257. *The Structure of Aromatic Systems.*

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The meaning and use of the term aromaticity are clarified. The relative importance of the ground-state resonance energy, the chemical reactivity and, for the ions, the equilibrium free energy, in determining the aromaticity of various compounds is discussed. Neutral aromatic systems are aromatic by virtue of a low chemical reactivity: the aromatic ions are aromatic by virtue of a favourable equilibrium. The low enthalpy of the ground state does not account directly for the aromaticity of the benzenoid hydrocarbons or for that of the ions. Some known and unknown mesomeric ions are discussed, the perturbation method developed earlier being used.

THE term aromaticity has come to have two different meanings. The classical meaning is " having a chemistry like that of benzene ": its modern theoretical meaning is " having a low ground-state enthalpy." The two usages are distinct, as the following discussion shows, and attempts to correlate them have been only accidently successful.

Aromatic compounds were first clearly recognised by their lack of chemical reactivity.[1] Later, they were found experimentally to have an abnormally low ground-state enthalpy [2] and this was explained by Hückel [3] who showed, by the molecular-orbital method, that cyclic systems of $(4\gamma + 2)$ $p\pi$-electrons are characterised by a low π-electron energy (high resonance energy). It has become the practice to consider the resonance energy of the ground state in discussing known aromatic systems and in searching for new ones.[4,5] In this theoretical development, the original meaning of the term aromatic has been lost: the characteristic stability of the aromatic systems is not a *direct* result of the low enthalpy of the ground state. The primary requirement, in the classical sense of the term, is a low

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[1] See Robinson, *Tetrahedron*, 1958, **3**, 323.

[2] Wheland, " Resonance in Organic Chemistry," John Wiley and Sons, New York, 1955, pp. 75—149.

[3] Hückel, *Z. Physik*, 1931, **70**, 204; 1932, **76**, 628.

[4] *Inter al.*, Roberts, Streitwieser, and Regan, *J. Amer. Chem. Soc.*, 1952, **74**, 4579; Baker and McOmie, " Progress in Organic Chemistry," Butterworths Scientific Publications, London, 1955, Vol. III, p. 44.

[5] Craig, " The Kekulé Symposium," Butterworths Scientific Publications, London, 1959, p. 20.

chemical reactivity, and the resonance energy of the ground state is only accidentally connected with this property.* Whether it is possible to have aromatic systems with low ground-state resonance energy is not clear: what is clear is that aromaticity in its classical sense requires a low chemical reactivity.†

The situation has been further complicated by the so-called "aromatic ions," the cyclopentadienyl anion and the tropylium cation, which have the aromatic sextet. These ions have a low ground-state enthalpy, for the same reason as in the case of benzene, but this has led to their being grouped together with benzene, implicitly or explicitly, as aromatic systems. But these ions are chemically very reactive and far from "benzene-like." These ions owe their stability to a favourable free-energy difference between the neutral form and the ion, not to a low chemical reactivity. The similarity between the ions and the neutral hydrocarbons as far as their ground states are concerned has obscured the fundamental differences in the reasons for their stability. If these ions are to be called aromatic, it must be kept in mind that the basic reason for this aromaticity is different from that of the neutral hydrocarbons or, alternatively, that the word is not being used in its classical sense. In this paper, the former procedure is adopted: the neutral hydrocarbons are aromatic because they have a low chemical reactivity, and the ions are aromatic because they have a favourable free-energy difference compared with their neutral partners. From this point of view, we can discuss the aromaticity of the neutral hydrocarbons and the ions in a quantitative fashion.

Neutral Hydrocarbons.—We are interested in the routes by which these compounds (A) decompose. The usual one is:

$$A + X \xrightarrow{\text{Irreversibly}} \text{Products} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where X is an atom or a small molecule. As we now have reasonably reliable theoretical methods of examining this process, we can measure aromaticity quantitatively. We will avoid the complication of steric effects by restricting the discussion largely to 5-, 6-, and 7-membered ring compounds.

The aromaticity of benzene is directly and simply attributable to its high localisation energy (see Table).‡ We can now understand the reduced aromaticity of naphthalene and azulene in a quantitative fashion by comparing the localisation energies of the most reactive positions. It is a serious difficulty of the resonance-energy criterion that one cannot say from it in any simple way whether naphthalene will be more, or less, aromatic than benzene: if one uses the resonance energy per electron, naphthalene should be more aromatic than benzene. The much discussed pentalene is an instructive example where concentration on the ground-state resonance energy has confused the issue. Its resonance energy (and its number of carbon atoms) is in fact intermediate between those of benzene and naphthalene, yet all attempts to isolate it have failed. The nucleophilic reactivity of the most reactive position is high (ε^- low), compared with, say, that of naphthalene, so the chemical-reactivity criterion suggests that it will be very reactive towards nucleophiles and not aromatic. Its free-radical localisation energy is low, but higher than that of heptafulvene, fulvalene, and fulvene, all of which can be obtained, at least in dilute

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* The connection is that the lower the energy of the ground state, the larger the activation energy, if the energy of the transition state is constant. But there seems no reason why, in the general case, the energy of the transition state should be even roughly constant. When the ground-state resonance energy can be successfully used in predicting aromaticity [the $4\gamma + 2$) rule of the benzenoid hydrocarbons] such a relation must occur; but it has no theoretical foundation and may break down without warning.

† This is also true for the inorganic compounds [5] and ferrocene,[6] but we have little information on their chemical reactivity, so it is still necessary to rely on the ground-state resonance energy here.

‡ Or by any other equivalent measure of chemical reactivity. It could be argued that a ground-state property is adequate for the estimation of the chemical reactivity. This may be true, but it would not be the resonance energy. We use the simple Hückel molecular-orbital technique as in previous papers: the symbols are defined there.[7]

[6] Moffitt, *J. Amer. Chem. Soc.*, 1954, **76**, 3386.

solution. It has been remarked earlier [7] that the isolable dibenzopentalene [8] has a reduced nucleophilic reactivity. Fulvene is a further example. Its resonance energy is quite high, but it has none of the properties of an aromatic system and this is explained immediately by its high nucleophilic and radical reactivity: the molecule is sensitive to bases and polymerises easily.[9] Benzofulvene and dibenzofulvene seem to be rather more stable [10] and they have a reduced nucleophilic reactivity. Fulvalene is stable to acids (ε^+ high), but is sensitive to bases (ε^- low) and polymerises easily ($\varepsilon^\bullet$ low): the molecule is not aromatic.[11] Heptafulvene is likewise not aromatic, since it is reactive towards acids (ε^+ low) and radical ($\varepsilon^\bullet$ low).

Resonance energies (R.E.) and localisation energies (ε) of neutral hydrocarbons.

	R.E.	R.E./π	ε^+	ε^-	$\varepsilon^\bullet$
Benzene	2·0	0·34	2·54	2·54	2·54
Naphthalene	3·68	0·37	2·30	2·30	2·30
Anthracene	5·31	0·38	2·01	2·01	2·01
Biphenylene	4·51	0·38	2·35	2·35	2·35
Azulene	3·36	0·34	1·93	1·93	2·24
Pentalene	2·46	0·31	2·03	1·54	1·96
Fulvene	1·46	0·24	2·00	1·01	1·61
Heptafulvene †	1·99	0·25	1·01	1·90	1·45
Benzofulvene ‡	3·33	0·33	—	1·16	—
Dibenzofulvene ‡	5·22	0·37	—	1·32	—
Fulvalene	2·80	0·28	1·99	1·36	1·68

* All in units of β. ε^+, ε^-, and $\varepsilon^\bullet$ are for attack by electrophiles, nucleophiles, and radicals respectively at the most reactive position. R.E./π is the resonance energy per π electron. The values are taken from Pullman and Pullman, " Les Théories Electronique de la Chimie Organique," Masson et Cie, Paris, 1952, and from Coulson and Daudel, " Dictionary of Values of Molecular Constants," The Mathematical Institute, Oxford, and the Centre de Chimie Théoretique de France, Paris.

† These localisation energies refer to the extracyclic carbon atom. The localisation energies of the other positions are 1·94, 2·12, and 2·27 for the 1-, 2-, and 3-position (Coulson and Daudel's numbering).

‡ ε^+ and $\varepsilon^\bullet$ of these hydrocarbons have not been reported. It is assumed that the extracyclic carbon atom will be the point of nucleophilic attack.

The chemical-reactivity criterion thus corresponds in a roughly quantitative manner to the organic chemist's idea of aromaticity: it shows clearly that we cannot expect aromaticity in any of the molecules below the line in the Table. It is, of course, not possible to fix this line with certainty, but it is reasonable to suppose that, if all the localisation energies are greater than about 2·0β, we may expect aromaticity. Since all the carbon atoms in an alternant hydrocarbon have the same values of the localisation energies for all three types of attack, these hydrocarbons will be stable to all reagents, or to none. In the non-alternant hydrocarbons, this equality of the localisation energies no longer exists and one finds mixed reactivity: a hydrocarbon may be quite stable to one type of reagent but very sensitive to another.[11]

The process depicted by equation (2) is an interesting but largely unexplored possibility. It represents an absolute or internal instability in that a single isolated molecule will

$$A \xrightarrow{\text{Irreversibly}} \text{Products} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

decompose spontaneously. Longuet-Higgins [12] has suggested that this is the reason for the instability of pentalene, decomposition occurring during a vibration to give two

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[7] Peters, *J.*, 1958, 1028.

[8] Blood and Linstead, *J.*, 1952, 2255, 2263.

[9] Thiec and Wieman, *Bull. Soc. chim. France*, 1956, 177.

[10] Courtot, *Ann. Chim.* (*France*), 1915, **4**, 202, 218.

[11] Doering, " The Kekulé Symposium," Butterworths Scientific Publications, London, 1959, p. 35; *Angew. Chem.*, 1956, **68**, 661.

[12] Longuet-Higgins, " The Kekulé Symposium," Butterworths Scientific Publications, London, 1959, p. 17.

molecules of acetylene and one of butadiyne. Reversible reactions also occur with the more reactive aromatic compounds,[13] but these also follow the localisation energies.

Hydrocarbon Ions.—Here we are not concerned primarily with the chemical reactivity but with an equilibrium:

$$\mathrm{A} + \mathrm{X} \rightleftharpoons \mathrm{B} \qquad (3)$$

since this is defined as measuring the aromaticity. X is a small molecule, such as water. Thus, the cyclopentadienyl anion will pick up a proton reversibly and the tropylium cation will react reversibly with water. The free energy change in these equilibria (ΔG) is given by

$$\Delta G = a + b\varepsilon^{\pm} \qquad (4)$$

where $\varepsilon^{\pm}$ is the localisation energy, the change in the π-electron energy when two or zero electrons are localised on a particular carbon atom; a and b are constants. It is assumed here that the only difference between the different hydrocarbons is in π-electron energy; changes in σ-bond energy, solvation energy, and entropy are constant or vary linearly with the π-electron energy changes. This localisation energy is identical with that used in studies of chemical reactivity, apart from the size of a parameter. Now this localisation energy can be obtained by solution of the secular equations, but it can also be obtained very easily by a minor modification of the perturbation method used earlier [7] for neutral systems. It turns out that the cross-linked cyclic anion [$(4\gamma + 1)$ carbon atoms, $(4\gamma + 2)$ $p\pi$ electrons] and the corresponding cation [$(4\gamma + 3)$ carbon atoms, $(4\gamma + 2)$ $p\pi$ electrons] have localisation energies $(\varepsilon^{\pm})$* given by:

$$\varepsilon^{\pm} = (E_{\pi}^{\text{ion}} - E_{\pi}^{\text{neutral}}) = 2\beta\left[1 + \frac{1}{n}\sum_{\text{cross}}^{\text{links}}\left\{\frac{\sin[(r+s)\pi/2]}{\sin[(r+s)\pi/2n]} \pm \frac{\cos[(r-s)\pi/2]}{\cos[(r-s)\pi/2n]}\right\}\right] \qquad (5)$$

where n is the number of carbon atoms in the ion, the cross-link is formed between atoms r and s, the plus sign is for the anion, and the minus sign is for the cation. The localisation energy of the un-cross-linked cyclic anion or cation is always 2β. The resulting values for some simple anions and cations are shown in the formulæ. The numbers in parentheses are those obtained by solution of the secular equations,[14] and the success of the perturbation method in reproducing these is clear.

These values reveal interesting trends. It must be borne in mind that these figures represent the π-electron energy required to produce an isolated carbanion (or cation) so that the molecule will protonate at the position where the numeral is smallest, and the smaller it is the lower will be the acidity of the neutral hydrocarbon. Fusion of one or two benzene rings to cyclopentadiene, giving indene and fluorene, reduces the acidity, as is well known.[15] The pK_a's of indene and fluorene are estimated [16] to be 21 and 25 respectively and that of cyclopentadiene is predicted to be 17, which agrees roughly with the fact that it forms the anion in t-butyl alcohol but not in ethanol.[15] Further linear addition of benzene rings reduces the acidity further. Angular addition, however, has a more complicated result: angular fusion to fluorene increases the acidity; to indene, it reduces the ease of protonation of the α-carbon atom, but increases that of the β-carbon atom until in compound (I) the latter position is the most readily protonated. Many of these compounds are known, including (I), but their acidity has not been examined and little is

* The sign convention is that used earlier: [7] the localisation energies are negative quantities, a positive number multiplied by β. In applying equation (5), the molecule must be numbered as a cycle, starting with the atom adjacent to, and finishing with, the localised atom. This ensures that the numbering is the same in the ion as in the localised molecule.

[13] Gold and Tye, *J.*, 1952, 2184; Plattner, Heilbronner, and Weber, *Helv. Chim. Acta*, 1952, **35**, 1036; Heilbronner and Simonetta, *ibid.*, p. 1049; Mackor, Hofstra, and van der Waals, *Trans. Faraday Soc.*, 1958, **54**, 66, 186.

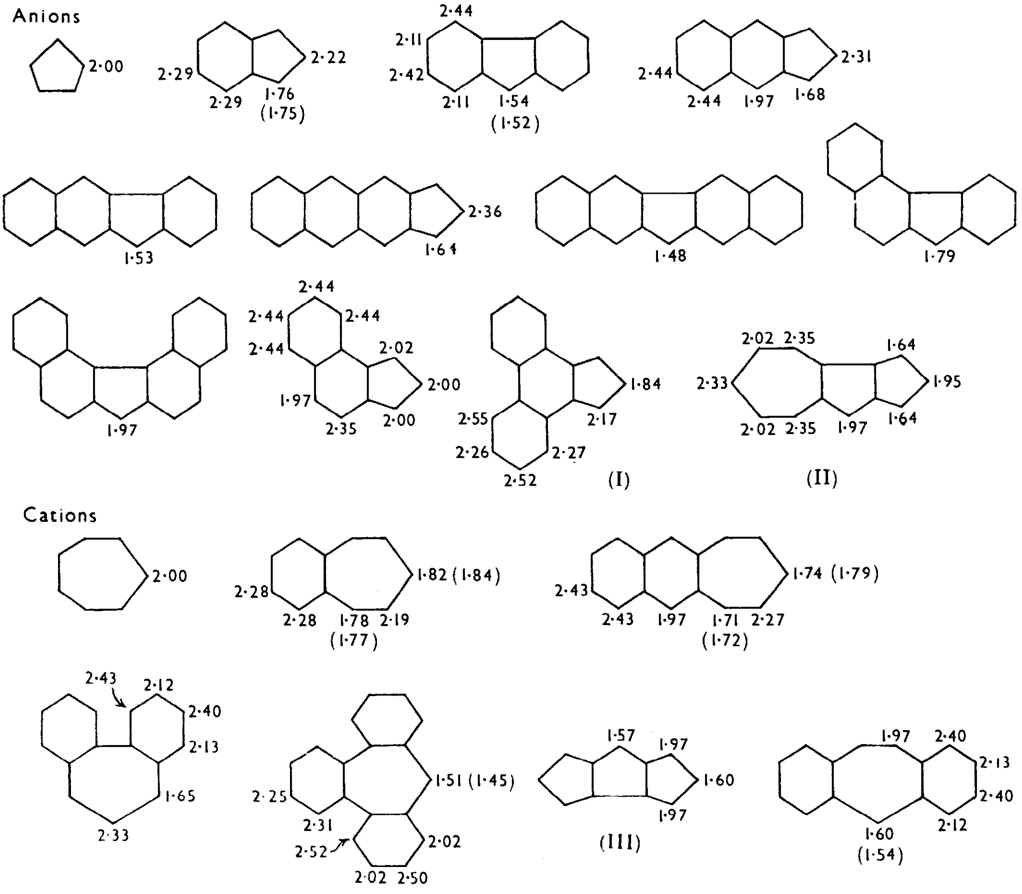
[14] Meuche, Strauss, and Heilbronner, *Helv. Chim. Acta*, 1958, **41**, 57, 414.

[15] Ziegler, Kühlhorn, and Hafner, *Chem. Ber.*, 1956, **89**, 434.

[16] Conant and Wheland, *J. Amer. Chem. Soc.*, 1932, **54**, 1212; McEwan, *ibid.*, 1936, **58**, 1124.

known about their chemistry. Compound (II) is of a novel type: the figures show that there is no reason to expect strong acidity for the protonated forms.

There is some systematic evidence available for the cations and successful use of the localisation energies has been demonstrated by Meuche, Strauss, and Heilbronner.[14]



Localisation energies (units of β).

Since the perturbation figures reproduce the secular-equation figures quite well, the former can be used with great ease on new ions. There is a concealed difficulty here, however, in that the ion may enjoy a favourable free energy, but the neutral form may decompose rapidly. This would probably be true of compound (III). For the ion to be isolable, therefore, conversion into the neutral form should be slow. Little is known about the rates of reaction of such ions, but if localisation energies are applicable here also, then a high localisation energy will serve the double purpose of giving a favourable free-energy balance and a low chemical reactivity. The localisation energies certainly predict the correct position of attack for indenyl and fluorenyl anions.

There is some qualitative information about the influence of inductive substituents on anions of this kind. The purely inductive ammonium ion substituent[17] stabilises the cyclopentadienyl anion markedly, and neutral, electron-withdrawing substituents do the

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[17] Spooncer, *Diss. Abs.*, 1956, **16**, 458.

same.[22] * The action of such substituents being represented by a change in the coulomb integral of the carbon atom to which they are attached, the change in the localisation energy ($\delta\varepsilon$) is given by:

$$\delta\varepsilon = (\delta E^{\text{ion}} - \delta E^{\text{neutral}}) = (q_r^{\text{ion}} - q_r^{\text{neutral}})k\beta$$

where q_r is the charge on carbon atom r. In the cyclopentadienyl anion, the charge is 1·2 and in cyclopentadiene it is 1·0. Since k is positive for electron-withdrawing substituents, these will increase the localisation energy and stabilise the anion. Essentially the same situation arises in the fluorenyl anion, which is known [23] to be stabilised by the electron-withdrawing nitro-substituent.

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* The phosphonium ion also stabilises the cyclopentadienyl anion,[18] but this is a less clear-cut case than the ammonium ion since the *d*-orbitals may intervene in the stabilisation [19] as they do for fluorenyl.[20] One would expect the ylides from indene and fluorene to be less stable than those from cyclopentadiene [21] since the former hydrocarbons are weaker acids.

[18] Ramirez and Levy, *J. Amer. Chem. Soc.*, 1957, **79**, 67.

[19] Kosower and Ramsey, *J. Amer. Chem. Soc.*, 1959, **81**, 857.

[20] Ingold and Jessop, *J.*, 1930, 713.

[21] Lloyd and Sneezum, *Tetrahedron*, 1958, **3**, 336.

[22] Linn and Sharkey, *J. Amer. Chem. Soc.*, 1957, **79**, 4970; Peters, *J.*, 1959, 1757.

[23] Hughes and Kuriyan, *J.*, 1935, 1609; Novelli and de Varela, *Ciencia e invest.* (*Buenos Aires*), 1948, **4**, 82; *Chem. Abs.*, 1948, **42**, 5912.