

## ON THE ROLE OF KEKULE VALENCE STRUCTURES \*

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**Abstract** - Individual Kekule valence structures of conjugated hydrocarbons are examined and the relative role of the opposing "aromatic" and "antiaromatic" contributions scrutinized. The work follows our previously proposed classification of conjugated systems based on the enumeration of  $4n+2$  and  $4n$  conjugated circuits. Here we would like to draw the attention to molecular formulas obtained by a partial superposition of selected Kekule valence structures and the situations in which they may play the dominant role and represent molecules adequately.

### INTRODUCTION

Kekule's idea of a hexagonal structure for benzene in 1865 offered important new insights to structural chemistry and laid the basis for the ensuing development of both theoretical organic chemistry and aromatic chemistry. One of the difficulties of quantitative description of a molecule with valence bond structures, such as Kekule valence structures, is a lack of information on the relative role that different structures have. It has been often assumed that all Kekule valence structures have a same weight. For example, Pauling's bond order concept (1) implies a same weight for all Kekule valence structures. However, there have been indications that some valence structures may be more important than others. As early as 1927, Fries (2) proposed an empirical rule suggesting that a better model is one in which the Kekule valence structure with the largest number of rings described by Kekule benzene valence structures has the dominant role. In the case of naphthalene, this means that valence structure 1 has greater weight than structure 2:

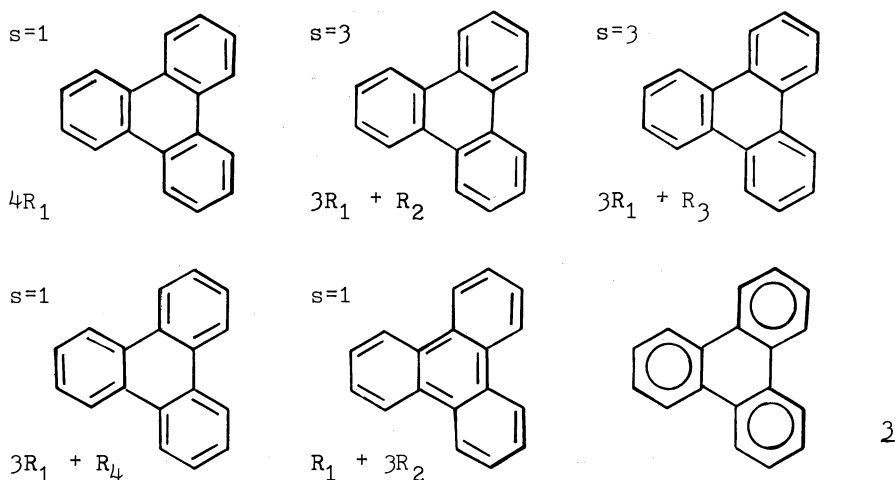


A comparison between the simple Hückel MO calculation for naphthalene and the more advanced SCF MO calculation showed that the difference in the predicted bond lengths indeed can be interpreted as the valence structure 1 having a greater weight (3). If one enumerates conjugated circuits for each of the shown Kekule valence structures of naphthalene, one finds a different count:  $2R_1$  in case of structure 1 and  $R_1 + R_2$  in case of valence structure 2. Here,  $R_1$  and  $R_2$  represent conjugated circuits involving a single ring and two rings respectively, or more precisely, rings of size  $4n+2$  with  $n=1$  and  $n=2$ , respectively. Since  $R_1$  makes considerably greater contribution to molecular resonance energy, it follows that the former structure is associated with a greater weight. The weight is determined by the partial contribution an individual valence structure makes towards molecular resonance energy, which can be calculated once numerical parameters for  $R_n$  contributions have been selected (4). Enumeration of conjugated circuits of different size within the collection of Kekule valence formulas represents an alternative partitioning of the molecular conjugation "content". The advantage of such viewing is that the components are all either  $4n+2$  or  $4n$  circuits to which one can ascribe usual "aromatic" and "antiaromatic" characteristics and thus delineate the role of the competing factors.

\* This work is dedicated to the memory of Franz Sondheimer

## CLAR'S STRUCTURAL FORMULAS

An alternative approach is to differentiate among the valence structures from the beginning and seek for consequences of such an assumption. Consider triphenylene, whose five symmetry non-equivalent Kekule valence structures are shown below (with their symmetry weights  $s$ ):



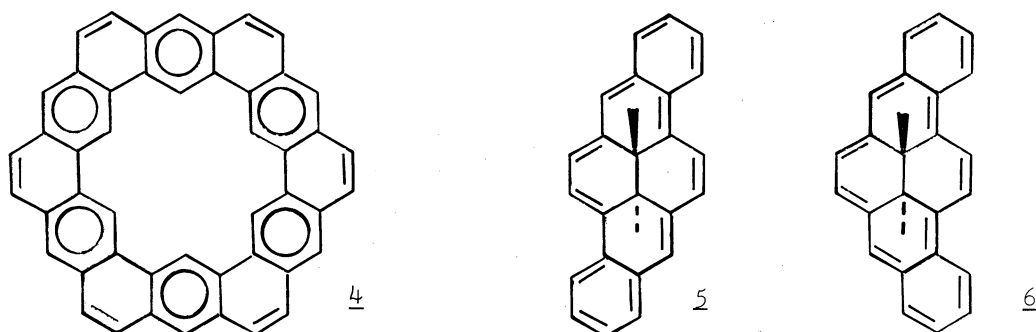
One may ignore the last Kekule valence structure arguing on the ground of chemical intuition, as Clar did (5), that such a structure cannot make a significant contribution, and proceed to view the molecule as a superposition of eight, rather than all nine Kekule valence structures. One then arrives at a structural formula 3 proposed by Clar and justified by Robertson and Clar, who advanced the notion of pi-electron sextets as a possible model for conjugated hydrocarbons. It appears that many have initially dismissed such a viewpoint, on grounds of an apparent arbitrariness--some Kekule structures are included but other valence structures are excluded in arriving at the final superposition which represents a molecule. Yet, the basic assumption that neglects some structures, is just as arbitrary or legal as the assumption that all valence structures make the same contribution. Although the truth may be somewhere in between, it seems to us that it is important to see how far one can proceed with the simple mathematical logic, based on binary weights of 0 and 1 (i.e., included and excluded structures). The final arbiter is the experiment and it is conceivable that Nature operates, or is better approximated, by binary weights, rather than by "uniform" superposition approximation. The concept of pi-electron sextet and the concept of conjugated circuits, together with the well known Hückel  $4n+2$  Rule, represent for the theory of valence probably the most significant evolution and advance since the early pioneering work of Kekule on the structure of benzene -- at least at the conceptual level.

## ILLUSTRATIONS OF SELECTED VALENCE STRUCTURES

Our primary effort here is to delineate the possible roles of different Kekule valence structures. This effort seems timely, in view of more recent evidence pointing to the predominant role of some Kekule valence structures, and in view of revived interest in Valence Bond calculations (6). Let me quote a few illustrations from the literature.

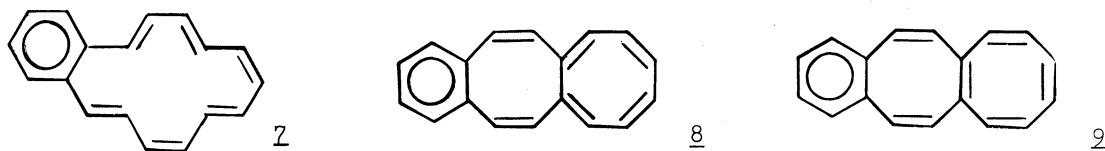
"The synthesis and properties of kekulene 4 were reported ... (7); however studies of the system now suggest similarities to phenanthrene. Only every other ring is aromatic, according to the bond lengths deduced from crystallographic studies, so that kekulene should not be regarded as a dodecabenzannulene system but more as a type of extended stilbene system." (8)

"Experimental evidence (9) has been presented that, other things being equal, the possibility, or not, of equivalent "Kekule" structures can have a profound effect on the diatropicity (aromaticity) of an annulene" (10). The compounds discussed are shown as structures 5 and 6, the one at left having equivalent Kekule valence structures while the one on right does not have such structures.



There are numerous illustrations of a similar situation when rings of different size are fused. An illustration of two fused  $4n+2$  rings is provided by benzo(14)annulene which has been described by the non-symmetrical structure 7 shown below on the basis of its NMR spectroscopy (11). This suggests that the induced diamagnetic ring-current in the (14)-annulene ring is weakened considerably by the annelation of the benzene ring.

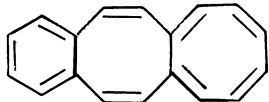
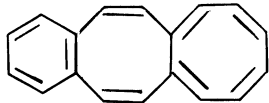
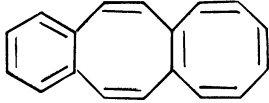
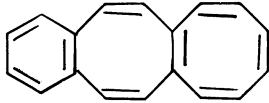
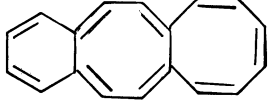
Stimulation for this work came, in particular, from the very recent work of Vogel and coworkers (12) on benz(c)octalene and dibenz(c,j)octalene. They found that benz(c)octalene exists in solution as an equilibrium mixture of the double bond isomers 8 and 9, whereas in its crystalline state only isomer 8 is present.



#### BENZ(C)OCTALENE

The first question we will consider is the differentiation between various Kekule valence structures. If we assume that one valence structure is preponderant, the question that follows is: What structural factors prevail in determining this particular structure over many others? We need some adequate and sufficiently general structural vocabulary to replace current imprecise, often vague, descriptions such as "similarity to phenanthrene," or "extended stilbene system." Clearly, as these attempts already show, one needs some auxiliary components to describe the system. We hope to demonstrate that "conjugated circuits" is a more suitable concept which is sufficiently general and has played a fundamental role in characterization of conjugated hydrocarbons. We will outline the basic notions by considering benz(c)octalene. In Table 1 we show the five Kekule valence structures for the molecule and the associated decomposition of the conjugation content in contributions from  $4n+2$  conjugated circuits, represented by symbol  $R_n$ , and from presence of  $4n$  conjugated circuits, represented by symbol  $Q_n$ . For instance, the first Kekule valence structure has, at one end, a benzene ring (i.e., six-membered ring with three alternating carbon-carbon double bonds) which makes the contribution  $R_1$ . The eight-membered ring at the other end represents formally cyclo-octatetraene and makes contribution  $Q_2$ . Finally, in addition to these two local conjugated circuits, each comprising a single ring, the molecular periphery also represents a conjugated circuit (i.e., the circuit in which there is formal alternation of carbon-carbon single and carbon-carbon double bonds). By counting pi-electrons involved we see that this is a  $R_4$  ring, i.e., a  $4n+2$  ring with  $n=4$ . In order to proceed, one needs some information on the relative magnitude of various  $R_n$  and  $Q_n$  contributions. In previous work and in comparison with available theoretical calculations we deduced plausible numerical values for the parameters involved (13). However, important structural deductions are possible already from an information on the relative magnitudes of these parameters. Rather than using a particular numerical magnitudes we will here only recognize that  $R_n$  are all positive and that they decrease in magnitude

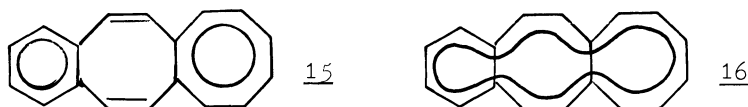
TABLE 1. Decomposition of Kekule valence structures of benzo(c)octalene into conjugated circuits

Kekule structure	Conjugated circuits
<u>10</u> 	$R_1 + R_4 + Q_2 > 0$
<u>11</u> 	$R_1 + R_3 + Q_2 > 0$
<u>12</u> 	$R_1 + Q_2 + Q_3 \sim 0$
<u>13</u> 	$R_1 + 2 Q_2 \sim 0$
<u>14</u> 	$R_3 + Q_2 + Q_3 < 0$

with  $n$ . On the other hand  $Q_n$  are negative and, in absolute magnitude, also decrease with  $n$ . Furthermore, we will assume that absolute values of  $R_n$  and  $Q_n$  alternate, with  $Q_n$  being larger than  $R_n$  for the same  $n$ . These assumptions are consistent with the numerical values selected for the contributions of rings of  $4n+2$  and  $4n$  size to molecular resonance energy by many authors. By not specifying the absolute scale, but merely the relative trends our conclusions are likely to have a general validity and will not be influenced by subsequent revisions of  $R_n$  and  $Q_n$  values. By considering the relative contributions of various  $R_n$  and  $Q_n$  components to the individual Kekule valence structures, one sees that structures 10 and 11 make a positive contribution, because  $R_1$ , the largest positive term, overcompensates the negative contribution of  $Q_2$ . The valence structures 12 and 13 make a little net contribution because the positive and the negative terms mostly cancel each other. However structure 14 clearly is destabilizing, making appreciable negative contribution to molecular resonance energy. Superposition of structures 10 and 11 gives structure 8 of Vogel and coworkers, while superposition of valence structures 12 and 13 gives structure 9 of Vogel et al. Hence we see that the additional stability of valence isomer 8 originates from its predominant "aromatic" character. The fact that this valence structure is the one eventually appearing in the crystalline state may well be due to its intrinsic stability, rather than to external (packing) factors. However, it would be premature to make definite deductions from considerations of an isolated case. All that we may conclude here is that the proposed model does not contradict experimental data.

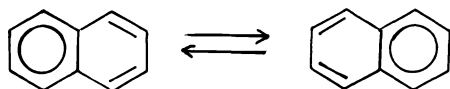
## ON PARTIAL SUPERPOSITION OF VALENCE STRUCTURES

Structures like 8 and 9, in which we locally identify a benzene ring with an isolated sextet of pi-electrons, have been suggested by Clar as a recognition of a particular stability that such clusterings effect on a molecule. Thus, according to Clar, one should view triphenylene as locally delocalized, the central ring being "empty", i.e., not involved in the overall conjugation, the other rings being similar to benzene ring. Application of Clar's approach to conjugated hydrocarbons generally proceeds without difficulty in recognizing valence structures that ought to be dismissed. But in some instances, a question may be posed as to why one stops halfway and uses structures 8 and 9 as Vogel et al., have done but not their superposition 15 or the superposition of all Kekule valence structures 16:



Structures 8 and 9 have been suggested by the experimental data, hence they are empirical in origin. They imply that partial superposition of valence structures may be a legitimate procedure and that a structure like 15 or 16 may lack reality. We would like to clarify the question of partial superposition of valence structures and demonstrate that indeed, if one wants to generalize the notion of pi-electron sextets of Clar and Robinson to non-benzenoid systems, one ought to stop with structures 8 and 9 (in case of benz(c)octalene), rather than attempting to combine these in a structure like 15 or 16.

Clar's structural formulas, with "isolated sextets," can be described informally as a "desire" of conjugated molecules to build closed shells of sextets. Consequently, exocyclic bonds to a sextet are, from our point of view, essentially single CC bonds. In some cases, like naphthalene, we may end with several equivalent Clar-type formulas



The molecule has to be viewed as a combination of corresponding structures resulting in "migration" of the sextet. Alternatively, we could speak of 10-tet, the next building block of various  $(4n+2)$ -tets, sextet being the case of  $n=1$ . Clearly, sextets dominate any higher  $(4n+2)$ -tets and determine localized delocalization. But in nonbenzenoid systems the tendency of  $4n$  contributions is toward localization and we lack the driving force for inducement of superposition of the components. As a result we obtain valence structures shown in Fig. 1

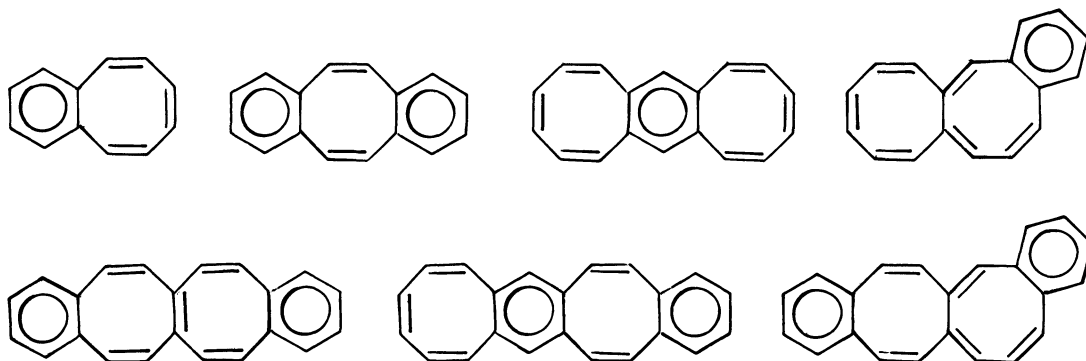
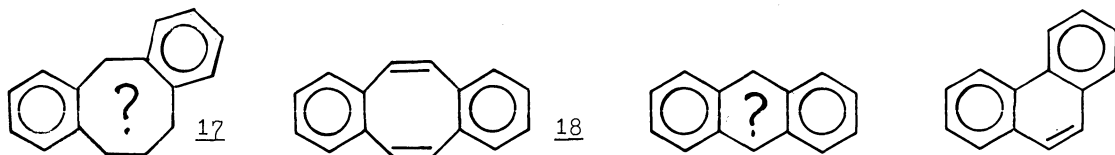


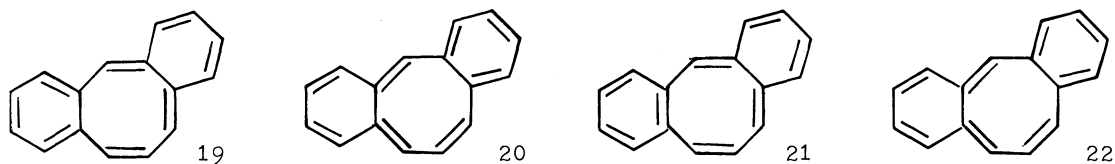
Fig. 1. Valence Structures for a selection of nonbenzenoid hydrocarbons

## ON NON-EXISTENT STRUCTURES

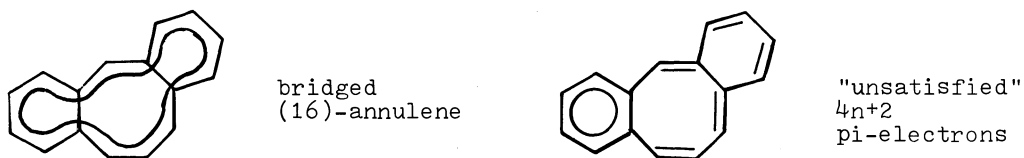
Examination of various nonbenzenoid systems shows interesting differences. Some compounds, like benz(c)octalene and dibenz(c,j)octalene lead to Clar's structures in which all benzene rings appear as isolated sextets. On the other hand, there are structures for which one cannot write down Clar's type formula in which all benzene rings would be represented as sextets. If one tries to force such a description, one ends with carbon atoms which cannot be paired unless "excited" valence structures are introduced. An example is 17 in contrast to 18:



Anthracene and phenanthrene represent the corresponding analogues in the case of benzenoid systems. But, as argued by Clar, the dilemma of anthracene can be resolved by the concept of migrating sextets, i.e., superposition of corresponding valence structures having isolated sextets. Presence of  $4n$  conjugated circuits hinders superposition of structures, as can be seen by examining the Kekule valence structures 19 - 22 :



Observe that superposition of valence structures 19 and 20, which make the major contribution to the molecular resonance energy, does not lead to a benzene sextet, but a bridged  $4n$  annulene. Thus such superposition is "destimulated" by its antiaromatic character. On the other hand, a superposition of the valence structures 19 and 21 produces only one benzene sextet with  $4n+2$  pi-electrons forced into a localized arrangement



Thus, neither superposition is compatible with the tendency of  $4n+2$  conjugated circuits toward an overall delocalization and aromaticity and the opposing tendency of  $4n$  conjugated circuits to form localized distribution of CC double bonds consistent with their antiaromatic character. No such contradicting tendencies are found in nonbenzenoid hydrocarbons of Fig. 1, which provide an illustration of molecules with well-defined "aromatic" parts and equally well-defined "antiaromatic" segments -- just as is the case with the formulas of Vogel et al., for benzo(c)octalene and dibenz(c,j)octalene. We can summarize the situation concerning a partial superposition of valence structures by proposing the following rule: "Structures for which one cannot write down a reasonable Clar's structural formula cannot exist." The rule is somewhat analogous to one suggested by Clar, indicating that structures for which one cannot write down Kekule valence structure cannot exist. A number of "non-existent" structures are depicted in Fig. 2. It is always risky to foretell the future but the main thrust of the proposed rule is not to totally disregard the eventual possibility of some such structure that would contradict the rule, but rather to point to the existence of such a class of compounds which is anticipated as elusive to synthetic efforts. In fact, Clar and Mackay (14) already attempted the synthesis of 1:14, 3:4, 7:8, 10:11 - tetrabenzoperopyrene, a "forbidden" structure according to Clar's postulate, having no Kekule valence structure. This should not be viewed as an effort to contradict the postulate, but as an effort to learn more about these currently "non-existent" structures. Our suggestion on non-existent structures, so to speak of a second kind, i.e., having Kekule valence structures, yet expected not to exist, is primarily

offered in order to help to systemize the present experience with nonbenzenoid conjugated hydrocarbons in particular and possibly to stimulate some future work.

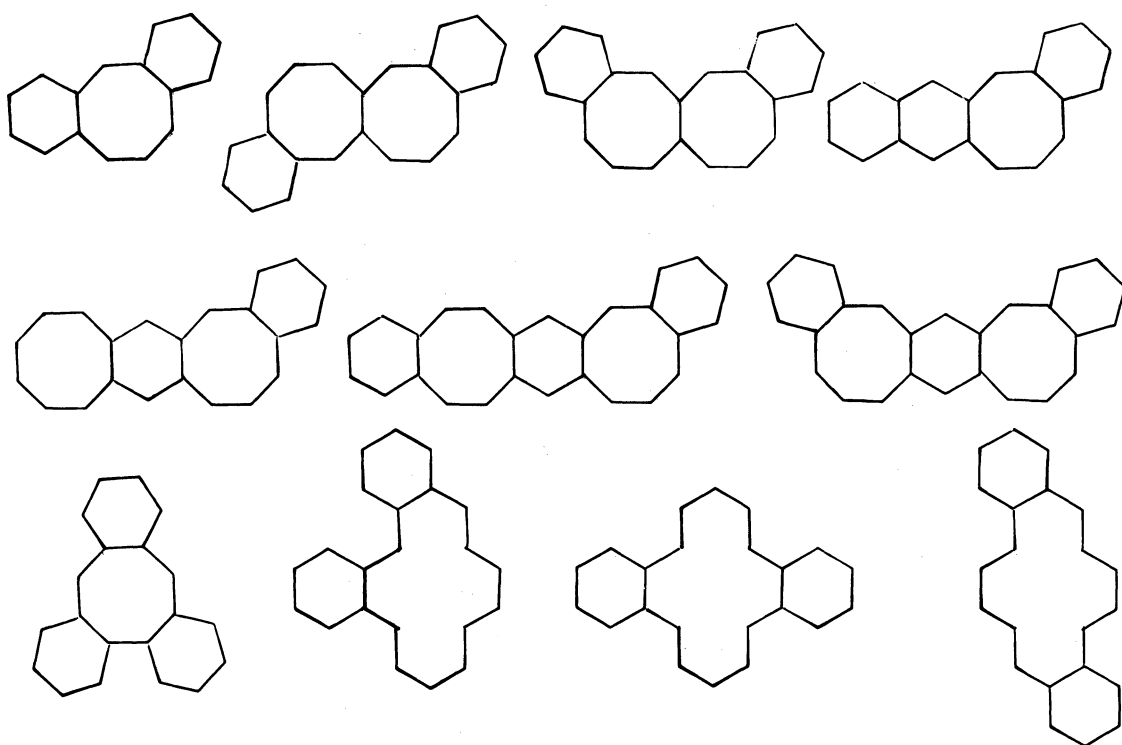
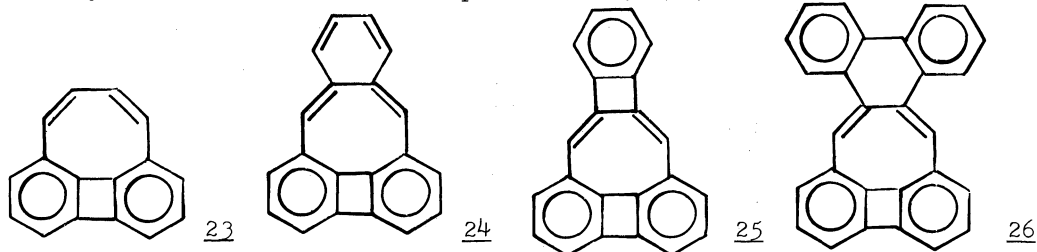


Fig. 2. Structures for which one cannot write down reasonable Clar's type valence formula

The opposing tendencies of  $4n+2$  and  $4n$  contributions are clearly discernible in benzocyclooctatetraene as discussed by Herndon. In such a structure, "...the delocalization of electrons that results in antiaromatic destabilization is mitigated by distortion to a more stable structure, and this is accompanied by a change to more evenly distributed bond orders in the aromatic ring. The delocalized annulene would have alternating bonds in the aromatic moiety, while normal alternating single and double bonds in the annulene ring give rise to more uniform bonds in the benzene portion."(15)

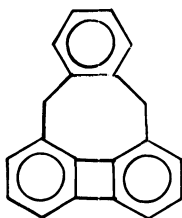
#### NETWORKS INVOLVING BIPHENYLENE

We have avoided in this report to include nonbenzenoid systems having a four-membered ring, such as biphenylene and related structures. The unusual strain in such systems may mask other regularities that can possibly be associated with  $4n$ -type rings. However, a number of nonbenzenoid unusual pi-networks involving four- and eight-membered rings have been synthesized and studied, by Wilcox and coworkers in particular (16)-(18):



The underlying basic structure is cycloocta(def)biphenylene 23 described as a structure that "... appears to hover at the borderline between olefinic,

aromatic and antiaromatic classification." (18) Structures 25 and 26 support a Clar's structural formula, but the same is not true for structure 24. Hence, 24 may evade synthetic attempts, and in its properties should dramatically differ from superficially related 26. The calculations of Wilcox and Grantham (18) are in harmony with our expectations. "Interestingly, -- concluded Wilcox and Grantham -- in contrast to the net paramagnetic ring currents predicted for 24 and 23, hydrocarbons 25 and 26 are predicted to exhibit net diamagnetic ring currents in spite of the presence of multiple fused 4n-membered rings. A measurement of diamagnetic susceptibility exaltation is therefore predicted to give a negative value for 24 and 23 and a positive value for 25 and 26, even though the protons on the eight-membered rings of all compounds are predicted to show substantial upfield shift in the NMR." Our analysis fully agrees with the above calculations on ring currents. Moreover, while ring current calculations give little insight into the cause for the observed results, and are used in an *a posteriori* fashion, we could anticipate different behavior of structures *a priori*. The localized bonds in 24 deprive the molecule to succeed in gaining an additional benzenoid ring. Thus, existence of 24, if synthesized, would not contradict the proposed rule, but it would imply that the additional ring is not benzene-like at all, just a polyene addition. Our rule restricts presence of a compound represented by a Clar-like formula



The calculation of Wilcox and Grantham support this prediction.

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