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TETRAHEDRON

Heteroaromaticity. 14. The Conjugation Energies and Electronic Structures of Nonbenzenoid Polycyclic Aromatic Systems[1]

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Abstract: The conjugation energies of a range of polycyclic nonbenzenoid hydrocarbons and aza derivatives have been calculated from their molecular dimensions. In most cases the values obtained reflect the number of π-electrons as is observed for their polybenzenoid counterparts and in contrast to that predicted by the Hückel 4n+2 rule and observed for monocyclic annulenes. The relative contributions of the various Kekulé forms for individual molecules do not support the explanation for this observation provided by the Platt hypothesis.

INTRODUCTION

The Hückel $(4n+2)$ rule is widely used as a basis for predicting aromaticity and is well illustrated by Figure 1 which is based upon data for annulenes presented in a previous paper.[2] In contrast to a similar theoretically derived relationship[3] the present data indicate that even $4n\pi$ systems possess some modest conjugation energy, and further that the conjugation energy increases with the size of the annulene. Hückel's rule is not strictly

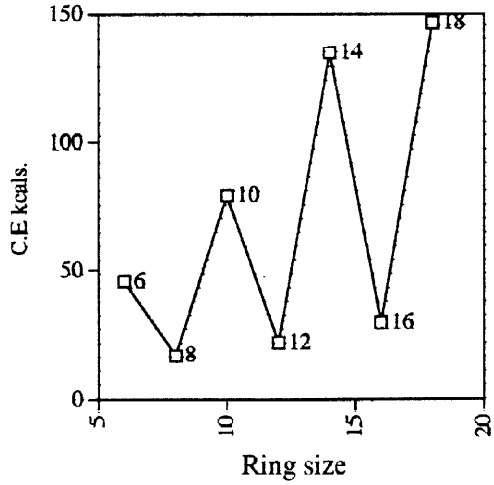

Figure 1. Resonance energies of annulenes as a function of ring size.

applicable to polycyclic systems and in the case of polybenzenoid compounds resonance energies increase steadily with increasing numbers of π-electrons.[4] Various attempts have been made to rationalise the situation. Platt suggested[5] that such polycyclic molecules should be regarded as peripheral polyenes, to which the Hückel rule applied, with intraannular cross links which could be regarded as small perturbations. Clar[6,7] pointed out that condensed benzenoid hydrocarbons often prefer to behave as a combination of aromatic subunits. This conclusion, which was originally based upon spectroscopic behaviour, has received support from both

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theoretical[8,9] considerations and from analysis of diamagnetic susceptibility enhancements.[10] More recently Randic[11] has proposed the concept of *conjugated circuits* which are defined as aromatic or antiaromatic depending upon whether or not they obey the Hückel rule. Systems having both $(4n+2)$ and $4n$ conjugated circuits are classed as intermediate showing partial aromatic character. So far most discussions in this area have either concentrated on polybenzenoid systems for which some experimental data are available, or in the case of non-benzenoid polycycles on the results of theoretical calculations.[12] Many of the latter group of compounds have been the subject of X-ray crystallographic structure determinations and are thus appropriate subjects for the direct calculation of conjugation energies and the respective contributions of their various Kekulé forms, using a procedure presented[2,13] in preceding papers.

The procedure entails calculating the energy, E_B, required to convert each bond of the conjugated system into the single or double bond of the corresponding Kekulé structure using the equation;

$$E_B = F\,(R_s \text{ or } R_d - R)^2\,(a - bR) \text{ kcal. mole}^{-1}$$

where R (Å) is the length of the bond.Summation of the E_B values for the Kekulé structure gives its conjugation energy, E. The lengths of the appropriate single (R_s) and double bonds (R_d) together with the values of the constants F, a and b are listed in Table 1.

Table 1. Constants used for bond energy calculations

Bond	R_s (Å)	R_d (Å)	F	a ($x10^3 Nm^{-1}$)	b($x10^4$ Pa)
CC	1.533	1.337	85.94	44.39	26.02
CN	1.474	1.274	62.19	43.18	25.73

A separate energy, E_i, has to be calculated for each Kekulé form and the energies for the n forms then summed to give the overall conjugation energy, CE, according to the following expression:

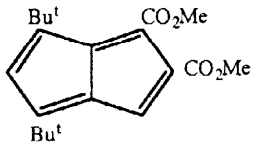
$$CE = n\,E_i\left(1/E_i \div \sum_{i=1}^{i=n} 1/E_i\right)$$

The summation coefficients provide the relative contributions of the individual Kekulé forms. Apart from its aforementioned application to annulenes, this method has been shown to reproduce satisfactorily independently determined conjugation energies for a wide range of azines and azoles. It is important to emphasise at this juncture that while the energies obtained are normally identical to the thermodynamic resonance energies for six-membered rings and other strain free systems this does not apply to most of the ring systems to be considered in this paper. Fortunately this will have little effect on the relative contributions of Kekulé forms for a specific molecule and are likely to be about the same for many of the compounds to be compared.

RESULTS AND DISCUSSION

As indicated in the introduction the aim of this paper is to present the conjugation energies that can be deduced for those non-benzenoid aromatic and heteroaromatic compounds for which appropriate molecular dimensions are available and, where applicable, assess their electronic structures in the light of the various proposals mentioned above.

8π and 10π Systems. The dimensions reported[14] for the substituted pentalene **1** indicate that the ring system comprises almost alternate single and double bonds and lead to a conjugation energy of 17.5 kcal. mole^{-1}. In contrast a much higher conjugation energy of 44.9 kcal. mole^{-1} is obtained for the diazapentalene[15] **2** whose four strongly electron donating substituents clearly offset the effects of inherent bond alternation.



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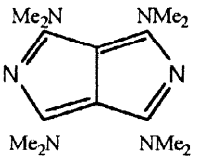

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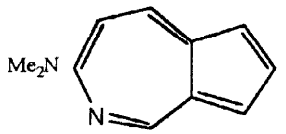
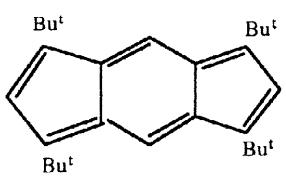


3

A conjugation energy of 81.4 kcal. mole^{-1} can be calculated for 1,3-bis(carboxymethyl)azulene.[16] Azulene itself gives rise to disordered crystals but dimensions derived[17] from its 1,3,5-trinitrobenzene complex provide a closely similar value of 78.8 kcal. mole^{-1}. The 6-dimethylamino-5-azaazulene[18] **3** provides a conjugation energy of 73.6 kcal. mole^{-1}. These values are much higher than the 47.1 kcal. mole^{-1} deduced[4] for azulene from thermochemical measurements, which also contain ring strain contributions, but are in keeping with values deduced from M.O. calculations. It is also notable that azulene displays a virtually identical diamagnetic susceptibility enhancement to that of naphthalene[4] with a resonance energy of 80.3 kcal. mole^{-1}.

12π-Systems. Although a conjugation energy of only 22 kcal. mole^{-1} was obtained[2] for a 1,7-methano[12]-



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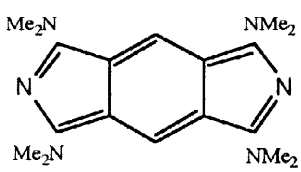

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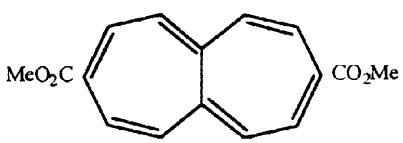

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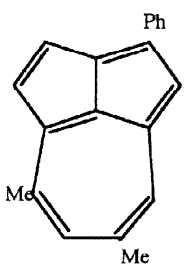
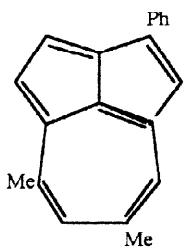
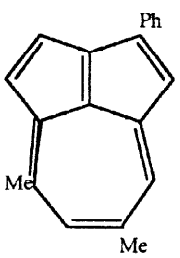


7a



7b

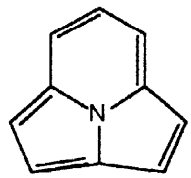


7c

annulene, respective values of 90.7 and 80.2 kcal. mole^{-1} can be calculated for the *s-i*ndacene **4**[19] and the diaza derivative **5**.[20] Even the heptalene **6**[21] manages a conjugation energy of 78.6 kcal. mole^{-1} despite existing in the form of two boat shaped rings. The tricyclic compound **7**[22] may be regarded as the azulene equivalent of acenaphthylene but its conjugation energy of 102.1 kcal. mole^{-1} represents a much larger increase over azulene compared to the 2.5 kcal. increase in proceeding from naphthalene to acenaphthylene.[4] Inspection of the three possible Kekulé contributors **7a,7b,7c,** with weightings of 26, 27 and 47 % respectively shows that an azulene circuit is present in all three while only the two minor contributors have a pentalene circuit in addition.

The cyclazine **8**[23], with a 10π electron periphery, poses an interesting question as to the role of the central nitrogen. Analysis of the dimensions of its trinitrobenzene complex indicates that the nitrogen is responsible for

16.7 of the total 87.3 kcal. mole^{-1} conjugation energy.



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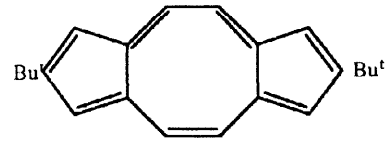
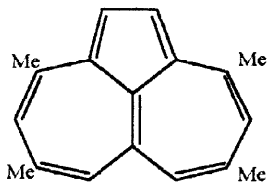
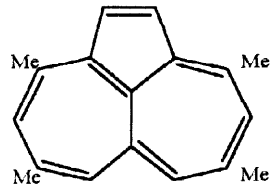


9

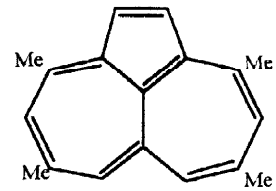
*14π-Systems.*The dicyclopenta[*a,e*]cyclooctene[24] **9** has a conjugation energy of 110.6 kcal. mole^{-1} comparable to the 111.5 kcal. mole^{-1} for anthracene. The tricyclic ring system **10**,[25] with a conjugation energy of 100.6 kcal. mole^{-1}, could be viewed as a a bridged heptalene, but the substantial difference (*vide supra* the comments on **7**) in conjugation energies points to an alternative rationale. This is provided by a consideration of the relative magnitudes of the three Kekulé contributors, **10a-c**, which shows that the azulene circuit is present in all three whereas the heptalene circuit is only present in the two minor ones, **10b**, **10c**.



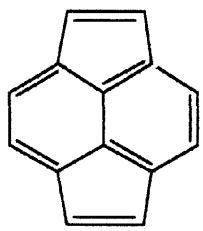
10a(50%)



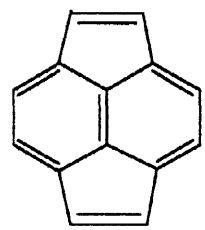
10b(25.3%)



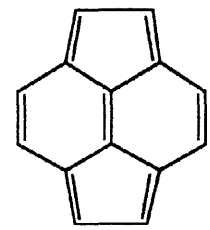
10c(24.7%)



11a(50.4%)

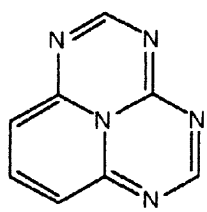


11b(38.3%)



11c(11.3%)Ä

The magnitude of the conjugation energy, 106.6 kcal. mole^{-1}, in pyracylene[26] **11a-c** points to considerable interaction between the naphthylene and ethylene subunits though this is only apparent in the case of the minor Kekulé contributor **11c**. As elsewhere in this paper only one of the possible mirror images of a particular Kekulé form is depicted although all have been taken into account in assessing relative weightings.



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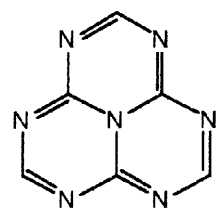
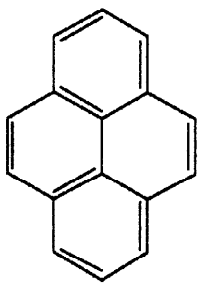


13

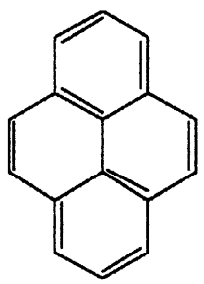
The dimensions of the tricyclic polyazines **12**[27] and **13**[28] lead to conjugation energies of 100 and 92.1 kcal. mole^{-1} respectively. As in the case of the cyclazine **8**, analysis of the contributions of the molecular fragments to

the overall conjugation energies indicates that the central nitrogens are responsible for *ca.* 7.5-9.5 kcals. of the total.

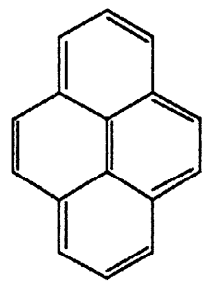
*16π-Systems.*Many of the initial discussions regarding the application of the Hückel rule to polycyclic benzenoid hydrocarbons have centred upon pyrene **14** with a resonance energy[4] of 141.4 kcal. mole^{-1}. From its dimensions[29] it is possible to derive the indicated relative contributions of the possible Kekulé forms. Of particular note is the fact that the preferred form **14c** according to the Platt hypothesis is not a major contributor.



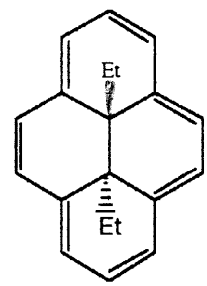
14a(36%)



14b(36%)



14c(28%)



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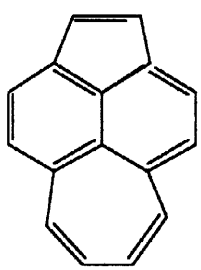
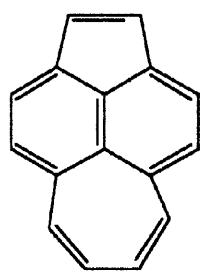
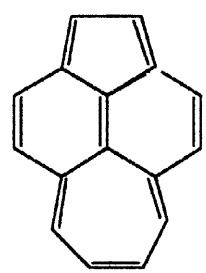


16a(51.4%)

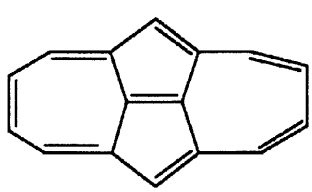


16b(34%)

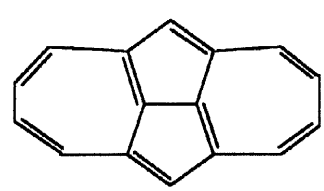


16c(14.6%)

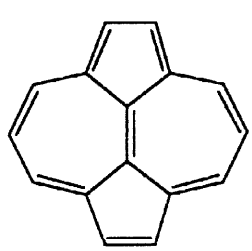
The contribution of the "additional" double bond is witnessed by the calculated conjugation energy of 106.5 kcal. mole^{-1} for the dihydropyrene **15**[30]. A somewhat larger contribution of structures **16b,16c,** having an outer



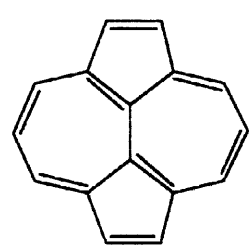
17a(52.2%)



17b(47.8%)

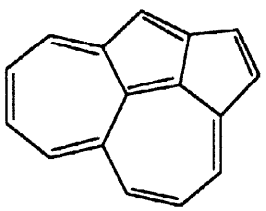


18a(56.1%)

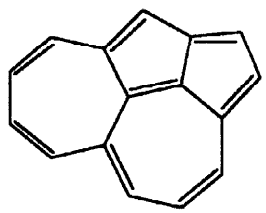


18b(43.9%)

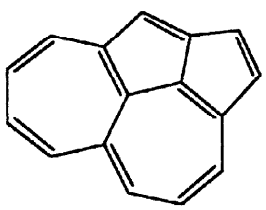
14π-electron periphery can be discerned in the case of acepleiadylene **16a-c**[31], which has a rather lower conjugation energy of 110.1 kcal. mole^{-1}. A resonance energy of 134.1 has been deduced[32] from heats of hydrogenation studies. The proportion of contributors having an outer 14π-electron periphery is appreciably



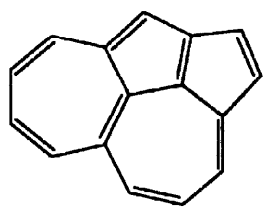
19a(28.2%)



19b(18.7%)

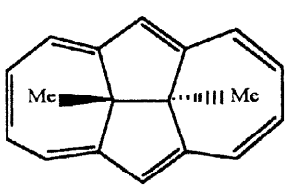


19c(18.2%)



19d(34.9%)

larger in the cases of **17a,b**,[33] **18a,b**[34] and **19a-d**.[34] Again comparison of the conjugation energy of 136.3 kcal. mole^{-1} calculated for **17a,b** with those of 112.6 and 106.4 kcal. mole^{-1} for **20**[36] and **21**[37] respectively, having peripheries with the same geometric disposition, further emphasises the substantial contribution of the "additional" double bond. The isomeric ring system in **22**[38] is appreciably nonplanar and not surprisingly it has a much lower conjugation energy of 74.8 kcal. mole^{-1}. Hückel molecular orbital calculations have been used to



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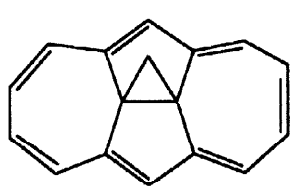

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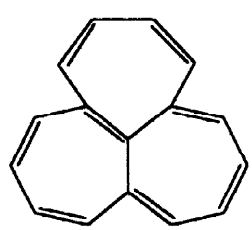

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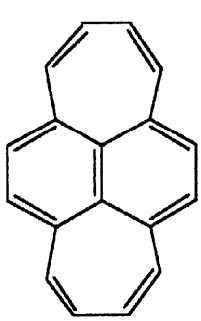
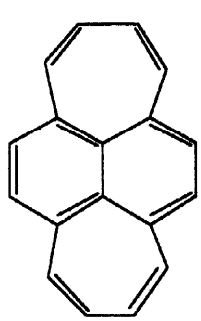
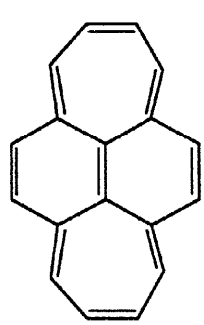


23a(33.3%)



23b(56%)



23c(10.7%)

predict[39] conjugation energies of 6.03ß, 6.05ß and 5.95ß for **17**, **18** and **19** respectively, which compare fairly well with the values of 136.3, 155.7 and 126.1 derived here. It may be noted that ^{1}H NMR spectra of the dicyclohepta[*cd,gh*]pentalene **17a,b** and ESR spectra of its anion have been interpreted[40] as favouring the electronic structure **17a** rather than **17b**.

18π-Systems There appear to be structural data available for only one example, namely dipleiadiene[41] **23.** The calculated conjugation energy of 117 kcal. mole^{-1} seems at first sight to be rather low, however inspection of the relative contributions of the possible Kekulé forms **23a-d** shows that only in the case of the minor contributor **23d** is there any conjugative interaction between the central naphthalene unit and the two peri butadienyl ones.

Conclusions

Inspection of the conjugation energies reported above shows that, with the exception of pentalene, there is a fairly steady increase in value with number of π-electrons as is observed with polybenzenoid systems although the magnitudes with the present ring systems are slightly lower. This is in direct contrast to the situation observed for monocyclic annulenes. Where applicable the weightings of the various Kekulé contributors for those molecules considered here do not support the Platt hypothesis[5] that 4n π–electron polycycles should be regarded as 4n+2 π-electron peripheries with essentially isolated intraannular ethylenic cross links; rather they seem to favour the Randic approach.[11]

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