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Chemistry

V. P. PARINI

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Abstract**Full Text***Chemistry***V. P. PARINI****ON THE INTERRELATION OF CERTAIN
FEATURES OF POLYNUCLEAR AROMATIC
COMPOUNDS***(Presented by Academician V. N. Kondrat'ev, 23 VI 1960)*

Unlike benzene, systems with condensed aromatic nuclei are characterized by a nonuniform distribution of electron density among the atoms forming the skeleton of the molecule; at the same time, the molecule becomes more readily excitable. In each individual case these situations can be quantitatively illustrated by calculations, and the literature contains many data obtained chiefly by the methods of MO theory. Among organic synthetic chemists who do not use calculations, it is customary to associate the excitability of polynuclear molecules with the total number of nuclei entering into the molecule; however, such an approach, as will be shown below, is incorrect.

Let us consider the simplest case—polynuclear aromatic hydrocarbons containing only six-membered rings. If, in the formulas of such compounds, the double bonds are arranged so that all electrons prove to be paired, then nuclei are often found which cannot be represented by means of canonical Kekulé benzenoid structures. Such nuclei, which below we shall call nonbenzenoid for brevity, must be assigned various types of quinoid structures, up to the triquinoxyl structure. The structure of the naphthalene molecule, for example, $[[\text{structural formula of naphthalene}]]$, can be depicted without resorting to quinoid structures; in other words, such a molecule contains zero nonbenzenoid nuclei, whereas the molecule of anthracene $[[\text{structural formula of anthracene with one marked ring}]]$ contains one nonbenzenoid nucleus, designat-

Table 1**Compounds used***(The numbers of the compounds correspond to the numbers in Fig. 1)*

No.	FormulaNo.	FormulaNo.	FormulaNo.	FormulaNo.	FormulaNo.	Formula
1	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]
2	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]
3	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]
4	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]
5	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]
6	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]
7	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]
8	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]

Figure 1. Four plots relating the number of nonbenzenoid nuclei to energetic and kinetic characteristics.

Figure 1: Figure 1. Four plots relating the number of nonbenzenoid nuclei to energetic and kinetic characteristics.

No.	FormulaNo.	FormulaNo.	FormulaNo.	FormulaNo.	FormulaNo.	Formula
9	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]
10	[[structural for- mula dia- gram]]	[[structural for- mula dia- gram]]	39	see 32		

...by a cross. This nonbenzenoid nucleus can be placed in the formula in various ways (in anthracene, for example, on either side), but its position does not affect our reasoning. The naphthalene molecule can also be depicted differently, with one nonbenzenoid nucleus, schematic naphthalene structure with a crossed ring, but in all cases we shall take into account only the most favorable structures,

Fig. 1. A—Relation between the number of nonbenzenoid nuclei and the value of the energy of the lowest unoccupied level according to data from (1). **B**—Relation between the number of nonbenzenoid nuclei and the value of the ionization potential according to data from (4, 5). **V**—Relation between the number of nonbenzenoid nuclei and the affinity for methyl, expressed through the logarithm of the reaction-rate constant according to data from (4). **G**—Relation between the number of nonbenzenoid nuclei and the value of the activation energy of conductivity (6).

containing the minimum possible number of nonbenzenoid nuclei, i.e., we assign the naphthalene molecule to the polynuclear structures that do not contain nonbenzenoid nuclei, giving naphthalene the first of the two structures shown above. In such reasoning we treat benzene separately, since, although it is the progenitor of polynuclear aromatic substances, it does not itself belong to them, and the distribution of electron density among the C atoms in benzene is uniform.

It turns out that the excitability of the molecule, and with it many energetic characteristics of a compound, are connected with the number of nonbenzenoid nuclei that are obtained when the double bonds are arranged in the formula of the given compound. This feature, being to a large extent formal and not

structural formula: fused aromatic system bearing two methylene groups, CH₂ and CH₂

Figure 2: structural formula: fused aromatic system bearing two methylene groups, CH₂ and CH₂

directly reflecting the actual structure of the molecules, nevertheless, along with its simplicity, proves sufficient for orientation with respect to certain essential properties of polynuclear aromatic compounds.

In the figures presented, the relationship is shown between the number of nonbenzenoid rings appearing in the structural formula of a substance and the energy of the lowest unfilled level (Fig. 1A); the ionization potential (Fig. 1B); the methyl affinity (Fig. 1C); and the “activation energy” of conductivity E in the equation $\sigma = \sigma_0 e^{-E/2kT}$ for 54 different hydrocarbons with condensed rings (Fig. 1D). From these same figures the interrelation of all the quantities mentioned is also clear. For the excitation energies into the biradical state, calculated by Dyatkina and Syrkin^(2,3), the same picture is obtained as for the energy of the lowest unfilled level.

As the number of nonbenzenoid rings increases from 0 to 4, the color of the compounds deepens regularly. The absorption maxima shift from the region of 200–300 mμ to the region of 600–700 mμ; in other words, the photon energy falls approximately from 4 to 1.8–1.9 eV.

In molecules, with an increase in the number of nonbenzenoid rings, a tendency toward easier excitability is observed. It is noteworthy that the data on the activation energy of conductivity fit the dependence given in Fig. 1D only in cases of natural packing of the molecules of the substance under study (the substance was obtained from solution by evaporation of the solvent). In the study of the conductivity of samples obtained by pressing the powdered substance⁽⁸⁾, such a dependence does not occur.

It is easy to see that the criterion we propose—the number of nonbenzenoid rings—may also be connected with the electron affinity, with an increase in the difference between the lengths of the bonds joining different carbon atoms in the molecule of one and the same compound, and with the growth of the maximum free-valence index, and hence also with the ability of the substance to inhibit certain autoxidation reactions⁽⁷⁾.

Judging from certain calculations and experimental data^(2,9), the same approach is applicable to meta- and para-oligophenylenes. In this case, extension of the chain in the absence of rings of nonbenzenoid structure does not change the excitability of the system. A different result may be expected for para-oligophenylenes, where, with a considerable increase in the chain length, an increase in the weight of the quinoid structure is probable, entailing easier excitability of the molecules. As the calculations of Dyatkina and Syrkin⁽²⁾ show, polynuclear compounds with side groups of the type

reaction schemes showing phenol–quinone-type tautomerism in several fused aromatic systems

Figure 3: reaction schemes showing phenol–quinone-type tautomerism in several fused aromatic systems

fit into the general picture described by us.

It is interesting to note that both the shift of the keto–enol tautomeric equilibrium of phenols toward the more stable structure, for example,

(the nuclei of nonbenzenoid structure are marked with a cross; possible resonance equilibria are sharply shifted toward structures with a smaller number of nonbenzenoid nuclei), as well as the lowering of the oxidation–reduction potential of polynuclear quinones—in other words, the relative chemical inertness of these quinones—apparently also fall within the scope of application of the criterion described.

Compounds whose structural formulas contain more than four nonbenzenoid nuclei are so unstable that attempts to synthesize them have until recently been unsuccessful. Here one may envisage the appearance of structures for which the radical state is the principal one.

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