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THREE TYPES OF CONJUGATED HYDROCARBONS BY THE UHF MO LCAO METHOD

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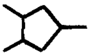
Using Hückel-type calculations Herndon and Ellzey discovered recently a new type of conjugated hydrocarbon structures, the so-called "closed shell biradicals" (CSB)[I]. According to the classification used there a molecule is considered to be a biradical if it has no K-structures. There are 5 types of conjugated hydrocarbons including 2 types of CSB.

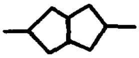
It should be noted that such conceptions as K-structures have in themselves only indirect connection to the spin properties which determine the radical character of any system. We shall analize here whether this "topological" classification may be justified on more sophisticated physical grounds. Three cases depending on the singlet-triplet energy difference E may be distinguished. If the singlet state is the lowest one ($E > 0$) we have the usual molecule, if the triplet is the lowest one then two unpaired electrons have parallel spins and the molecule is spin-paramagnetic. Finally if $E \sim kT \sim 0.02$eV the spins of unpaired electrons have the arbitrary relative orientation and the system behaves as a biradical. (In the last case the system is in a mixed state rather than in a pure one). The proposed singlet-triplet energy difference is of order calculated by McConnell in typical biradicals [2].

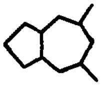
Apparently , the Hückel method which can never give $E \neq 0$ is inadequate for the determination of the hydrocarbon type. Therefore we have used the SCF MO LCAO method. For every system considered in [I] the net charge-bond order matrix and energy of the lowest singlet state of molecule, dianion and dication have been calculated. Then by the method of [3] the approximate solution for these quantities and the spin density of the unrestricted Hartree-Fock triplet state were obtained. The π-electron Hamiltonian parameters used were the same as in [4].

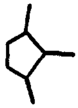
Calculated E-values (in eV) are given below

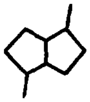

I)-I.24

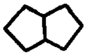

II)-I.0I

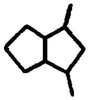

III)-0.93

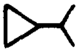

IV)-0.83

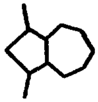

V) I.54

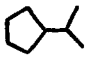

VI) I.04

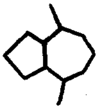

VII) 0.66


VIII) 0.03


IX) 0.23


X)-0.32


XI)-0.32


XII)-0.05

These results (which will be published completely elsewhere) clearly show that I-IV which according to [I] were thought to be "true" biradicals are in fact triplet molecules. Cyclobutadiene (E = -2.87eV) also belongs to this type. Probably its instability should be ascribed to this fact. In V-VI, which according to [I] are molecules, the singlet is about I-I.5eV lower than the triplet. Pentalene (VII) takes an intermediate position. By the same method we have also calculated E in "normal" alternant molecules such as naphtalene (E = 2.65), anthracene (E=I.68) and transbutadiene (E=3.22) where agreement with experiment and our previous CI-calculation [4] was achieved. In VIII-XII, which according to [I] are CSB, E is considerably nearer to zero. Dibenzobutalene (E = -0.29) is also a member of this class.

Thus, it can be concluded that the structures which by the topological classification [I] were believed to be CSB are most probably true biradicals, especially VIII,XII, whereas "biradicals" I-IV are unstable triplet molecules. The projection of the UHF triplet state performed in accordance with[5] does not alter this conclusion (e.g., projected E in I is -I.384 in IX is 0.230)

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