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On the Number of Aromatic Sextets in a Benzenoid Hydrocarbon[1]

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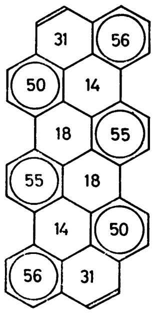
Synopsis. For a benzenoid hydrocarbon with a single sextet formula, the number of aromatic sextets in it is very close to the number of sextet-type resonance interactions per Kekulé structure.

An aromatic sextet is a benzene ring which can be isolated from a benzenoid hydrocarbon on condition that, if there is some residual π-system, at least, one Kekulé structure can be written for it.[2,3] One or more aromatic sextets may be further isolated from the residual π-system. Clar has long stressed the importance of writing the structural formula of a benzenoid hydrocarbon with a maximum of aromatic sextets.[2,3] These aromatic sextets, isolated from each other, have been considered as the only origin of aromatic stabilization. The structural formula thus defined is termed a sextet formula. Recently, Herndon showed,[4,5] with the aid of a simple resonance theory, that the Dewar-type resonance energy[6—8] of a benzenoid hydrocarbon is primarily associated with sextet-type resonance interactions, *i.e.*, resonance interactions related by a permutation of three double bonds within individual six-membered rings (sextets) of the structure.

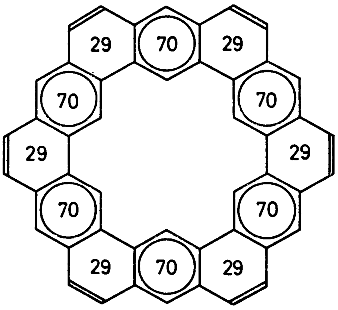
In this article, I would like to point out that Clar's way of enumerating the sextets which give rise to aromaticity in the hydrocarbon is essentially the same as Herndon's, except for polyacenes and their derivatives. A somewhat complicated situation for the polyacenes with plural sextet formulas has already been examined in a separate paper.[9] The present discussion will, hence, be limited to the benzenoid hydrocarbons for which only one sextet formula can be written.

Let N_C be the number of aromatic sextets in Clar's sextet formula of a benzenoid hydrocarbon,[2,3] and let N_H be the number of sextet-type resonance interactions, divided by the number of possible Kekulé structures. According to Herndon,[4,5] the sextet-type resonance interactions are enumerated by the excision of each six-membered ring of the structure in turn, with a summation of the number of possible Kekulé structures for the residual π-systems. The present problem is thus reduced to a comparison of the two quantities, N_C and N_H. For this purpose, N_H-values are calculated for almost all the relevant hydrocarbons imaginable.

Those adopted first are 52 benzenoid hydrocarbons from benzene (C_6H_6) to tetrabenzoheptacene ($C_{42}H_{22}$), which are all cited in Ref. 2. For example, 157 Kekulé structures can be written for dipyreno-(1'.3': 10.2); (1''.3'': 5.7)-pyrene (I). The number of sextet-type resonance interactions assigned to each six-membered ring is entered in the ring concerned. The aromatic sextets specified in the sextet formula are therein marked with circles. Note that the number of the resonance interactions of this type is comparatively large at these aromatic sextets. This aspect of the aromatic sextets is common to all the hydrocarbons studied. The N_H-value is then calculated to be 5.707 for I, while the sextet formula is composed of six aromatic sextets and two fixed double bonds. Note, again, that the N_C-value of this compound agrees with the N_H-value within an accuracy of 5.1 percent of the latter value. The N_C-to-N_H value is 1.051. The analogous ratios for common hydrocarbons are as follows: phenanthrene, 1.000; pyrene, 1.000; dibenz[*a,h*]anthracene, 1.000; dibenz[*a,j*]anthracene, 1.000; triphenylene, 1.039; picene, 0.975; benzo[*d*]pyrene, 1.031; benzo[*ghi*]perylene, 1.000; peropyrene, 0.964; violanthrene, 0.988; ovalene, 1.000.



(I)



(II)

As may be suggested from these figures, the N_C-to-N_H ratios for the 52 benzenoid hydrocarbons were found to be densely distributed around 1.000. Interestingly, the number of aromatic sextets in the sextet formula nicely approximates the number of sextet-type resonance interactions per Kekulé structure, namely,

$$0.937 < N_C/N_H < 1.075. \qquad (1)$$

It is noteworthy that, despite a variety of molecular geometries, the ratio for any compound with a single sextet formula is close to unity. It is possible to include in this relation two other hydrocarbons, coronene and circobiphenyl, which are classified as superaromatic species.[3] Clar's sextet formulas for these two compounds can be written in two ways, although they are far from polyacene derivatives. Among the hydrocarbons investigated, coronene has the minimum ratio of 0.9375, while hexa-*peri*-benzocoronene has the maximum ratio of 1.0749.

It goes without saying that the same features of the aromatic sextets are encountered in other kinds of benzenoid hydrocarbons which have not been referred to by Clar. In 1970, [12]coronaphene (II) was first prepared by Jenny *et al.*[10] 200 Kekulé structures can be written for this compound. The N_C-to-N_H ratio for II is calculated to be 1.010 with the use of $N_C=6$ and $N_H=5.940$. The numerical difference between the two ways of enumerating the sextets is only one percent of either value.

In conclusion, we can safely say that, as long as a maximum number of aromatic sextets are fixed in a benzenoid hydrocarbon, Clar's simple aromatic sextet theory[2,3] can predict the number of sextet-type resonance interactions in it; hence, it gives a rough estimate of the Dewar-type resonance energy.[7,8] Remember that the Dewar-type resonance energy, which has been the best aromaticity index available, is roughly proportional to N_H.[4,5] In this sense, Clar's concept of an aromatic sextet is evidently a simplified version of Herndon's theory of aromaticity.[4,5]

This resemblance between them reminds us of the correlation between Pauling's and Coulson's definitions of the bond order.[11] When only a single Kekulé structure is possible for a conjugated hydrocarbon, the double bonds in it indicate the correct locations where Coulson's bond order reaches its maximum values. In the same manner, we might say that, when a benzenoid hydrocarbon has a single sextet formula, the aromatic sextets in it specify the locations where the resonance energy is densely distributed.

References

1) Presented at the Symposium on Molecular Structures, Tokyo, Japan, October 1974.

2) E. Clar, "Polycyclic Hydrocarbons," Vols. I and II, Academic Press, New York, N. Y. (1964).

3) E. Clar, "The Aromatic Sextet," Wiley, London (1972).

4) W. C. Herndon, *J. Am. Chem. Soc.*, **95**, 2404 (1973).

5) W. C. Herndon and M. L. Ellzey, Jr., *J. Am. Chem. Soc.*, **96**, 6631 (1974).

6) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685 (1965).

7) M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc.*, **91**, 789 (1969).

8) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y. (1969), Chapter 5.

9) J. Aihara, *Bull. Chem. Soc. Jpn.*, **48**, 3637 (1975).

10) W. Jenny, P. Baumgartner, and R. Paioni, in "Proceedings of the International Symposium on the Nonbenzenoid Aromatic Compounds," Sendai, Japan (1970), pp. 183—186.

11) W. B. Smith, "Molecular Orbital Methods in Organic Chemistry: HMO and PMO," Marcel Dekker, New York, N. Y. (1974), Chapter 3.