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CLOSED-SHELL BIRADICAL STRUCTURES

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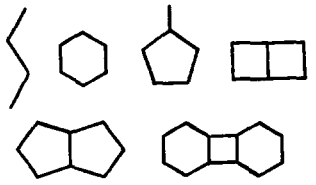
Within the Hückel molecular orbital (HMO) formulism, three main types of π-structures with even numbers of p-orbitals have been discussed.[1,2] The first of these types is exemplified by the molecules shown in group 1 below, all of which can be represented by Kekule structures. Each compound in 1 also has a closed-shell of completely occupied bonding MO's, not excluding pentalene which happens to have an empty non-bonding energy level. Cyclobutadiene and dibenzobutalene 2 are members of a second group with Kekule structures, in which HMO calculations predict degenerate non-bonding half-filled MO's.[3-5] Trimethylenemethane and triangulene 3 belong to a third class with biradical structures and half-filled non-bonding MO's.[6,7]



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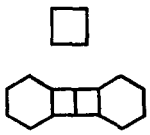

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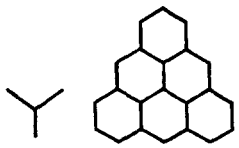

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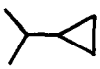
Using graph theoretical techniques we have identified another interesting group of molecular structures, and we have induced algorithms for constructing structures of this kind.

The two smallest members of this fourth genotype are 2-cyclopropenylallyl 4 and 2-cyclopentadienylallyl 5. Both systems are required to have biradical valence-bond structures, but each also has a closed-shell of electrons according to HMO theory. Single non-bonding energy levels calculated for both structures are filled in 4, and empty in 5. This pattern of energy levels holds uniformly for higher members of series corresponding to each



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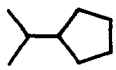

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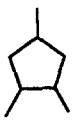
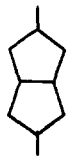
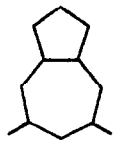
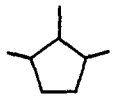
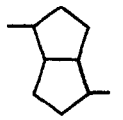
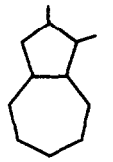
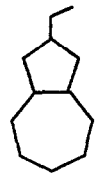
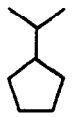
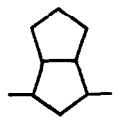
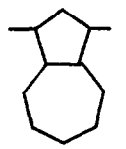
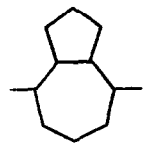
parent structure. If examples with the prerequisites of type 4 compounds are prepared, dicationic species should be obtainable, whereas dianions of type 5 compounds might well be the expected stable forms.[8] The pentalene energy pattern is like that of 5, and the pentalenyl dianion has been prepared by treating dihydropentalene with n-butyl lithium.[9]

HMO resonance energies per electron (REPE), and energies of highest occupied and lowest unoccupied orbitals (HOMO and LUMO) are given below for a few normal biradicals, closed-shell compounds, and closed-shell biradical structures. Although HMO calculations have been judged

Biradicals					
REPE(β)	0.00	0.149	0.229	0.244	
Closed-shells					
REPE	0.217	0.225	0.288	0.287	0.317
HOMO	0.618	0.362	0.431	0.131	0.477
LUMO	-0.414	-0.445	-0.158	-0.329	-0.360
Closed-shell Biradicals					
REPE	0.199	0.209	0.262	0.261	0.277
HOMO	0.0	0.504	0.477	0.0	0.359
LUMO	-0.705	0.0	0.0	-0.555	0.0

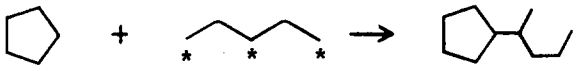
as inaccurate in thermodynamic applications,[10,11] we believe that the correct orders of stabilities for the isoelectronic π-systems are given correctly. One notes that the closed-shell structures are predicted to be significantly stabilized relative to the open-shell biradicals. Also, in the closed-shell biradicals the HOMO-LUMO energy gaps are not excessively small, and thermally populated biradicaloid ground states can inferentially be ruled out.[12]

The results described above were obtained by hand calculations. Factored secular

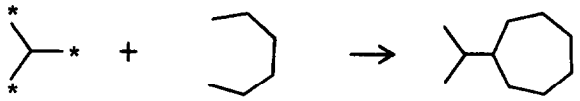
polynomials were written by inspection of symmetry reduced graphs of the molecular systems. The expected energy-level patterns were then confirmed in all cases by counting sign changes in the terms of the secular polynomials according to Descarte's rule. The polynomials were then reduced further by factoring out interger roots, the remaining lowest negative and the positive eigenvalues being found using Newton's method.[13,14] A substantial savings in time was noted over that required for the preparation of data cards for digital computer calculations.

Any number of biradical structures with HMO closed shells can be constructed using the following rules.

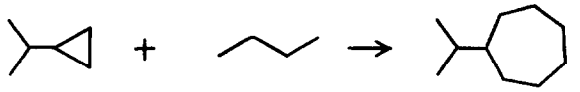
(a) Connect an arbitrary vertex of the structural graph of an odd non-alternant to any inactive (non-starred) vertex in the graph of any odd alternant. The odd non-alternant system must be void of non-bonding orbitals. Possible starting systems are monocyclic odd systems and their benzoannelated derivatives. Example:

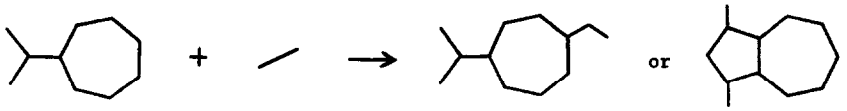


(b) Join an active vertex of an even alternant biradical graph to two vertices of an even alternant graph so that a non-alternant system is obtained. Example:



(c) After creation of structures according to rules (a) and (b) one may use theorems outlined by Gutman and Trinajstić to enlarge the parent systems.[15] The insertion of a four vertex chain, or the attachment of one vertex of an even alternant graph to the parent system by one or two edges will not alter the energy level pattern nor the required biradical structure. Examples:





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