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## FOREWORD

THIS volume contains all but four of the papers which were submitted for presentation at the Third Conference on Carbon. Two of the papers were divided to give appropriate credit to those whose work is discussed. It is with a great deal of pride that this volume is presented to the reader. This is the second volume of the series; the first one contains papers presented at the first two Conferences. While the previous volume was published by the University of Buffalo, with the financial support of a number of industrial organizations, the present one is being published by the Pergamon Press Incorporated and it is to this publishing house that thanks are due for satisfying all our wishes with regard to the publication of this book. The cooperation of all of the authors in the preparation of this volume is greatly appreciated.

The Third Conference on Carbon was co-sponsored by the University of Buffalo, the National Science Foundation and the U.S. Office of Naval Research and was held at the University of Buffalo on June 17-21, 1957. The Steering Committee was composed of Messrs. E. N. Adams, H. Brooks, G. J. Dienes, S. Mrozowski (chairman) and J. Platt; in addition to those named above, Messrs. G. R. Hennig, C. R. Kinney, M. L. Studebaker, J. R. Tinklepaugh and P. L. Walker cooperated on the Program Committee. Thanks are due to each of these people, to the co-sponsoring institutions (in particular to Mr. J. H. McMillen of the National Science Foundation and Mr. F. B. Isakson of the Office of Naval Research) and to all the others whose enthusiastic cooperation and support have helped in making the Conference a success. There can be no doubt that the biennial Carbon Conferences have become well established. At the Third Conference, a Carbon Committee was elected, which later has been considerably expanded, the purpose of which is to keep in contact people interested in the field of carbons by continuing the biennial and/or organizing other conferences if necessary, by continuing the publication of the Proceedings and by any other means considered beneficial for this cause. A complete list of the membership of the Carbon Committee is given on the reverse page.

S. MROZOWSKI  
M. L. STUDEBAKER  
P. L. WALKER

Buffalo, New York  
*April* 1958

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PART I

**SYMPOSIUM**

FROM BENZENE TO GRAPHITE AND TO DIAMOND



# ON SOME ELECTRONIC PROPERTIES OF LARGE AROMATIC SYSTEMS

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(Manuscript received October 4, 1957)

After a brief indication of the possibilities of the molecular orbital method in the field of the electronic properties of large aromatic systems, the author considers in more detail some of these properties as a function of the size and the shape of the system. Whenever possible the study is extrapolated to the infinite layer of graphite. The electronic properties considered are in particular: resonance energy including the extension-compression correction; distribution of bond orders and free valences, especially in connexion with the chemical reactivity of the systems; the distribution of mobile electrical charges which is shown, on the basis of recent S.C.F. calculations, to be probably uniform (contrary to results by Pritchard and Sumner which are criticized). The interrelation between different electronic indices (free valence, singlet-triplet transition, electron affinity) is examined, and, in connexion with a recent paper by Matsen, a procedure is shown by which the role played by these different indices in the reactivity of the hydrocarbons towards free radicals can be differentiated. The possible correlation between electrical conductivity of hydrocarbons and their singlet-triplet excitation energy, postulated by Northrup and Simpson, is examined and it is shown that it fails for a number of hydrocarbons, recently studied by Inokuchi. In connexion with recent new experimental results of Akamatu on the diamagnetic anisotropy of the acenes, it is shown that a slight refinement in the classical calculations further improves the agreement between the theoretical and experimental values of the anisotropy in these compounds.

“From benzene to graphite”, and I would add “through carbons”, is a wonderful title for a symposium, but it is a long way too. Our first approximation will be to consider single planes of condensed benzene rings, the approximation being justified by the weakness of intermolecular, interlayer forces in this type of solid. Then, the different steps on the road from “benzene to graphite” are represented by the polynuclear aromatic hydrocarbons of increasing size and I guess that the idea underlying the choice of the subject of this symposium was that this increase in size should be accompanied by a regular evolution of the principal electronic properties of the hydrocarbons in such a way that they should approximate those of graphite as a limiting case.

Now, not only is the way from benzene to graphite a very long one, but the number of electronic properties of the intermediate compounds which may be taken into consideration is quite large too. From the quantum mechanical point of view, we possess,

as you all certainly know very well, two basic, fundamental methods of studying these properties: the valence bond method and the molecular orbital method. The first of these methods seems, however, rather inadequate for the study of compounds of the size which we want to consider here. As far as my information goes, the largest aromatic hydrocarbon that has ever been studied quantitatively by the valence bond method is naphthacene, which has only four fused benzene rings, and even already, for this molecule, some very important approximations and simplifications had to be adopted, such as grouping together all the formulas of the same degree of excitation, total omission of ionic formulas, etc.<sup>1</sup> So, we are left essentially with the molecular orbital method, but this, on the contrary, at least in its classical approximations, does not offer any fundamental difficulty for the study of even

<sup>1</sup> A. Pullman, *Ann. Chim.* **2**, 5 (1947); A. Pullman and B. Pullman, *Experientia* **2**, 1 (1946).

large aromatic systems. The essential difficulty is that of increasing labor, though other difficulties appear also when we want to use recent more refined versions of the MO method, like the self-consistent field MO method or that of configuration interaction. Practically, we shall limit ourselves mostly to the consideration of the results obtained by the classical approximations of the method, though on a number of occasions we shall refer to more refined results too.

But, even in the classical LCAO approximation, the possibilities that the method offers for the study of the electronic properties of large aromatic systems are extremely numerous and varied. I have summarized the different possibilities in Table I<sup>2</sup>.

A few comments may be useful in connexion with this table. The two basic quantities obtained by calculations are the energies of the individual molecular orbitals and the coefficients of the atomic orbitals comprising the different molecular orbitals.

The energies of the individual molecular orbitals enable us to obtain the total energy of the mobile electrons and this quantity leads directly to the well-known *resonance energy* which indicates the gain in stability due to the delocalization of the  $\pi$ -electrons. The applications of resonance energy are countless, particularly in problems concerned with chemical equilibrium (e.g. tautomerism, oxidation-reduction potentials of reversible systems, formation and stability of free radicals, acid and base strength etc.). Other important structural indices of conjugated molecules like *bond order* or *electrical charge* are also directly related to the total energy. The energies of the individual molecular orbitals enable us also to establish the values of the different electronic transitions and in the first place of the so-called

$N \rightarrow V$  and  $N \rightarrow T$  transitions: electronic transitions obtained by excitation of an electron from a bonding to an antibonding orbital. The classical molecular orbital method does not distinguish between singlet and triplet states, but a distinction may be obtained, on a semi-empirical ground, by using different values for the  $\beta$  or  $\gamma$  integrals for the two types of transitions.  $N \rightarrow V$  transitions are too large a subject to be considered here but we shall be interested to some extent in the  $N \rightarrow T$  transitions.

The energies of the *individual* molecular orbitals are also of interest, particularly those of the highest filled and the lowest empty orbitals, which are related respectively to the ionization potential and the reduction potential of hydrocarbons. They are even, in fact, particularly useful in the study of the evolution of the electronic properties related to them, in the series from benzene to graphite, because for graphite  $k_i$  or  $m_i$  tends to zero and extrapolations are thus easily possible<sup>3</sup>. From the experimental point of view, the ionization potentials of the aromatic hydrocarbons are, unfortunately, practically unknown, though we do know those of the extremes: 9.2 eV for benzene, 8.2 eV for naphthalene<sup>4</sup> and 4.39 eV for graphite (work function)<sup>5</sup>. The polarographic reduction potentials are much better known, mostly due to the recent work of Bergman<sup>6</sup>, who has measured them for a great number of large aromatic systems, containing up to 10 fused benzene rings. Matsen has shown (*vide infra*) that the reduction potentials are related to the electroaffinity of the hydrocarbons.

<sup>3</sup> See in particular F. A. Matsen, *J. Chem. Phys.* **24**, 602 (1956).

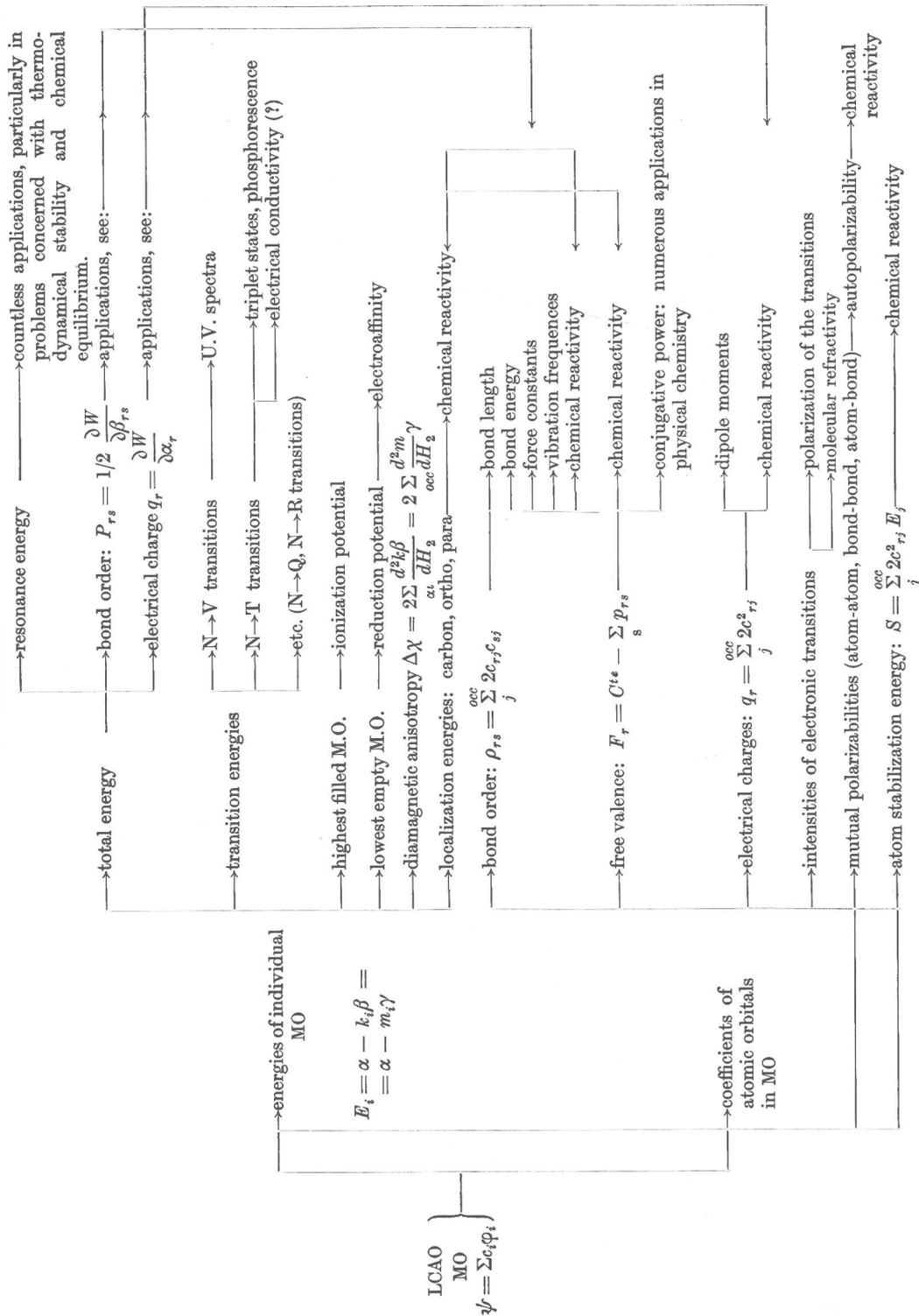
<sup>4</sup> K. Higasi, I. Omura and T. Tsuchiya, Tables of ionization potentials of molecules and radicals. Monographs of the Hokkaido University, Sapporo, Japan (1956).

<sup>5</sup> A. Braun and G. Busch, *Helv. Phys. Acta.* **20**, 33 (1947).

<sup>6</sup> I. Bergman, *Trans. Faraday Soc.* **50**, 829 (1954); **52**, 690 (1956).

<sup>2</sup> For a detailed description of the method and its applications, see e.g. B. Pullman and A. Pullman, *Les théories électroniques de la Chimie organique*, Masson Ed., Paris (1952); C. A. Coulson, *Valence*, Oxford (1952).

TABLE I



We have also indicated, as deriving from the energies of the molecular orbitals, the so-called *localization energies*. These quantities are very important in the theory of chemical reactions and measure the essential varying part of the activation energy for substitutions and additions occurring on highly conjugated systems<sup>7</sup>. In fact, they are not obtained directly from the same equations as those which lead to the energies of the molecular orbitals in the hydrocarbons, but from related secular determinants from which certain rows and columns have been struck out. We shall be particularly interested here in localization energies for radical substitution reactions.

The quantities which are related to the coefficients of the atomic orbitals composing the molecular orbitals: bond orders, free valences, electrical charges etc., are becoming to-day classical indices of electronic structures with numerous applications. Another property which depends on these coefficients is the intensity of electronic transitions; the dipole moment of the transition, which is a fundamental quantity concerned with the intensity, is related to the coefficients of the atomic orbitals in the molecular orbitals involved in the transition.

Finally, there is a certain number of indices like the mutual polarizabilities, introduced by Coulson and Longuet-Higgins<sup>8</sup> which depend both on the energies and coefficients.

Because of the shortage of time, we cannot consider here all the electronic properties. We do not need to do it either because some of them (electronic levels, diamagnetic susceptibility) will be dealt with by other speakers (Coulson, Pacault). We shall thus center our attention on certain of the properties: resonance energies, bond orders, elec-

<sup>7</sup> See <sup>2</sup>; R. D. Brown, *Quart. Rev.* **6**, 63 (1952); B. Pullman, *Cah. Phys.* **42**, 48 (1954); M. J. S. Dewar, *J. Amer. Chem. Soc.* **74**, 3355, 3357 (1952); see also <sup>13</sup>.

<sup>8</sup> C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. A* **191**, 39 (1947); *ibid.* **192**, 16 (1947); *ibid.* **193**, 447 (1948).

trical charges, free valences, these last indices in connexion with localization energies and problems of chemical reactivity. We shall also consider properties related to the highest filled and lowest empty orbitals, partly because they play a role in the same phenomena as those in which the preceding indices intervene and then also for their proper significance. In no way are we going to consider in detail the numerical values of these different indices in a great number of compounds. We shall try rather to stress some points of general interest.

To start with, let us consider two basic electronic indices: the resonance energies and bond orders.

#### I. RESONANCE ENERGY

When considering *resonance energies* and bond orders (which means immediately bond lengths) in aromatic hydrocarbons of increasing size and varying shape, mention must be made in the first place of a paper by Coulson and colleagues<sup>9</sup>, published a few years ago, where this problem has already been studied to some extent for a large number of structures intermediate between benzene and graphite. I cannot in this lecture give a detailed account of their results, but I shall just mention that they have been interested essentially in the *mean* values of the  $\pi$ -electron energy per carbon atom and the *mean* mobile bond order of the CC bonds (which means the mean C-C bond lengths). They have been able to show that the mean mobile binding energy per C atom increases regularly with increasing size of the conjugated system and that for a given number of C atoms, the greatest energy corresponds to the more condensed form (Fig. 1). They have shown also that, on the contrary, the mean bond order decreases regularly with increasing number of C atoms and that

<sup>9</sup> M. Bradburn, C. A. Coulson and G. S. Rushbrooke, *Proc. Roy. Soc., Edinb.* **62**, 336 (1948); C. A. Coulson and G. S. Rushbrooke, *ibid.* **63**, 350 (1948).

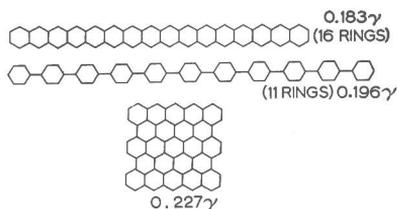


FIG. 1.

practically the mean C-C bond length is very close to that in graphite already for condensed structures of about 50 C atoms.

I should like in the first place to make some supplementary remarks on the problem of resonance energy.

Following the LCAO calculations, the resonance energy per C atom is equal to 0.33  $\beta$  in benzene and to 0.58  $\beta$  in graphite<sup>10</sup>. If we fix the empirical value of  $\beta$  on the basis of the experimental resonance energy of benzene (which is 5.94 kcal/carbon), we deduce  $\beta = 18$  kcal. We may use this value to predict the resonance energy per carbon in graphite. We obtain 10.44 kcal/g-atom. Now the most recent empirical evaluations are due to Barrow<sup>11</sup> who gives 10 kcal/g atom and to Colladay<sup>12</sup> who gives 11 kcal. The predicted value is thus in very good agreement with experiment so that this property probably evaluates quite regularly in the series with increasing size.

However, the situation is more complex than this, for two reasons:

(1) In the first place, the empirical value of  $\beta$  which is 18 kcal when based on benzene is less than this if larger hydrocarbons are considered. This can be seen in Table II which contains the most recent results of empirical evaluation of resonance energies<sup>13</sup>. Now the mean value of  $\beta$  is approximately 16.5 kcal which leads to a resonance energy per carbon in graphite of only 9.55 kcal.

TABLE II

Compound	Resonance energy (kcal)	Resonance energy ( $\beta$ )	$\beta =$ (kcal)
Benzene . . . . .	36.0	2.00	18
Naphthalene . . . . .	61.0	3.68	16.6
Anthracene . . . . .	83.5	5.31	15.7
Phenanthrene . . . . .	91.9	5.45	16.8
Naphthacene . . . . .	110.0	6.93	15.9
Benzanthracene . . . . .	111.6	7.10	15.7
Benzophenanthrene . . . . .	109.6	7.19	15.3
Chrysene . . . . .	116.5	7.19	16.1
Triphenylene . . . . .	117.7	7.27	16.2

The situation is, however, safe because if we had taken into account, as we should have done, the fact that the  $\beta$ 's should vary inside each molecule as a function of interatomic distance, we should then have obtained, for hydrocarbons other than benzene, resonance energies which, in  $\beta$  units, would be smaller than the ones quoted in the table. This would lead to an increase of the value of  $\beta$ . Thus the resonance energy of coronene obtained, with different  $\beta$ 's for different bonds, is only 9.48  $\beta$ <sup>14</sup> instead of 10.58  $\beta$  in the classical approximation. The difference is approximately 10% and corresponds just to what is needed in order to re-establish the previous situation.

(2) The second difficulty is related to what is called the *compression-extension correction*. The correction arises from the following fact<sup>15</sup>: the theoretical resonance energy,  $R_{\text{theor}}$ , of a molecule, is the difference in energy between a kekulé structure and the actual conjugated structure.

$$R_{\text{theor}} = R_{\text{Kek}} - R_{\text{Ac}}$$

where  $R_{\text{Kek}}$  refers to a reference state of non-interacting single and double C-C bonds with bond lengths equal to those in the conjugated molecules.

<sup>14</sup> Unpublished calculations by the author.

<sup>15</sup> C. A. Coulson, *Valence*, Oxford (1952); R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Amer. Chem. Soc.* **63**, 41 (1941); J. van Dranen, Thesis, Amsterdam (1951).

<sup>10</sup> G. W. Wheland, *J. Chem. Phys.* **2**, 474 (1934).

<sup>11</sup> G. M. Barrow, *J. Chem. Phys.* **22**, 953 (1954).

<sup>12</sup> G. S. Colladay, *J. Chem. Phys.* **22**, 2085 (1954).

<sup>13</sup> G. W. Wheland, *Resonance in Organic Chemistry*, John Wiley, New York (1955).

Now the empirical reference state contains single and double C-C bonds equal in length to 1.54 and 1.34 Å. It is the difference of energy between these two reference states which represents the compression-extension correction, that is, the energy needed to shorten the standard C-C bonds and lengthen the standard C=C bonds to the observed conjugated length.

So that:

$$R_{\text{theor}} = R_{\text{emp}} + C_{\text{comp-extn}}$$

The value of this correction has been calculated numerically in a number of simple hydrocarbons and the results show that the correction is approximately a constant and quite large fraction of  $R_{\text{theor}}$  of the mean order of 80%. This result, if extrapolated to graphite, would lead to a theoretical value of the extension-compression correction of the order of 80% of 10.44 kcal = 8.35 kcal/C atom.

Now, the experimental value of the correction has been evaluated for graphite by Colladay<sup>12</sup> and found to be equal to 8.5 kcal/g-atom. The agreement between the theoretical and the experimental value is thus excellent so that obviously in this field the extrapolations from compounds of limited size to graphite are very successful.

## II. BOND ORDERS AND FREE VALENCES

Let us now consider another important type of electronic characteristic of condensed aromatics—namely their bond order and the closely related indice of free valence. I have already quoted the work of Coulson and co-workers on the evolution of the *mean* value of bond order with increasing size of the aromatic hydrocarbons, the general phenomenon being a steady decrease of the bond order from the values 0.6667 in benzene to 0.5254 in graphite, corresponding to the

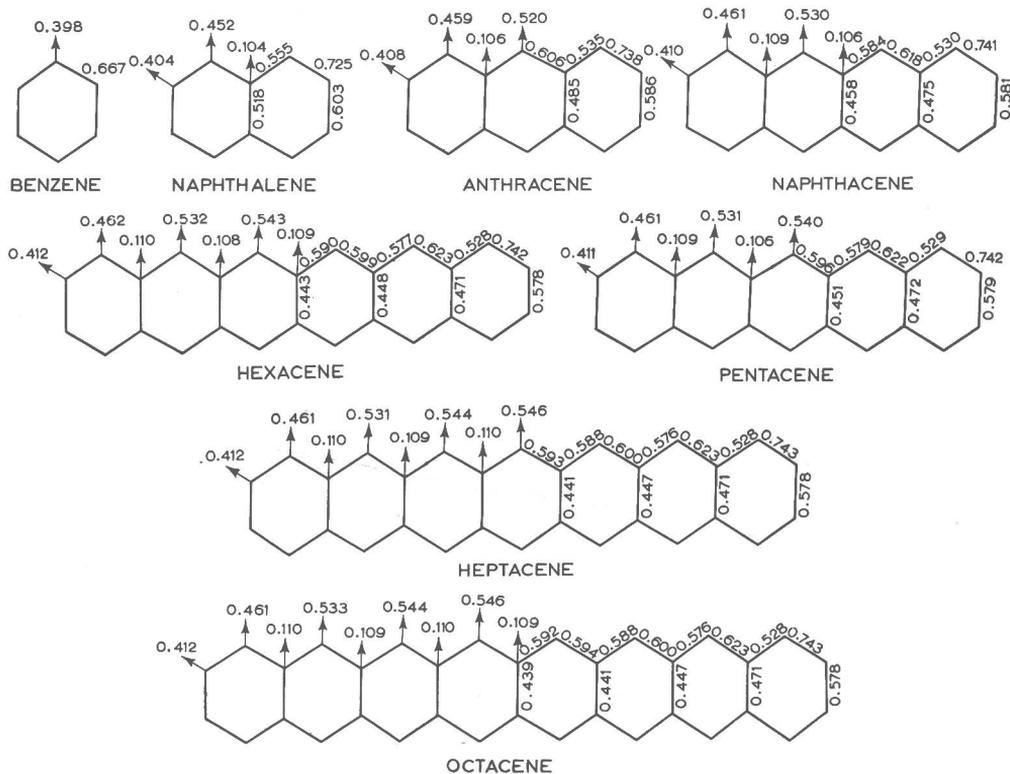


FIG. 2.