ Willstätter and Waser, *Ber.*, **44**, 3428 (1911). Willstätter and Hatt, *ibid.*, **45**, 1478 (1912). Willstätter and Heidelberger, *ibid.*, **46**, 517 (1913).

¹⁶ For an excellent synopsis of Baeyer's work on this problem, see Cohen, Ref. 12, pp. 395-403.

¹⁷ In a paper presented at the meeting of the California Section of the American Chemical Society, held in conjunction with the meeting of the American Association for the Advancement of Science, at Berkeley, Calif., August 5, 1921; also in the author's thesis for the degree of Doctor of Philosophy at the University of California, which will shortly be published. A short preliminary article has appeared in *Science*, **55**, 679 (1922).

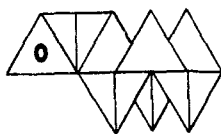
¹⁸ Hull, *Phys. Rev.*, [2] **10**, 692 (1917).

¹⁹ Debye and Scherrer, *Physik. Z.*, **18**, 294 (1917).

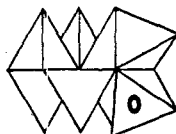
cules in crystals of benzene and a considerable number of its derivatives are similarly close-packed, and *the dimensions of the elementary hexagon, computed from the crystallographic data, are the same (within a few per cent.) as the corresponding dimensions in graphite,* thus proving this structure of benzene to be the correct one.

Conjugation with the Ring.—In a molecule possessing a double bond in the position indicated by the formula $C_6H_5-A=B$ (and sometimes in compounds of the type $C_6H_5-A-B=D$) the side chain is "conjugated with the ring,"²⁰ giving one or the other of the two kinds of structure depicted in Fig. 16 for benzaldehyde. It seems probable that where there is "double conjugation," as in naphthalene (Fig. 17), anthracene (compare Fig. 24), phthalic acid (Fig. 18), phthalic anhydride (Fig. 19), and stilbene, $C_6H_5-CH=CH-C_6H_5$ (Fig. 20), the first arrangement is the actual one, while in other cases the decision as to which is correct must await further experimental work.

In this connection it may be noted that, almost without exception, *meta*-directing groups are those which we should expect to conjugate with the ring, non-conjugating groups directing to the *ortho* and *para* positions.



A



B

Fig. 16.—Benzaldehyde.

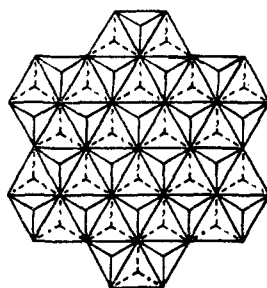


Fig. 15.—A close-packed layer of benzene centroids.

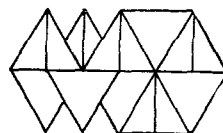
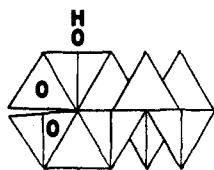
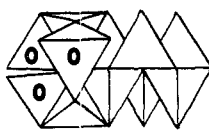
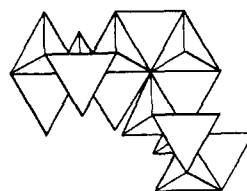


Fig. 17.—Naphthalene.

Objections to the Centroid Structure.²¹—The objections which have been raised to Körner's benzene model may be grouped into three

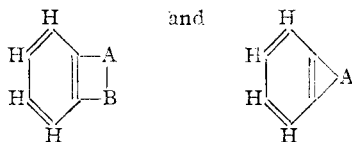
Fig. 18.
Phthalic acid.Fig. 19.
Phthalic anhydride.Fig. 20.
Stilbene.

²⁰ Compare the evidence from molecular-refractivity and magnetic-rotation data, Cohen, Ref. 11.

²¹ Compare Graebe, *Ber.*, **35**, 526 (1902). Werner, "Lehrbuch der Stereochemie," Fischer, Jena, 1904, p. 370.

classes. (1) Compounds might be expected in which an atom or group of atoms is attached to 2 *meta* carbon atoms, while such linkages between *ortho* atoms (as in phthalic anhydride) would at first sight appear unlikely. (2) Similar linkages between the 1 and 8 positions in naphthalene (as in acenaphthene and naphthalic acid) appear impossible. (3) The unsymmetrical di- and tri-substitution products of benzene should give stereoisomers. Attempts to separate such isomers have so far proved fruitless.

Let us consider the first of the above. A side chain which conjugates with the ring is not in a position to react with an atom or group of atoms in the *meta* position, but two such side chains which are *ortho* to each other (as in phthalic acid, Fig. 19) are in close proximity; hence, the fact that phthalic anhydride and similar *ortho* derivatives are known, but not the corresponding *meta* derivatives, is a point in favor of this theory rather than against it. It might be possible, however, by using suitable non-conjugating side chains, to obtain linkages between *meta* carbon atoms. Because this has not been done does not mean that it cannot be done, but merely that proper means have not yet been employed. From Kekulé's formula one would expect compounds of the type represented by the formulas



but attempts to prepare them have proved fruitless.²²

There is another possible reason why the benzene ring has not yet been bridged between *meta* positions. The electron sextet at the center of the

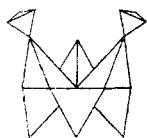


Fig. 21.—Benzene, with two of the hydrogens, *meta* to each other, substituted by other atoms; illustrating the nature of the probable distortions of the molecule.

centroid must exert a greater repulsion on each single bond electron pair connecting a ring carbon atom to another atom, than do the pairs at the corners of the centroid hexagon. The carbon tetrahedra in the centroid must therefore be distorted somewhat as indicated in Fig. 21 and, because of the tendency for bond electron pairs to be on the straight lines joining atomic centers,²³ the atoms attached to the centroid carbons (even when they do not conjugate with the ring) are forced away from the center of the structure, as shown in the illustration. Furthermore, (also because of the electron sextet in the center) the centroid tetrahedra are considerably larger than

²² Perkin, Jr., *J. Chem. Soc.*, **53**, 1 (1888).

²³ Huggins, "Electronic Structures of Crystals. I," soon to be published in *THIS JOURNAL*.

the valence tetrahedra of nitrogen, oxygen, or aliphatic carbon atoms.²⁴ Thus it is evident that groups which are *meta* to each other are not in very close proximity after all.

Turning now to the second class of objections, it may be seen from Fig. 22 that such compounds as acenaphthene and naphthalic anhydride may easily be accounted for by the present theory if they be considered 1, 5 instead of 1, 8 derivatives. The methods which have been used to determine the orientation of naphthalene substitution products differentiate between the 5 and 8 (and between the 6 and 7) positions only by such means as the anhydride formation of naphthalic acid, which were valueless as long as the true structure of naphthalene remained in doubt. In view of the present evidence, we may conclude that the numbering of many substitution products of naphthalene is in error, the 5 and 8 positions being interchanged, and likewise the 6 and 7.

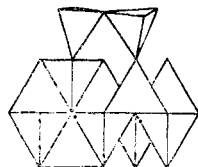
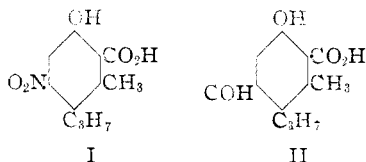


Fig. 22.—Acenaphthene.

The evidence in regard to the stereo-isomerism of the substitution products of benzene is also very weak. Several investigators have attempted to separate such isomers. Le Bel²⁵ has reported a negative result of an attempt to separate salts of *o*-toluidine by means of mold. Lewkowitsch²⁶ attempted to grow fungi in solutions of 2-methyl-3-nitrobenzoic acid, but they did not thrive. He also tried to resolve 2-methyl-6-hydroxy-, 2-methyl-3-hydroxy-, and 2-methyl-3-methoxybenzoic acids by converting them into their cinchonine salts, finding that although these salts crystallized well, the acids thrown down from their solutions by ammonia were optically inactive. Meyer and Lühn²⁷ found that compounds of the formulas I and II were too poisonous to permit good



resolution by means of mushroom fungi, but by adding other nutritive material to dilute solutions, some optical rotation was produced. This, they state, may have been caused by the added food. Attempted resolution of these same acids and also of 3-hydroxybenzoic acid by means of their salts with various alkaloids gave negative results.

²⁴ In diamond the edge of the valence tetrahedron is 1.26 Å. The oxygen and nitrogen tetrahedra are smaller than this. In graphite and in many aromatic crystals the tetrahedron edge (between electron sextets) is about 2.5 Å.

²⁵ Le Bel, *Bull. soc. chem.*, [2] **38**, 98 (1882).

²⁶ Lewkowitsch, *J. Chem. Soc.*, **53**, 781 (1888); *Ber.*, **16**, 1576 (1888).

²⁷ Meyer and Lühn, *Ber.*, **28**, 2795 (1895).

It is evident that the attempted separations by means of fungi give us no evidence one way or the other in regard to the problem. The failure to obtain resolution by means of the alkaloid salts is purely negative evidence and is by no means conclusive (although it has apparently been considered so). There are quite a few substances which, according to generally accepted theory, should be optically active, but they have resisted all attempts at resolution.²⁸ The experimental results with the benzene derivatives can be accounted for in a number of ways. The acids used are all fairly strong acids (probably the cause of their toxic properties). If the compounds formed between these and the alkaloid bases are *ionized*, resolution need not result. Other possible explanations are that the isomers of these salts have but slightly different solubilities (repeated frac-

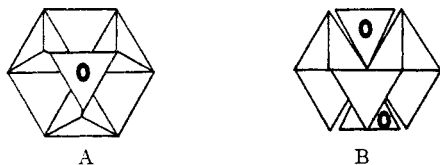
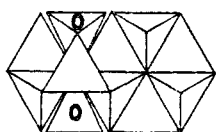
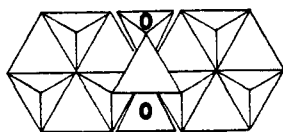
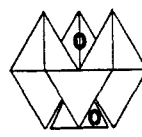


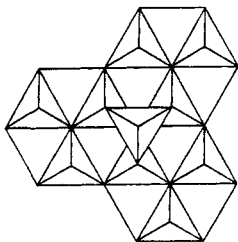
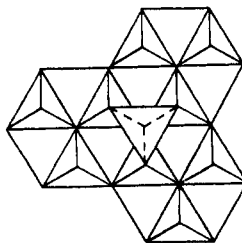
Fig. 23.—Quinone.

tional crystallization was apparently not tried in any of the above cases), or that the isomers of the optically active acids, after resolution, rotate polarized light very little or not at all.

Benzene Derivatives and Related Compounds.—Except for the crystal structure evidence, perhaps the most potent argument in favor of the cen-

Fig. 24.
Naphthaquinone.Fig. 25.
Anthraquinone.Fig. 26.
 γ -Pyrone.

troid structure for the benzene nucleus is that the properties of its derivatives and of related compounds (such as furane, thiophene, pyrrole) may be much more adequately represented by models of the centroid type than by the ordinary formulas or the models based on them. Space does

Fig. 27.
Triphenylmethane.Fig. 28.
Triphenylmethyl.

²⁸ Ref. 12, p. 186.

not permit of a further consideration of this question here, but the centroid structures of a few of the more interesting aromatic compounds are shown in the illustrations. In the quinones (Figs. 23, 24 and 25), it may be noted, the *centroid bond* consists of 8 electrons surrounded by 8 atomic kernels; in the pyrones (Fig. 26) the centroid bonds also contain 8 electrons, but each of these is surrounded by 8 kernels; while in triphenylmethyl (Fig. 28) there is a centroid bond of 7 electrons in the center of a group of 7 atoms. In furane, thiophene and pyrrole, there are 6 electrons in the center of each molecule, each of these being surrounded by 5 atomic kernels.

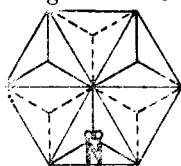


Fig. 29.
Pyridine.

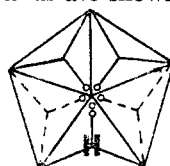


Fig. 30.
Pyrrole.

Summary

Probable mechanisms for the simplest types of organic reactions are given and explained by means of an assumed maximum in the force-distance curve representing repulsion between electrons. As intermediate steps in these reactions, bonds of 3, 4, or more electrons surrounded by 3, 4, or more atomic kernels are assumed. The reactivity of double and triple bonds is explained from this viewpoint. Conjugation is then briefly considered and the structure of typical compounds given, some of these being similar to those proposed by Erlenmeyer, Jr. Keto-enol tautomerism and its relation to conjugation are discussed.

Applying this idea of conjugation to benzene leads to a structure of the *centroid* type first proposed by Körner. The evidence for and against this structure is briefly reviewed. It is shown that the objections raised to it are all invalid or inconclusive. On the other hand, the known properties of benzene and of its derivatives are very adequately represented by their centroid structures. Furthermore, recent evidence from crystal structures proves this benzene structure to be the correct one.

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