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THE STRUCTURE OF BENZENE

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G. V. Chelintsev

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The structure of benzene is just about the most pressing special question in the central problem of chemical science in the present stage of its development i.e., the structural problem. Butlerov is the founder of the doctrine of molecular structure. In place of the former metaphysical theories, he created a ~~methodologically valuable~~ structural theory ^(which is completely valid methodology) which played a decisive role in all subsequent developments of chemical science.

One extremely important aspect of the structural theory is the study of chemical structure -- of the differences between chemical and mechanical phenomena and of the existence in chemical phenomena of a supra-mechanical, chemical regularity. This regularity is expressed in structural formulas showing the presence in molecules not only of general mechanical, but also of certain particular, localized, chemically unifying atomic interactions. The understanding of the above mentioned regularity made it possible not only to express the whole known diverse ^{particles} multiformity of chemical molecules with simple formulas, but even to predict the existence of hundreds of thousands of new molecules.


Although he was convinced of the validity of the science of chemical structure, Butlerov foresaw nevertheless the possibility of the discovery of a diverse multiformity of ^{particles} molecules transcending his structural theory and therefore realized the necessity for further development of the latter. And in fact, soon thereafter, the discovery was made of stereoisomeric and complex compounds, of


ions and of radicals the theoretical interpretation of which was embodied in the stereochemical, co-ordinative^{ion} and electron theories.

Butlerov's ~~study~~^{theory} of chemical structure remained the guiding light in all the new theories. It is enough to glance at the ~~simple~~^{unequivocal} formulas of these theories for each molecule, with electron orbits localized in one or two atoms, to be convinced that these formulas express not the quantitative, but the qualitative differences in the interrelations between atoms and atoms, electrons and nuclei, and also express how the concept of chemical structure cannot be reconciled with that of the mechanical status of molecules. The new theories, because of their methodological correlation with the structural theory, can be united with it under the general name of Butlerov's classical theory.

The classical theory was developed because Butlerov's concept of the structure of particles corresponded to the observed and predicted diverse multiformity of particles. In this theory it is stated that the entire known diverse multiformity of particles is encompassed by simple classical formulas with electron orbits localized in one or two atoms. In other words, in the classical theory formulas the concept of chemical structure is expressed as the law of localization of electron orbits in one or two atoms. It is very important to note that even today we do not know about ~~such~~² a supplementary diverse multiformity of particles ^{which would} requiring the introduction of formulas with three or more atomic electron orbits and the revision of the classical law of orbit localization in one or two atoms. ✓

However, in the description of certain molecules, there were offered formulas with delocalized orbits. That was because the classical formulas assigned to the molecules did not always correspond to one property or the other of said molecules. More often than not these discrepancies could be eliminated by pointing out the peculiarities of the mechanical condition of chemical structures, i.e. the peculiarities of distribution of electron density and atomic nuclei of the given chemical structure defined by the mutual influences of atoms and atoms and of electrons and nuclei. But in other cases such explanations were insufficient and it was necessary to admit the inadequacy of the classical formulas assigned to the molecules.

Benzene offers the clearest example. Not one of the formulas with orbits localized in one or two atoms suggested for Benzene fully corresponds with all of its properties. The inadequacy of the best of these --- the hexatrienic formula of Kekulé:  was decisively proven by data obtained through physical means defining the uniformity of the six intercarbon bonds in the benzene ring.

In connection with this, Thiele's formula:  has acquired a predominant significance. It is used nowadays as an explanation of the evenly distributed density of hexaelectronic clouds on the hexatomic orbit encompassing all the carbons of the benzene ring. Thiele's formula upsets the law of localization of electron orbits in one or two atoms and therefore denies the validity of the Classical Theory as applied to benzene.

Thiele's formula has acted as springboard for the development, mainly by Anglo-American chemists, of the "mesomeric resonance" theory.

The basic postulate of the mesomeric resonance theory is the delocalization of electron orbits in all the atoms, and is directly opposed to the classical law of orbit localization in one or two atoms. Thus, the concept of chemical structure of molecules as an aggregate of particular, supra-mechanical, chemically unifying interrelations between atoms and atoms, and between electrons and nuclei, was reduced to the level of a generic aggregate of mechanical interrelations between electrons and nuclei. At the same time the classical formulas expressing chemical structure with localized orbits and bonds were declared fictitious, good only for occasional and inaccurate presentations of nuclear distribution and of the total electron cloud density in the molecules. Thus the mesomeric resonance theory denies the classical theory.

As a result of discarding the law of localization of orbits in one or two atoms, the mesomeric resonance theory introduced a limitless number of formulas expressing various nuclear distributions and electronic densities in the molecules. Consequently these formulas⁵ were sufficient to describe any chemical or physical property of the molecules. (These formulas should appear as designations of atoms with more or less heavy plus and minus signs and with more or less heavy connecting lines. They should also appear in any number of combinations, not limited by valency, and octet rules, but adapted for the expression of the required

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distribution, with respect to the nuclei, of the total electron cloud density. The formulas of Thiele serve as prototypes thereof.

Unfortunately, instead of such formulas which simply and obviously express the delocalization of orbits, the formulas of Ingold and Pauling have been used, which disguise the meaning. (This has led to a number of misunderstandings.) However, this success was achieved at a heavy price. The balance between the number of possible formulas and the number of actual molecules, as defined by the localization of orbits law, was lost. The actual particles were hopelessly submerged by the numberless possible combinations of electron and nuclear distributions and became subject to chance rather than scientific prediction. (And science, according to T. D. Lysenko, is the enemy of chance.) The mesomeric resonance theory, universal as far as descriptive properties are concerned, appeared to be lacking in the powers of prediction, which made it fruitless in practice.

The practical fruitlessness of the mesomeric resonance theory stems from its methodological defectiveness. Butlerov's concept of the supra-mechanical chemical structure, similar to Engels' concept of supra-mechanical chemical motion, corresponds to the phenomena of the discrete nature of molecules and the intermittance of reactions, while the negation of this concept reduces the molecule to the level of a stable electronic and nuclear aggregate, and the reaction to the level of an uninterrupted mechanical shifting of nuclei and electronic density. The mesomeric resonance theory appears to be an attempt to bring

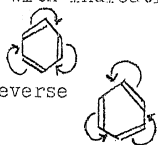
of the "free will of the electron".

If the false impersonation by the mesomeric resonance theory of the quantum mechanical theory in chemistry aided its spread, then certainly the technique of expressing "real" structures with delocalized orbits by means of "fictitious" classical formulas with localized orbits offered by its authors should be considered the main factor of this spread. Such techniques, complemented by scholastic arguments intended to create an appearance of correctness opened the possibility of a parasitic exploitation by the mesomeric resonance theory of the "fictitious" classical formulas in their usual, real chemical and physical form.

Techniques of expressing "real" structures by means of "fictitious" formulas are elaborated in two variations -- in the mesomeric theory of Ingold and the resonance theory of Pauling.

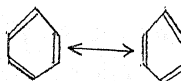
For instance, in the mesomeric theory the "real" structure of benzene is expressed by the fictitious formula of Kekule equipped with indications as to the delocalization of electron

orbits:



or, in reverse

In the resonance theory the curved arrows are discarded and replaced by a connecting double arrow:



indicating that the fictitious formulas of Kekule should be considered not apart, but in superposition. Both variations underscore the oneness of meaning of the new formulas with the formula of Thiele in its electron interpretation described above. The

expediency of substituting the formula of Thiele (which best of all expresses the concept of orbit delocalization in benzene) with new formulas is usually characterized by the fact that these are more familiar to the chemist. The upsetting of the orbit localization law and of the rules of valency is presented in a masked form.

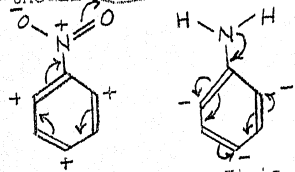
However, the question lies not only in this comparatively harmless "advantage" of the Ingold and Pauling formulas over that of Thiele. The main "advantage" is that the Ingold and Pauling formulas open the possibility for scholastic play with the concepts of the fictitiousness and reality of the classical formulas employed therein. Thus, for instance, in the argument of the energy origin of the real structure of benzene, one mentions the gain of energy deriving from the mesomeric perturbation of "alternate", or resonance-"forming" hexatrienic structures. Obviously, if the classical formulas are truly fictitious, then the structures expressed by them can neither be disturbed nor resonate -- they cannot give a physical effect of energy gain. This way the establishing of the fictitiousness of classical formulas is combined with their use in the usual real sense.

✓ The main "advantage" of the Ingold and Pauling formulas appears still more obviously in the arguments used to explain the chemical properties of molecules. The arguments used to explain the rules of substitution orientation in the benzene ring can serve as example. These explanations are considered to be extremely important accomplishments of the mesomeric resonance theory.

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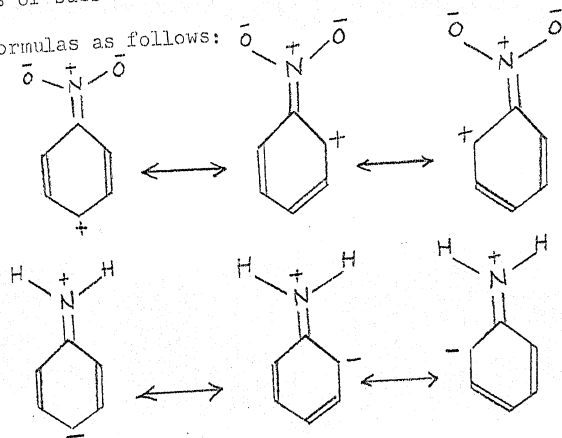
interpretations given by the alternate mesomeric theory result in the following formulation.

For instance, in the alternate mesomeric theory they take the following shape:



Such formulas are absurd in themselves. It is obvious that the curved arrows from bond to bond, and from bond to atom, are distributed arbitrarily and that by combining them appropriately with their combinations one can place plus and minus signs on any carbon of the benzene ring, in other words one can "explain" anything. But even more essential is the fact that the displacements of electron density in the benzene ring by introduction into it of a substitute are analyzed not in connection with the "actual" formula of Thiele, but with the "fictitious" formula of Kekule.

In the alternate resonance theory, the explanations of the rules of substitution orientation in the benzene ring are given in formulas as follows:



It is easy to see that if the quinonoid structures determine the distribution of the electronic density in the benzene ring, then the corresponding formulas are not fictitious.

Consequently, both in the mesomeric and resonance alternates of the mesomerism resonance theory the explanations of the rules of substitution orientation in the benzene ring are reached by means of a parasitic usage, in an accepted, real sense, of the allegedly fictitious classical formulas. These "explanations" (just like all other "explanations" of the mesomerism resonance theory) are only illusions -- the fruit of scholastic contrivances. ✓

The processes of the mesomeric resonance theory described above are based on the concept of mesomerism according to which the real structures are intermediate in relation to the structures expressed by the "fictitious" classical formulas. The ponderously Machistic meaning of the concept of mesomerism is characterized by the fact that the fictitiousness of the classical formulas tested by the description and prediction of hundreds of thousands of molecules, in other words the fictitiousness of our reliable knowledge, is confirmed simply by saying that here reality is understood and expressed through fiction.

Thus the mesomeric resonance theory was spread by means of Machistic scholasticism. The falsity of this theory is exposed in my book (1). It is not surprising that this book met with hostility from the followers of Ingold and Pauling. Even so, they were forced to maneuver. In particular, sensing the lack of dependability of the concept of mesomerism, Ingold's and Pauling's followers endeavor to reduce it to the level of the "phenomenon" of electron orbit delocalization. The insolvency of the quantum-mechanical basis of the electron orbit delocalization postulate

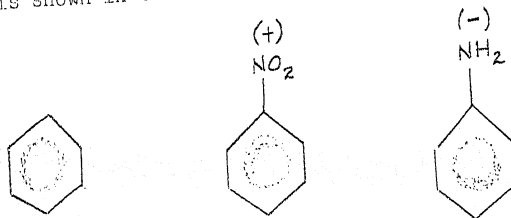
has been mentioned above. The only serious basis of this postulate is the nonconformity of the molecular properties to the classical formulas assigned to them and, above all, the nonconformity of the hexatrienic formula of Kekule to the uniformity of the benzene intercarbon bonds. This last fact was the main encouragement to the growth of the mesomeric resonance theory. It becomes clear therefore how important the structure of benzene is in defining the ways of development of the structural problem. A successful solution of the structure of benzene in line with the classical theory would be equivalent to a direct denial of the orbit delocalization postulate and, consequently, of the whole mesomeric resonance theory.

As shown below such a solution is possible. Consequently, the promotion of the concept of benzene orbit delocalization to the rank of actual phenomenon was wholly unwarranted. One can only compare the worths of the two solutions of the structure of benzene, one of which is based on the postulate of orbit delocalization, and the other on the law of orbit localization in one or two atoms.

The benzene formula must first of all satisfy two extremely important conditions presented by the aggregate of its chemical and physical properties: the uniformity of the intercarbon bonds in the benzene ring and the alternating of positive and negative carbons, or "alternating polarity" in the benzene ring. The latter condition is fulfilled in the mesomeric resonance theory (as shown above) by utilizing the allegedly fictitious classical formulas in a real capacity. Let us leave

mesomeric scholasticism alone and see what Thiele's formula, best expressing the concept of orbit delocalization, can give us to satisfy the conditions already mentioned.

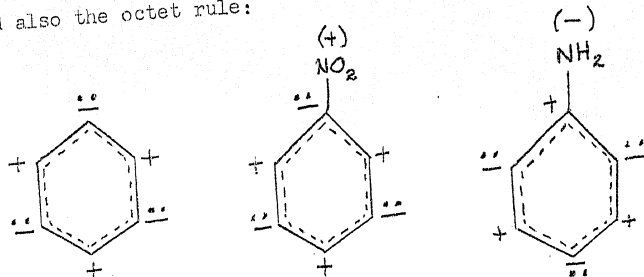
We find that Thiele's formula, which satisfies the first condition, in no way satisfies the second. For instance, according to Thiele's formula, the introduction of the substitute into the benzene ring must be accompanied by a uniform movement of the density of the six-electron cloud towards the positive, or away from the negative substituting atom (the density of the cloud is shown in the sketch):



However such a movement of the electron cloud density can in no way lead to alternating polarity and is not in concordance with the rules of orientation in the benzene ring. Thus, outside of scholastic expediency, the concept of orbit delocalization is not only inadequate for a complete formulation of benzene, but leads to conclusions directly contradicting the properties of benzene.

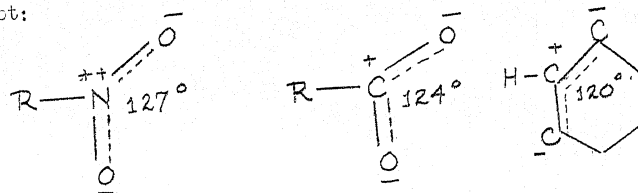
A complete formulation of benzene is possible only on the basis of the classical law of orbit localization in one or two atoms. The impression of inadequacy of the classical theory in the formulation of benzene is the result of not solving this

problem by means of the double electrovalent-covalent (semipolar) bond. I have shown (2) that by using this concept one can create the "contact formula" of benzene subject to the law of orbit localization in one or two atoms, to the rules of valency (electrovalent bonds come to being not according to the rule of valency numbers, but according to the rule of higher co-ordinative numbers), and also the octet rule:



According to the contact formula, three electronic doublets of the aromatic sextet are distributed over three monoatomic orbits of the benzene ring metacarbons. This corresponds to the uniformity concept of the six intercarbon bonds and to the alternating polarity in the benzene ring.

I have shown the conformity of the contact benzene formula with all experimental chemical and physical data. Here I will cite only the comparison of the contact benzene formula with the formulas of molecules in which the semipolar bond characteristic is beyond doubt:



Inasmuch as this comparison clearly shows the similarity between benzene and the indicated molecules both in bond angles and, particularly, in planar configuration, it can serve as clear testimony to the semipolar nature of the benzene intercarbon bonds and, consequently, to the accurateness of the benzene contact formula.

Thus, the classical formula, based on the law of orbit localization in one or two atoms, appears to be the only benzene formula conforming with the conditions of both bond uniformity and alternating polarity. This deprives the postulate of orbit delocalization and the mesomeric resonance theory itself of their most important support. The nonconformity of the Kekule formula with the properties of benzene does not indicate the insolvency of the classical theory, but simply suggests the necessity to replace Kekule's formula with another classical formula.

The creation of the benzene contact formula and of other similar formulas eliminating the factor of nonconformity of the properties of molecules with their assigned classical formulas has necessitated the development of the classical theory into a "new structural theory". (3)

The principal traits of the new structural theory is the establishment of the qualitative difference between covalent and electrovalent bonds and the consequent possibility of a homeopolar^r electrovalent bond (resulting from the deformation of the electron shells in oppositely charged atoms.) The latter concept does not exist in the minds of the mechanistically thinking followers

of Ingold and Pauling, for whom the concept of electrons belonging to the nuclei is equivalent to the concept of electron density distribution as related to the nuclei. And yet this concept finds itself in full accord with Butlerov's teachings on chemical structures and the classical law of orbit localization in one or two atoms which define the impossibility of reconciling the chemically unifying interrelations between atoms and atoms, and between electrons and nuclei with their power and space interrelations. The new structural theory is a logical development of the practical and methodologically valid classical theory of Butlerov.

The current state of chemical science is characterized by the opposition of the mesomeric resonance theory and the new structural theory. The struggle between the two theories is nearing its second stage. For several years the patriotic followers of Ingold and Pauling simply defended their theories. But nowadays, retreating step by step, they find themselves on the antiquated positions of Thiele's theory. The defense of Ingold's and Pauling's theories now mainly assumes the form of a rabid attack upon the new structural theory. Ingold's and Pauling's theories, however, are doomed to collapse. Their followers should redeem their clumsy errors by working on the development of the advanced, Soviet chemical theory based on the teachings of A. M. Butlerov.

CONCLUSIONS

(1) The insolvency of the classical theory in the formulation of benzene is condition^{ed} not by its falsity, but by its lack of development. The logical development of the classical theory into a "new structural theory" makes it possible to assign to benzene a "contact formula" conforming to the above law, and which satisfies all physical and chemical experimental data.

(2) The achievements of the mesomeric resonance theory in the formulation of benzene are illusory. As a consequence of the creation of the benzene contact formula, the mesomeric resonance theory is deprived of its main support and loses its right to existence.

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Literature: (1) G. V. Chelintsev, Notes on organic chemistry theory, Goskhimizdat, 1949.

(2) G. V. Chelintsev, *ibid.* pp 107-114.

(3) G. V. Chelintsev, *ibid.* pp 87-119.