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THE ANTIAROMATICITY OF CYCLOBUTADIENE[†]

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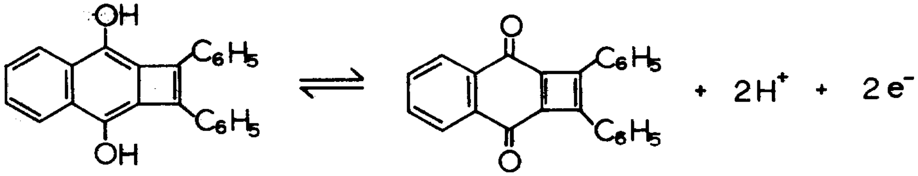
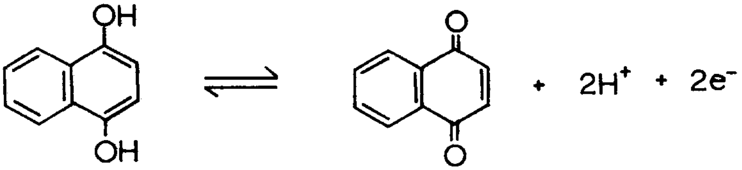
Breslow and coworkers have reported experimental evidence in support of the antiaromaticity of cyclobutadiene.[1] Their most recent work dealt with the polarographic oxidation of I and III where it was found that I is more difficult to oxidize than III by 12.4 kcal/mole.



I　　　　II



III　　　　IV

The difference was attributed to destabilization of II by the cyclobutadiene ring formed in the oxidation. The same experiment on the dianions of I and III gives a difference of 16 kcal/mole. Compound II is of course not cyclobutadiene itself, and Breslow concludes that the antiaromatic destabilization of cyclobutadiene is probably considerably more than this 12-16 kcal/mole.

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Dewar, Kohn and Trinajstić[2] using the Pariser-Parr-Pople method compute the resonance destabilization of cyclobutadiene to be 18 kcal/mole. This cannot be compared directly with Breslow's result since II does not contain a cyclobutadiene ring isolated from the remaining π system of the molecule. Further, I as written contains a 3,4-dimethylenecyclobutene grouping which is itself predicted to have considerable antiaromatic character.[3] In addition, an alternative valence bond structure containing the cyclobutadiene structure can be written for I. Thus, as Breslow indicates, it is uncertain whether the 12-16 kcal from his experiments represents a large or small part of the cyclobutadiene resonance destabilization and therefore whether or not Dewar's theoretical result is in agreement with experiment. A theoretical prediction of the cyclobutadiene antiaromaticity would be more satisfactory if one first checked whether the same theory gives Breslow's numbers when applied to compounds I-IV.

We have shown that the simple Hückel method, *if used with the proper reference structure,* can give predictions of aromaticity and heats of atomization as accurate as those of the more elaborate Pariser-Parr-Pople theory.[4-8] Using our computed heats of atomization for compounds I-IV gives a difference of 7 kcal/mole between the two energies of oxidation, in reasonable agreement with Breslow's measured 12 kcal/mole. (Note that the Hückel method, like the Pariser-Parr-Pople, does not include σ angle strain. This is of no consequence if we may assume the ring strain to be approximately equal in I and II.) In the same way we compute the antiaromaticity (*i.e.*, the resonance destabilization exclusive of ring strain)to be $-1.07\beta = 33$ kcal/mole for cyclobutadiene. This is nearly double Dewar's result and does indeed suggest that Breslow's measurement reflects only a portion of the destabilization of cyclobutadiene. Figure 1 shows our computed resonance energy per π electron (REPE) for cyclobutadiene and higher members of the annulene series. The predicted oscillation about non-aromaticity (REPE = 0) is in agreement with the observed behavior of these compounds,[9] and also with the Pariser-Parr-Pople calculations of Dewar[10] and the iterated Hückel results of Figeys.[11]

The annulenes form a particularly simple series whose orbital energies can be obtained in closed form.[12] Summing these over filled orbitals,[13] and taking the limit as the ring size becomes infinite gives, in the notation of ref. 4, a limiting REPE of $4/\pi - 1/2\cdot(E^{\pi}_{22} + E^{\pi}_{12}) = 0.0053\beta = 0.16$ kcal/mole which is identical to the limit for an infinite polyene chain. Thus the limiting behavior of both series is essentially nonaromatic. This is in accord with the work of Longuet-Higgins and Salem[14] who predict alternation of bond length in both large

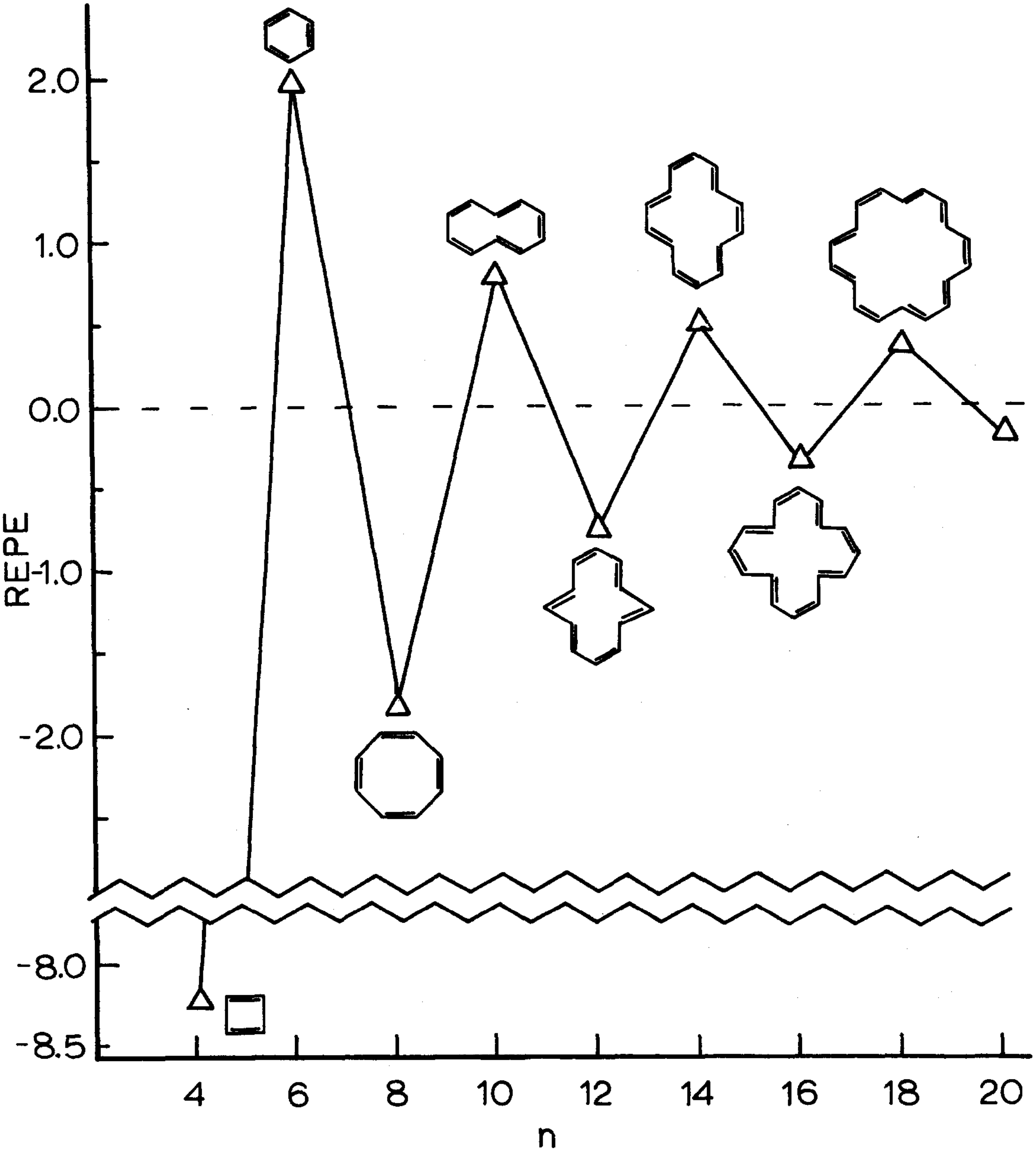

FIGURE 1. Resonance energy per π electron (kcal/mole) of the annulenes *vs.* n (number of π electrons). Note that to retain a negative REPE for antiaromatics, the opposite sign convention from that of ref. 4 has been used.

linear polyenes and large annulenes. The present results further establish the usefulness of the Hückel method as currently employed in dealing with ground state energies of conjugated systems.

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