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High-Spin Carbenes[†]

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Abstract: A general class of π-network hydrocarbons that includes the possibility of dangling σ-bonds at carbene centers in the π-network are investigated theoretically. Several semiempirical approaches are treated: the simple valence-bond model, a "modified" molecular-orbital scheme, and complete configuration interaction calculations on Parisier–Parr–Pople-type models. Often these three approaches agree with one another in the prediction of ground-state spin S, as well as with experiments when available. We find that for alternant π-networks a very simple rule seems to accurately predict the value of S.

I. Introduction

Interest in high-spin hydrocarbons seems to be continually developing.[1] Experimentally there has been[2-5] some success in synthesizing and studying these nonclassical compounds. Species with spin as great as $S = 4$ (i.e., nonet spin multiplicity) have been prepared.[5] There have also been several theoretical ideas developed[4,6-12] to help identify such possible species. In addition there have been numerous quantum chemical calculations[8,10-16] for individual molecules and polymer chains, including some[8,16] accurate ab initio configuration interaction (CI) calculations.

Several theoretical rules of note have been developed[7-12] to predict the ground-state spin S of conjugated π-systems. In one simple approach, Hückel theory is supplemented with Hund's (first) rule to make predictions, but this evidently sometimes overestimates[8-11] S. For this, modified molecular-orbital (MO) arguments have been developed[8-10] that recognize that Hund's rule is ineffective for exchange coupling between two singly occupied orbitals when little differential overlap occurs. In an alternative approach[7,11,15] the simple valence-bond (VB) model for carbon π-networks has also been investigated. For this VB model, Ovchinnikov[7] conjectured that the ground-state spin for "alternant" networks is simply half the difference between the number of "starred" and "unstarred" sites. Later it was noted[11] that this[17] and several other results[18] may be rigorously proved. Often this simple VB result agrees with the modified MO approach (involving some analysis of the nonbonding MO's) as well as with more accurate complete CI computations on Parisier–Parr–Pople (PPP) models, extensive ab initio CI computations, and experiment. Thus it seems appropriate to explore more fully such simple arguments and VB models, as we do here for a wider class of alternant hydrocarbons that include some nonbonded (i.e., singly occupied) σ-orbitals.

A natural extended class is that of π-conjugated networks including carbene centers. Indeed several such species have long been known, there being several reviews both on the experimental[19] and theoretical[20] sides. Most of this work has focused on single carbene centers (independently of whether it was associated to a π-network) and the reactions they undergo. Studies from the groups of Itoh[2,5,21] and Iwamura[5] and of Wasserman[22,23] seem to provide the primary examples of systems such as will be emphasized here as high-spin candidates. An example of a very simple carbene species is shown in Figure 1, where only the σ-bonds are explicitly indicated; four valence electrons remain to be distributed amongst the dangling σ-orbital of the central carbon and the three π-orbitals of the carbons. In the absence of ligands of rather different electronegativity it seems[20] likely that the ground state is dominated by configurations in which the dangling σ-orbital on the carbene centers is singly occupied. This presumption is made for the species considered here, examples of which are indicated in Figure 2, where now the solid lines indicate the π-network and the dashed lines are appended to carbene centers, with a (singly occupied) dangling σ-orbital. Thus structure **2** of Figure 2 represents the species of Figure 1. Several of the species

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(16) See, e.g., Kollmar, H.; Staemmler, V. *J. Am. Chem. Soc.* **1977**, *99*, 3583. Jaffra, J. A.; Newton, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5012. Borden, W. T.; Davidson, E. R.; Feller, D. *Tetrahedron* **1982**, *38*, 737.

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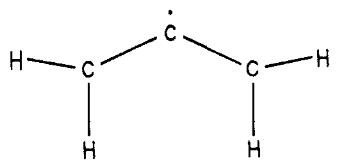

Figure 1. The σ-electron network in an example species, with one (unshown) π-electron on each C atom.

of Figure 2 are known experimentally and are observed to exhibit a variety of ground-state spins.

The predictions in this paper of ground-state spins are made from three points of view. The associated models are a covalent VB model, a Hückel-type MO model, and a PPP-type model. For each of these three points of view a matter of crucial importance is the manner of exchange coupling and particularly the signs of exchange "parameters". Hence this topic is addressed in section II. In sections III–V the three models are described, and corresponding predictive methods are noted. In section VI predictions for the ground-state spin are compared to each other and (when available) to experiment. For systems with alternant π-networks, an especially simple to apply VB theorem seems to be fairly reliable. Section VII presents some quantitative VB and PPP-type results for systems with about 9 or fewer π-centers.

II. Exchange Coupling

In systems with singly occupied orbitals exchange coupling can arise. The relevant singly occupied orbitals may be (possibly nonorthogonal) atomic orbitals (as in VB approaches) or (possibly degenerate) MO's. The exchange coupling interaction between two such orbitals, say i and j, may[24] be expressed as

$$J_{ij}(ij) \qquad (2.1)$$

where (ij) is an exchange operator and J_{ij} is an exchange parameter (measuring the strength of the interaction). Here we take (ij) to permute spin indices for orbitals i and j (so that via the Dirac identity this could be expressed as $2S_i{\cdot}S_j + {}^1/_2$, if so wished).

Different low-order formulas apply for J_{ij}, depending on whether or not the orbitals are orthogonal. For the case of atomic-like orthogonal orbitals, the inclusion of the effects of ionic configurations is crucial and leads to an expression:[25]

$$J_{ij} = \left\{\sqrt{(U/4)^2 + \beta_{ij}^2} - \frac{U}{4}\right\} - K_{ij} \cong \frac{2\beta_{ij}^2}{U} - K_{ij} \qquad (2.2)$$

where β_{ij} is a (Hückel-type) resonance parameter (or integral), K_{ij} is a (direct) exchange integral (which is necessarily nonnegative), and U is a (Hubbard-type) electron-repulsion parameter (expressing the *relative* repulsion of two electrons both in the same orbital). For the case of atomic-like nonorthogonal orbitals, an alternative derivation[26] identifies dominant contributions to arise via covalent configurations and yields a quite different expression:

$$J_{ij} = \frac{S_{ij}^2C_{ij} - K_{ij}}{1 - S_{ij}^2} \cong S_{ij}^2C_{ij} - K_{ij} \qquad (2.3)$$

where S_{ij} is the overlap integral, K_{ij} is the (direct) exchange integral, and C_{ij} is a (nonnegative) Coulomb parameter (or integral). Notably both (2.2) and (2.3) express J_{ij} as the difference between two nonnegative terms.

III. Valence-Bond (VB) Model

The simple VB model is defined on the space of covalent structures with each of the singly occupied atomic orbitals having a single electron with either spin up or down. As indicated in section II, this leads to a model Hamiltonian:[27]

$$H = \sum_{i<j} J_{ij}(ij) + \text{constant} \qquad (3.1)$$

where the chemical structure of the molecule is embodied in the choice of the exchange parameters J_{ij}. More simply the J_{ij} are taken to exhibit but few values, say: $J_{ij} = J_{\pi\pi}$ if i and j are for neighboring π-orbitals; $J_{ij} = J_{\sigma\pi}$ if i and j are a σ,π-pair of orbitals on the same (carbene center); and $J_{ij} = 0$ otherwise. It is a crucial point that $J_{\pi\pi}$ and $J_{\sigma\pi}$ may differ (rather substantially), as may be seen on considering either of the J_{ij} formulas of section II. Both formulas express $J_{\pi\pi}$ as the difference of two positive terms, the first of which dominates; thus $J_{\pi\pi}$ is antiferromagnetically signed (i.e., >0 for the present sign convention) favoring singlet spin pairing. For the other nonzero case, of $J_{\sigma\pi}$, the two orbitals are orthogonal by symmetry so that $S_{ij} = \beta_{ij} = 0$; thus $J_{\sigma\pi} = -K_{ij}$ then is ferromagnetically signed, favoring a triplet spin alignment. Though $K_{\pi\pi}$ is quite small in comparison to $J_{\pi\pi}$ (or $C_{\pi\pi}$ as in (2.3)), the exchange integral $K_{\sigma\pi}$ is between two orbitals on the same center and as a consequence should be somewhat larger than $K_{\pi\pi}$. As a rough guess we take

$$J_{\sigma\pi}/J_{\pi\pi} \cong -1 \qquad (3.2)$$

In the inorganic literature[28] just such arguments are widely discussed for models as in (3.1) (termed Heisenberg models).

Sometimes consequences of the VB model may be easily made without recourse to quantitative calculations. In particular there are theorems[17,18] for a few ground-state properties, whenever the system is such that the (singly occupied) orbitals can be partitioned into two (disjoint) sets A and B such that $J_{ij} < 0$ only if i and j are in the same set. Then the ground-state spin is

$$S_{\mathrm{VB}} = ||A| - |B||/2 \qquad (3.3)$$

where $|A|$ and $|B|$ are the orders of A and B. (A final point that the splitting to the next higher spin state is nonzero, holds under mild conditions, met here.) In fact Itoh's π-alternants[2] satisfy this condition: the π-orbitals are divided into "starred" and "unstarred" sets as usual (with sites of one set bonded only to sites of the other set), and then each nonbonded σ-orbital is placed into the *same* set as the π-orbital on the same center.

IV. Hückel Molecular-Orbital (MO) Model

Most simply this approach utilizes the Hückel model. First one locates all the nonbonding π-MO's, as is readily done by hand.[29] In the Hückel approximation these orbitals do not couple to the σ-orbitals, so dangling σ-bonds are grouped with the nonbonding MO's. Next each nonbonding MO is given an appropriate number of electrons (here one to each MO). Finally one proceeds beyond the simple (one-electron) model to include "exchange" couplings or, in a more formal description, applies degenerate perturbation theory to the zero-order Hückel-model eigenspace of determinants with singly occupied nonbonding MO's of various possible spin alignments. The result (in low order) is an effective Hamiltonian with interactions as in (2.1), with i and j now being labels for nonbonding MO's. In *first order*, the formulas for J_{ij} are like those of (2.2) and (2.3), but since the orbitals are eigenfunctions to the one-electron system Hamiltonian, they are now orthogonal (i.e., the $S_{ij} = 0$) and the one-electron couplings vanish (i.e., the $\beta_{ij} = 0$). Thus one anticipates all the $J_{ij} = -K_{ij} < 0$, which is the Hund's rule result. Thence one makes the ground state spin prediction

$$S_{\mathrm{HHMO}} = N_{\mathrm{NBMO}}/2 \qquad (4.1)$$

where N_{NBMO} is the total number of nonbonding MO's.

In a more careful version,[8-10] one makes a further check on the applicability of Hund's rule. This entails the realization that in

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[23] Trozzolo, A. M.; Murray, R. W.; Smolinski, G.; Yager, W. A.; Wasserman, E. *J. Am. Chem. Soc.* **1963**, *85*, 2526.

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[26] See, e.g., Simpson, W. T. *J. Chem. Phys.* **1956**, *25*, 1124.

[27] Usually the VB model for conjugated hydrocarbons has been expressed otherwise, but the equivalence to the form (3.1) has long been noted, e.g., by Simpson[13] or perhaps first by Van Vleck, J. H.; Sherman, A. *Rev. Mod. Phys.* **1935**, *7*, 167.

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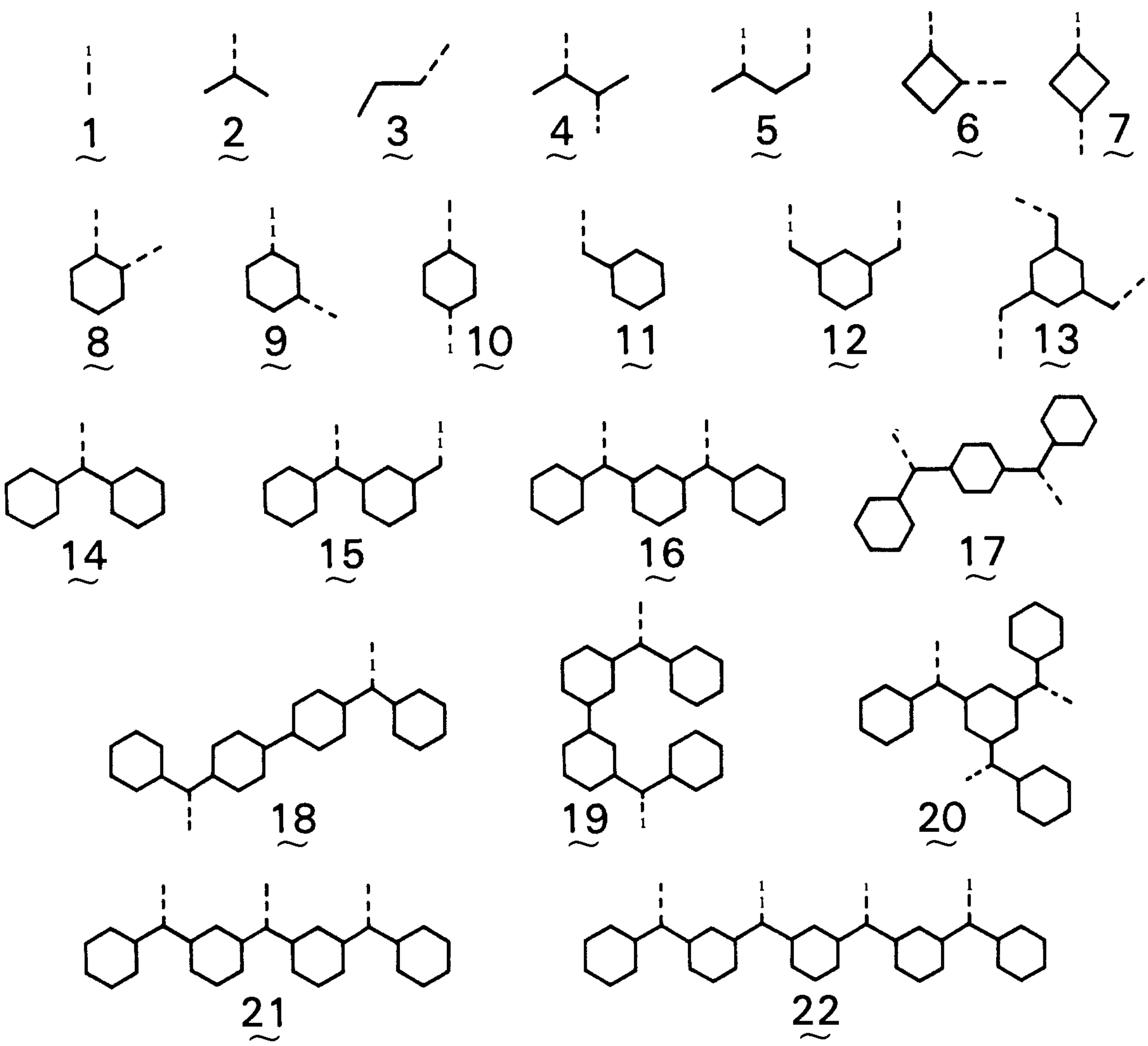

Figure 2. A sampling of π-conjugated hydrocarbons with nonbonded σ-electrons (located by dotted lines).

our preceding discussion one should check to see if $K_{ij} > 0$ (noting it is necessarily nonnegative), for if $K_{ij} = 0$ (or is exceedingly small) one should proceed to seek higher order (degenerate-perturbation-theoretic) corrections to the J_{ij}. Indeed if there is little differential overlap between orbitals i and j, then $K_{ij} \cong 0$. Thus[8,9] if the ith and jth nonbonding MO's can be chosen localized on disjoint sets of centers, then $K_{ij} \approx 0$. Further it seems to be[8] a general rule that the higher order corrections are positive, so that if $K_{ij} \approx 0$, then $J_{ij} > 0$. However, in the present situation there is an important exception: the J_{ij} coupling between a σ- and a π-orbital should remain negative even if the π-orbital has no component on centers near that of the σ-orbital (since $K_{ij} > 0$ is in fact the only spin-dependent coupling from a σ-orbital to any part of the π-system, in the ordinary semiempirical schemes). Still if a nonbonding π-MO has no density on the center on which a σ-orbital resides, then the coupling should be very small and will here be neglected (i.e., J_{ij} set to 0). The J_{ij} coupling between two σ-orbitals should typically be of even smaller magnitude and also will be set to 0.

Once the exchange couplings are specified there still remains the problem of determining the ground state again. Most simply, if all the J_{ij} are negative, then the maximum spin results, as in (4.1). At the other extreme, if all the J_{ij} are both positive and of (nearly) the same size, then the minimum spin results (singlet or doublet, as there are an even or odd number of electrons). If there are J_{ij} of opposing sign or if the J_{ij} are nonnegative but of variable sizes, then the result is more delicate. In some cases the theorem of section II can be applied. The more general case, which depends upon the quantitative details of the more complete perturbed Hamiltonian and upon the details of the degenerate perturbation treatment, will not be considered further in this work.

V. Parisier-Parr-Pople-Type Models

A model more complete than those of the preceding sections would include explicit electron-electron interaction (and correlation) over the manifold of π-configurations. A reasonable choice for the interaction Hamiltonian within the π-system is that of a PPP-type (or Hubbard) model[30]

$$H_\pi = \beta \sum_{i\sim j}^{\pi}(E_{ij} + E_{ji}) + \tfrac{1}{2}U\sum_{i}^{\pi}(E_{ii}^2 - E_{ii}) \qquad (5.1)$$

where β is a (Hückel-type) resonance integral and U is a relative on-site electron-electron repulsion parameter (given[31] in terms of the usual Coulomb integrals as $U \cong \gamma_0 - \gamma_1$). The sums are restricted to π-orbitals, with $i\sim j$ indicating a nearest-neighbor pair. The E_{ij} are[30,32,33] infinitesimal generators for the unitary group and shift an electron (of arbitrary but fixed spin) from orbital j to i. They may be expressed in terms of common creation and annihilation operators as[33]

$$E_{ij} = a^+_{i\alpha}a_{j\alpha} + a^+_{i\beta}a_{j\beta} \qquad (5.2)$$

Interactions involving the dangling σ-orbitals need also be considered. With the neglect of direct interactions between (typically rather distant) carbene units the occupancy of the dangling σ-orbitals becomes fixed, since the σ,π resonance integral is zero

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(30) See, e.g., Matsen, F. A. *Acc. Chem. Res.* **1978**, *11*, 387.

(31) (a) Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc.* **1960**, *A257*, 445. (b) Murrell, J. N.; Salem, L. *J. Chem. Phys.* **1961**, *34*, 1914.

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(34) Arnold, D. R. *J. Am. Chem. Soc.* **1974**, *96*, 3708.

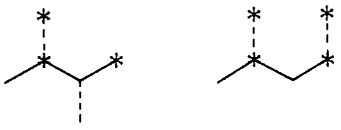

Figure 3. Illustration of the starring construction for species **4** and **5**.

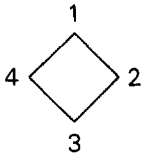

Figure 4. The labeling used for the (cyclobutadiene) π-network of species **6** and **7**.

by symmetry. For the presumed single electron occupying these σ-orbitals, the dominant interaction then should be that of exchange, with the exchange parameter $J_{ij} = -K_{ij}$ as seen in section II. Though the orbital energy of the σ-orbitals differs from that of the π-orbitals, one need not explicitly include either in the Hamiltonian since they both represent conserved quantities, i.e., good quantum numbers. (Of course if states with different occupanices of σ- and π-orbital spaces were to be compared, these orbital energies, and electron–electron interaction terms involving σ-orbitals, would be crucial.) Thus the relevant interaction involving σ-orbitals currently is

$$H_{\sigma\pi} = -K_{\sigma\pi}\sum_{\mathrm{i}}^{\sigma}(E_{\mathrm{ii'}}E_{\mathrm{i'i}} - E_{\mathrm{ii}}) \tag{5.3}$$

where the i sum is over all dangling σ-orbitals and i′ denotes the π-orbital on the same center as i. With singly occupied σ-orbitals, the unitary group operator in the sum here is in fact equivalent to a transposition, denoted (ii′) in section II. The overall PPP-type model then is

$$H = H_{\pi} + H_{\sigma\pi} \tag{5.4}$$

which (again) is reasonable for fixed σ-orbital occupancy.

VI. Qualitative Predictions

The methods of the preceding sections can be used to predict the ground-state spins for the species in Figure 2. The VB predictions are especially simple to make and are conveniently aided via a diagrammatic construction as in Figure 3 for species **4** and **5**. First, one places stars on alternant sites of the π-network (as usual); second, one appends stars to those σ-nodes that are attached (via a dashed bond) to a starred π-node; and third, half the difference of the number of starred and unstarred nodes is taken to give the spin (being 0 and 1, for species **6** and **7**, respectively).

The MO considerations, though by many standards simple, are a little more involved. For instance, for species **6** and **7** the nonbonding π-MO's are

$$\psi_{\mathrm{a}} = \frac{1}{\sqrt{2}}\chi_1{}^{\pi} - \frac{1}{\sqrt{2}}\chi_3{}^{\pi} \qquad \psi_{\mathrm{b}} = \frac{1}{\sqrt{2}}\chi_2{}^{\pi} - \frac{1}{\sqrt{2}}\chi_4{}^{\pi} \tag{6.1}$$

where the $\chi_{\mathrm{i}}{}^{\pi}$ are (orthogonalized) π-orbitals for π-centers labeled as in Figure 4. Since ψ_{a} and ψ_{b} occupy disjoint sets of sites, the modified Hund's rule predicts $J_{\mathrm{ab}} > 0$; however, the coupling to the σ-orbitals $\chi_{\mathrm{i}}{}^{\sigma}$ (or $\chi_{\mathrm{j}}{}^{\sigma}$) are ferromagnetically signed or zero if the coefficient of the corresponding $\chi_{\mathrm{i'}}{}^{\pi}$ (or $\chi_{\mathrm{j'}}{}^{\pi}$) is zero in the π-MO considered. The resulting coupling patterns may be depicted as in Figure 5, with nodes identified to nonbonding MO's and edges to exchange couplings, which are positive or negative as the edge is a solid or dashed line. Application of the theorem of eq 3.3 then yields respective spin predictions of 0 and 1 for **6** and **7**, in agreement with the predictions of the VB and PPP-type models.

The various predictions for the species of Figure 2 are given in Table I. In some cases the modified Hückel MO predictions (as developed in section IV) fail to predict a splitting (as when the nonbonding π-MO's have no density on a carbene center); the different spins that are thence predicted to be degenerate are then listed. The MO predictions are seen to come into closer agreement with the VB predictions on using the modified Hund's rule formulation. Notably in all the cases of Table I where either experimental results are available or (presumably) more reliable computations on PPP-type models have been made agreement with the VB predictions is obtained. Of some note is species **17**; the experimental value as earlier measured[23] was in disagreement with the VB result, but more recent measurement[21] now agrees with the VB prediction.

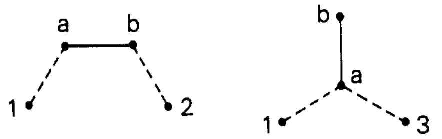

Figure 5. The exchange-coupling patterns among the four nonbonding MO's of species **6** and **7**, respectively. The π-MO's are identified by labels as in (6.1), while the σ-MO's are identified by the labels of their carbon center, as in Figure 4.

Table I. Ground State Spin Predictions

	ground-state spin				
molecule	Hund HMO	modified Hund HMO	VB	Hubbard PPP	expt
1	1	1	1	1	1 (ref 19, 20)
2	1	0, 1	0	0	
3	1	1	1	1	1 (ref 34)
4	1	0, 1	0	0	
5	1	0, 1	1	1	
6	2	0	0	0	
7	2	1	1	1	
8	1	0, 1	0	0	
9	1	0, 1	1	1	
10	1	0, 1	0	0	
11	1	1	1	1	1 (ref 22)
12	2	2	2	2	2 (ref 22)
13	3	3	3		
14	1	1	1		1 (ref 22)
15	2	2	2		
16	2	2	2		2 (ref 2)
17	1	0, 1	0		0 (ref 21)
18	1	0, 1	0		
19	2	0	0		0 (ref 2)
20	3	3	3		
21	3	3	3		3 (ref 2)
22	4	4	4		4 (ref 5)

VII. Quantitative CI Computations

For VB and PPP-type models quantitative full configuration interaction (CI) computations can be used to predict splittings amongst states of various spin multiplicities. With the use of modern unitary group techniques, or with modern VB (or Rumer) basis approaches,[25] and with the restriction to just a few low-lying eigenstates one can[32] handle systems with up to nearly a million basis states. For the PPP-type and VB models, this currently limits system sizes to about $N = 12$ and $N = 24$ electrons, respectively.

For most of the systems of Figure 2 that fall into this computationally accessible category, we have carried out such brute-force CI computations. This has been done for a manifold of potentially low-lying states that correspond in number to those that would be obtained from the coupling of a given number n of singly occupied orbitals. This number n is taken to be a sum $n = n_{\sigma} + n_{\pi}$ where n_{σ} is the number of singly occupied (carbene) σ-orbitals and n_{π} is the number of nonbonding Hückel π-MO's. That is, n_{π} is the number of singly occupied π-MO's that might be only weakly exchange coupled, these in turn being exchange coupled to the singly occupied σ-orbitals, so that within the 2^n-dimensional manifold of states splittings might include the lowest lying ones. For $n = 2$ then we consider the lowest singlet and lowest triplet, while for $n = 4$ the two lowest singlets, the three lowest triplets and the lowest quintet are considered. The parameterization of the Hubbard model is taken to have

$$|\beta|/U = 1/2 \tag{7.1}$$

Table II. Ground-State Energies and Singlet–Triplet Splittings in Units of $J = \sqrt{(U/4)^2 + \beta^2} - U/4$

	spin		VB model		Hubbard model	
molecule	ground state	excited	ground state	splitting	ground state	splitting
1	1	0	−1.000	+2.000	−1.000	+2.000
2	0	1	−4.000	0.438	−3.725	0.204
3	1	0	−3.903	0.903	−3.800	0.769
4	0	1	−6.340	0.199	−6.012	0.067
5	1	0	−6.266	0.202	−6.030	0.077
8	0	1	−10.231	0.215	−10.085	0.090
9	1	0	−10.121	0.234	−10.031	0.040
10	0	1	−10.191	0.161	−10.061	0.055
11	1	0	−10.496	0.809	−10.439	1.035

as is reasonable.[30,31]

In Table II results are reported for those systems for which both VB and PPP-type computations were carried out. The VB calculations are reported with the constant of (3.1) chosen to be

$$\text{constant} = -J_{\pi\pi}N_{\pi} \qquad (7.2)$$

where N_{π} is the number of π-bonds, and the exchange parameter $J_{\pi\pi}$ is as given by (2.2) with $K_{ij} = 0$. Thence the VB- and Hubbard-model energies in units of $J_{\pi\pi}$ are more directly comparable, as verified in Table II. For systems with 4-membered rings, it has long been known that there is lack of agreement of energies (say as embodied in Hückel's $4n + 2$ rule) between the simple VB and Hückel MO models, and this persists on comparing VB and PPP models. Thus only systems without 4-cycles have been reported in Table II. The ground-state energies are similar and, though the differences in the ground-state energies via the two models are comparable to the singlet–triplet splittings, these splittings are of the same sign for the two models. There is some qualitative agreement in these splittings via the two models. There appears to be a tendency for the VB splitting to exceed that of the Hubbard model, with the ratio of VB splitting to Hubbard-model splitting increasing as the value of the splitting decreases. Moreover, the qualitative features here do not appear to depend strongly on the particular parameter values, of t/U or of $J_{\sigma\pi}/J_{\pi\pi}$. For instance, the choice of the ratio $J_{\sigma\pi}/J_{\pi\pi}$ of eq 3.2 as "small" as −0.10 has been tested, and like orderings of levels for the PPP-type and VB models was found.

VIII. Conclusion

The ground state spin predictions via the simple VB model for aromatic carbene species seems to be in remarkable agreement both with the results from brute-force computations on the PPP model and with the experimental evidence. Further examples in which the VB model predictions agree with experiment are found in ref 35. Moreover, the graph–theoretic construction for making this prediction for alternants is very simple. Some semiquantitative agreement is found between VB and PPP-type models.

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Ab Initio Calculations on the Ring Opening of Cyclopropane Radical Cation. Trimethylene Radical Cation Is Not a Stable Intermediate

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Abstract: Ab initio calculations with the 6-31G* basis set find no chemically significant stability for trimethylene radical cation (**2**). Although, with inclusion of electron correlation at the MP2 level of theory, there is apparently an energy minimum for a geometry of **2** with C_s symmetry, the barrier to hydrogen migration to form propene radical cation (**3**) is found to be less than 0.2 kcal/mol. At the MP2 level of theory the rearrangement of cyclopropane radical cation (**1**) to **3** involves conrotatory ring opening and passage over a transition state of C_2 symmetry. After correction for zero-point energy differences, the transformation of **1** to **3** is computed to be exothermic by 10.3 kcal/mol and to require an activation energy of 21.9 kcal/mol. The importance of electron correlation for correctly calculating the relative energies of species with localized and delocalized wave functions is demonstrated, and the finding that, with inclusion of sufficient correlation, the (0,0) geometry of **2** is stable to asymmetric distortion of the C–C bond lengths is discussed.

Observation of trimethylene radical cation (**2**), formed by ring opening of cyclopropane radical cation (**1**), has been claimed both in CF_2ClCCl_2F matrices[1] and in the gas phase.[2] Recently, however, we[3] and others[4] have reported the results of ab initio calculations that call into question whether the irreversible opening of **1** to **2** is possible energetically. In this paper we describe the results of additional calculations which indicate that **2** can re-

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