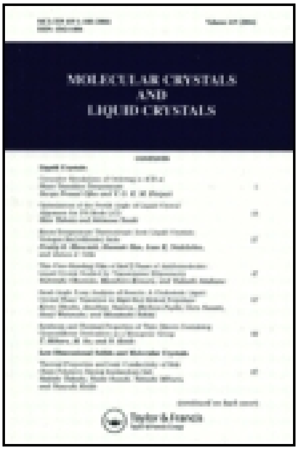

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POLYRADICALS AND HIGH-SPIN HYDROCARBONS

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Abstract Semiempirical descriptions of conjugated-hydrocarbon polyradical species are considered, with special note given to predictions of the ground-state spin. Comparisons of these predictions are noted for a systematic listing of alternant radicaloid species. A simple rule emerges.

INTRODUCTION

Recently organic polyradicals and the possibility of organic ferromagnets have evoked much interest. There have been several reviews, as in refs. 1-5, and there have been reports[6,7] of organic ferromagnets (at fairly reasonable temperatures), though structures were not well characterized. Further efforts to synthesize higher temperature organic ferromagnets are presumably underway. A good theoretical understanding is desirable.

Here we focus on a particular feature: the correlation between chemical structure and ground-state spin multiplicity. The predictions considered are via several semiempirical models for an important special class of species: uncharged alternant conjugated hydrocarbons without heteroatoms. As such the various chemical structures are identified by a molecular graph with sites representing pi-centers and edges representing neighboring pairs of sites (connected by a σ-bond). These graphs specify our considered models and thence a ground-state spin prediction. The alternant feature assumed here plays a crucial role, this assumption being that the sites of the molecular graph may be separated into two disjoint sets of sites of starred and unstarred sites such that bonds of the graph occur only between sites in different sets.

In the following we briefly describe the models considered. Some computations are then reported, and found to strengthen a simple rule for the ground-state spin. Finally references to some related extensions are noted.

PREDICTIVE METHODS

Several semiempirical schemes for predicting the ground-state spin have been studied. They are of varying degrees of difficulty in application and include:

First, the Hund-Hückel molecular-orbital (HHMO) scheme simply assumes that the non-bonding MOs are singly occupied and that Hund's rule applies. This is based upon a standard consideration of the interaction between a pair of singly-occupied orthogonal orbitals, a and b, being governed by an exchange integral $(ab|v_{12}|ba)$, which is generally nonnegative. Then the predicted spin is just half the number of non-bonding MOs.

Second, a classical structure (CS) approach concerns an assignment of a maximal number of disjoint double bonds, with the remaining unpaired sites assumed to couple together with aligned spins. Again Hund's rule might be invoked to justify this coupling. Then the predicted spin is half the number of remnant unpaired sites.

Third, a modified Hückel molecular-orbital (MHMO) scheme assumes singly-occupied non-bonding MOs are to be localized as much as possible and thence to couple in pairs with or against Hund's rule. If two such non-bonding MOs have non-zero MO coefficients on the same site, the associated exchange integral is assumed to be positive, so that Hund's rule applies. On the other hand if they do not share such a site, Borden and Davidson[1,8] have emphasized that the two non-bonding MOs have little differential overlap, the exchange integral is near zero, and one should look to the effects of admixture of higher-energy configurations. One could assume that these higher-order considerations are always counter to Hund's rule, with their effect simply being overwhelmed whenever the (lower-order) exchange contribution is non-zero. With 2 (or 3) non-bonding MOs localizable so as not to share a site this leads to a singlet (or doublet) ground state prediction; whereas if not so localizable the ground state is predicted to be triplet (or quartet). For greater numbers of non-bonding MOs the predictions are a more delicate matter, depending upon the pattern (and perhaps sizes) of the exchange couplings amongst the various non-bonding MOs.

Fourth, another modified Hückel molecular-orbital (M'HMO) scheme proceeds with many of the same ideas, except that when a pair of singly-occupied non-bonding MOs occur on disjoint sets of sites the coupling is taken with different signs. It is taken to conform with or against Hund's rule as the MOs occur on "like" or "unlike" sites. This comparison of MOs may be expressed[9] in terms of parity, with the parity being even or odd as the MOs are localized on starred or unstarred sites. Then the ground-state spin is predicted to be half the difference between the numbers of even- and odd-parity non-bonding MOs.

Fifth, the valence-bond (VB) model of Pauling and Wheland in its simple form with only nearest-neighbor interactions turns out to be equivalent to the Heisenberg model of solid-state physics. The determination of the ground-state wavefunction and energy is in general a difficult task, evidently limited with present tools to about two dozen pi centers. However, Lieb and Mattis[10] have proven results[11,12] which give the ground-state spin of this model as simply half the difference between the numbers of starred and unstarred sites.

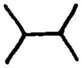
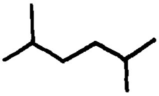
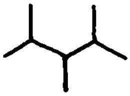
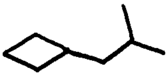
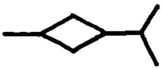
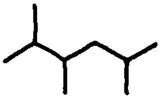
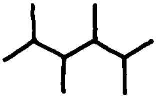
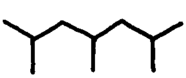
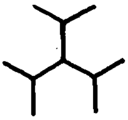
Sixth, the Parisier-Parr-Pople (PPP) model may be simplified to the Hubbard model, wherein Coulomb interactions are limited to (pi) electrons on the same site. It is believed that the Hubbard model agrees well with the PPP model for the "homo-polar" states including the lowest state of each spin multiplicity. See, e.g., refs. 13 and 14. There seems to be little in the way of theorems for the ground-state spin multiplicity, so that complete configuration-interaction computations are utilized, though this currently limits results to about 10 pi centers.

RESULTS AND DISCUSSION

The systems we treat are labelled by molecular graphs which are constrained: to be connected; to have sites only of degrees 1, 2 or 3; to be alternant (or bipartite); and to have an embedding in the plane (without crossing bonds). Upon initiating a systematic listing of such graphs we find 89 with 8 or fewer sites. From amongst these we find 28 have a HHMO spin prediction that differs from some other spin prediction. Of these 28 we find that the remaining five predictive schemes explored here agree amongst themselves in all but 5 cases.

These 5 species, along with 3 other larger species exhibiting a similar behavior, are listed in the following:

Table of Spin Predictions for Crucial Species of the Text

Molecular Graph	Spin Predictions					
	HHMO	CS	MHMO	M'HMO	VB	Hubbard
	1	1	0	0	0	0
	1	1	0	0	0	0
	1	1	0	1	1	1
	1	1	0	1	1	1
	1	1	0	0	0	0
	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
	1	1	0	0	0	0
	2	2	0	2	2	2
	2	2	1	2	2	2

Examination of the results reported in this table supports several theses. In particular the ground-state spin of (homo-atomic, planar) alternants appears to be correctly given (without exception) by:

(i) the nearest-neighbor VB (or Heisenberg) model;
(ii) the second modified Huckel molecularorbital (M'HMO) scheme;
(iii) the Hubbard (and presumably PPP) model; and
(iv) the simple formula $S = |N_* - N_o|/2$ where N_* and N_o are the numbers of starred and unstarred pi-centers in the molecule.

Further agreement with more accurate ab initio computations[8,15] on a few species has been summarized elsewhere[12].

Qualifications need to be mentioned in extending these ideas. Quantitative predictions for exchange splittings seems to be more difficult. The nearest-neighbor VB model appears to be inaccurate in this regard for systems containing rings of size 4. Improved VB models as in ref. 13 have been less well tested. Treatments of nonalternants and heteroatomic species have been made less often, and any general rule might be more complicated because of the potential greater relevance of admixing ionic states.

Some qualitative extensions seem to be quite successful. This includes qualitative theorems for the ground state of the simple VB model regarding[3,16] point-group symmetries as well as signs of spin densities and expectation values of exchange interaction operators. The spin-density theorem in particular agree qualitatively with numerous computations, as in ref. 17. Extensions to alternant carbene systems with exchange coupling to singly-occupied methylenic σ-orbitals show[3,4,18] much promise. The theorematic VB approach to the prediction of ground-state spin also supports[3] an argument due to McConnell[19] concerning the sign of intermolecular exchange coupling.

Overall it seems there is progress from several points of view. Presumably the emerging (often simple) rules can aid in the design of novel magnetic species.

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