Two-State Model of Antiaromaticity: The Triplet State. Is Hund's Rule Violated?

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A theoretical and computational study of the lowest lying triplet state of cyclic hydrocarbons having an even number ($2n$) of π electron bonds (antiaromatic compounds) is presented. In these systems, the ground singlet state of the most symmetric structure is distortive, being a transition state for the reaction exchanging two bond-alternating structures. As a resonance hybrid of two equivalent valence bond (VB) structures, this singlet is a stabilized biradical of B_{1g} symmetry. The lowest lying triplet of the most symmetric form is strongly bound, similar in geometry to the 1^1B_{1g} singlet transition state, *and is always higher in energy*. The energy difference between the two states is remarkably constant regardless of the ring size. This apparent violation of Hund's rule is derived from the symmetry properties of the system. The triplet state is treated as a resonance hybrid of n equivalent covalent structures, each having $n - 1$ singlet electron pairs and one pair of two spin parallel electrons (triplet pair); part of the exchange resonance stabilization is lost in the triplet, making the singlet more stable. Thus, this effect is due to the difference between the static resonance stabilization of the triplet and the singlet states. In contrast, Hund's rule always holds for biradical systems having only one dominant VB structure. Spectroscopic observation of these biradical triplets is possible by photodetaching an electron from the monoanion, as recently demonstrated experimentally. The model predictions are confirmed computationally for several examples including H_4, H_8, cyclobutadiene, cyclooctatetraene, pentalene, and heptalene.

1. Introduction

Hund's rule violations have been noted in many systems that are considered as having a biradical character. Examples include the 90° twisted form of ethylenes[1] and the ground state of the most symmetric form of antiaromatic molecules. Cyclobutadiene (CB) has been extensively discussed in this context.[2−4] Various explanations based on MO theory were offered, including dynamic spin polarization[5,6] and the pseudo Jahn Teller effect.[3] The possible role of 4-fold symmetry was pointed out,[7] and the need to include configuration interaction in order to account for apparent violations of Hund's rule has been repeatedly emphasized.[8] It was recognized that whereas in a single configuration the exchange interaction always makes the triplet of lower energy, when more configurations are added, electron correlation may outweigh it. However, a general prescription was not given.

Ovchinikov[9] used a Heisenberg Hamiltonian to describe the perfectly correlated polyelectronic wave function of hydrocarbons, including cyclic ones. Klein and co-workers[10] developed the concept further and gave it a more rigorous mathematical foundation. These treatments are sometimes dubbed as valence bond ones, in which spin pairing is maximized.

A VB-based account for exceptions to Hund's rule was given by Voter et al.[11,12] for the cases of twisted ethylene and square CB. They showed that resonance stabilization between two equivalent structures is dominant in making the singlet state more stable than the triplet. The physical basis for this stabilization is the contribution of all four electrons involved in the bonding of these system, as first suggested by Mulder.[13]

Recent experimental studies have considerably increased the interest in these systems. Negative ions may be prepared in the gas phase by electron attachment[14] or by a chemical reaction.[15,16] Photodetachment of the electron prepares the neutral with the initial geometry of the negative ion, and measurement of the electron's kinetic energy allows the mapping of the neutral's low lying electronic states. This has been recently done for cyclooctatetraene (COT)[17] and some other biradicals,[18] confirming experimentally that the singlet states of many biradicals are lower in energy than the triplets. Matrix isolation spectroscopy has been a major source of information on reactive species such as biradicals. Recently, pentalene was isolated and investigated in an argon matrix.[19] These experimental findings on "classical" antiaromatic molecules and related biradicals led us to reconsider the relative stability of low lying singlet and triplet states.

We base our approach on the assumption that these molecules are two-state systems, namely systems that may be considered as resonance hybrids of two covalent structures.[20] The valence bond (VB) approximation is a convenient method for dealing with such systems and will be used extensively. We are particularly interested in systems having an even number of electron pairs, as is the case in antiaromatic molecules. The model, which was previously used to consider the properties of transition states in valence isomerization reactions and their singlet twins,[21] has been used in ref 22 (henceforth referred to as paper 1) to analyze the properties of the singlet states of antiaromatic systems; It is now extended to the lowest lying triplet. It is shown that the first singlet state, S_0, which is formed by an out-of-phase combination of the two VB structures, is the ground state in this case and that the triplet state lies very close to it, but always at a higher energy. The S_0 state is a transition state so that the triplet, which usually is found only about 0.6 eV above it, is the lowest lying bound state of the system. The mode that serves as a reaction coordinate between the two distorted forms of S_0 has a very high frequency in the T_1 state.

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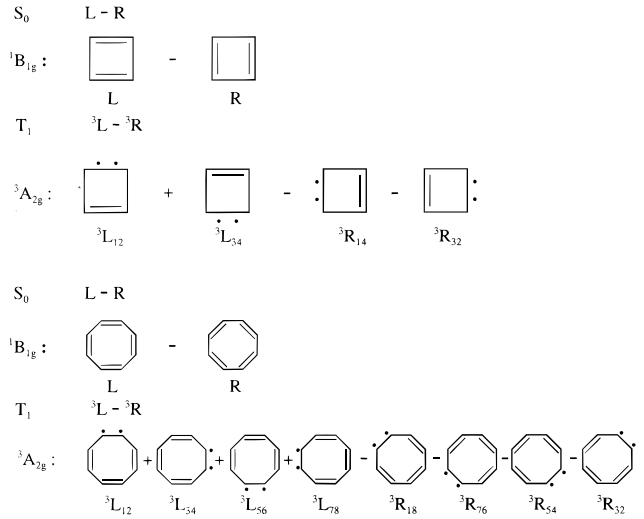

Figure 1. VB structures of the lowest lying singlet and triplet states of CB and COT.

2. Model

The model is based on the approach presented previously[20,22] for the singlet states. Consider a cyclic system having $2n$ equivalent bonds formed by singlet electron pairs. Examples are H_{2n} ($n = 2, 4, ...$) molecules, with $4n$ σ electrons, or $C_{2n}H_{2n}$ ($n = 2, 4, ...$), with $4n$ π electrons. As shown in Figure 1 of Paper 1, pairing of all the binding electrons can be achieved in two equivalent ways: using the H_{2n} system as an example, these are H_1H_2, H_3H_4, ..., $H_{2n-1}H_{2n}$ and H_1H_{2n}, $H_{2n-1}H_{2n-2}$, ..., H_3H_2. These two structures correspond to two VB Kekulé, which will be termed $|L\rangle$ and $|R\rangle$ and may be described by the shorthand notation introduced earlier:[20,22]

$$^1|L\rangle = (1\bar{2}-\bar{1}2)(3\bar{4}-\bar{3}4)...(2n-1\overline{2n}-\overline{2n-1}2n) \quad (1)$$

With L containing a normalization factor and all permutations over the atomic orbital wave functions i ($1 = 1, 2, ..., 2n$). Likewise, the other Kekulé wave function, $|R\rangle$, has the form

$$^1|R\rangle = (1\overline{2n}-\bar{1}2n)(2n-1\overline{2n-2}-\overline{2n-1}2n-2)...(3\bar{2}-\bar{3}2) \quad (2)$$

The actual wave function of the system is constructed from the combination of the two VB structures L and R. Two combinations are possible, an in-phase one, $L + R$, and an out-of-phase one, $L - R$. In the case of an even number of electron pairs (as pertains for the present case), the out-of-phase combination is the ground state.[20]

Triplet states are formed by inverting one of the spin functions in one of the electron pairs, keeping all others paired. There are n possible ways of doing this for each of the structures L and R of a cyclic molecule having $4n$ electrons, as exemplified in Figure 1 for cyclobutadiene (CB) and cyclooctatetraene (COT), giving a total of 4n possible structures. However, not all of them are independent.[23] The spin functions of the two electrons may be written as $\alpha\beta$-$\beta\alpha$ for the singlet state and $\alpha\alpha$, $\beta\beta$, and $\alpha\beta + \beta\alpha$ for the triplet, with α denoting spin 1/2 and β denoting spin $-1/2$. For comparison of the singlet and triplet states of the same configuration, it is convenient to use the $\alpha\beta + \beta\alpha$ triplet function, which in the absence of a magnetic field is degenerate with the other two.

Let us consider first the special case of CB (or any four-electron problem). This problem was extensively dealt with previously,[11,12,24] and is used as an example before discussing the general case. The L and R singlet functions may be written as

$$^1|L\rangle = (1\bar{2}-\bar{1}2)(3\bar{4}-\bar{3}4) = 1\bar{2}3\bar{4}-1\bar{2}\bar{3}4-\bar{1}23\bar{4}+\bar{1}2\bar{3}4 \quad (3)$$

$$^1|R\rangle = (1\bar{4}-\bar{1}4)(3\bar{2}-\bar{3}2) = 1\bar{4}3\bar{2}-1\bar{4}\bar{3}2-\bar{1}43\bar{2}+\bar{1}4\bar{3}2 = -1\bar{2}3\bar{4} + 12\bar{3}\bar{4}+\bar{1}\bar{2}34-\bar{1}2\bar{3}4 \quad (4)$$

so that

$$^1|L-R\rangle = 2(1\bar{2}3\bar{4}+\bar{1}4\bar{3}2)-1\bar{2}\bar{3}4-1\bar{2}3\bar{4}+1\bar{4}\bar{3}2+\bar{1}43\bar{2} \quad (5)$$

The two L triplets (see Figure 1) may be written as

$$^3|L_{12}\rangle = (1\bar{2}+\bar{1}2)(3\bar{4}-\bar{3}4) = 1\bar{2}3\bar{4}-1\bar{2}\bar{3}4+1\bar{2}3\bar{4}-\bar{1}2\bar{3}4 \quad (6a)$$

$$^3|L_{34}\rangle = (1\bar{2}-\bar{1}2)(3\bar{4}+\bar{3}4) = 1\bar{2}3\bar{4}+1\bar{2}\bar{3}4-1\bar{2}3\bar{4}-\bar{1}2\bar{3}4 \quad (6b)$$

and the two R triplets as

$$^3|R_{14}\rangle = (1\bar{4}+\bar{1}4)(3\bar{2}-\bar{3}2) = 1\bar{4}\,3\bar{2}-1\bar{4}\bar{3}2+\bar{1}43\bar{2}-\bar{1}4\bar{3}2 = -1\bar{2}\,3\bar{4}+12\bar{3}\bar{4}-\bar{1}2\bar{3}4+\bar{1}2\bar{3}4 \quad (7a)$$

$$^3|R_{32}\rangle = (1\bar{4}-\bar{1}4)(3\bar{2}+\bar{3}2) = 1\bar{4}\,3\bar{2}+1\bar{4}\bar{3}2-\bar{1}43\bar{2}-\bar{1}4\bar{3}2 = -1\bar{2}\,3\bar{4}-12\bar{3}\bar{4}+\bar{1}\bar{2}34+\bar{1}2\bar{3}4 \quad (7b)$$

It is easily seen that $^3|L_{12}\rangle + {}^3|L_{34}\rangle + {}^3|R_{12}\rangle + {}^3|R_{34}\rangle = 0$ so that only three of the four possible triplet structures are independent. In this special case, we find that the wave function corresponding to the out-of-phase combination $|L-R\rangle$ is

$$^3|L-R\rangle = {}^3|L_{12}\rangle + {}^3|L_{34}\rangle - {}^3|R_{14}\rangle - {}^3|R_{32}\rangle = 1\bar{2}3\bar{4}-\bar{1}2\bar{3}4 \quad (8)$$

The energy of this state is

$$E^3(L-R) = \langle 1\bar{2}3\bar{4}-\bar{1}2\bar{3}4|H|1\bar{2}3\bar{4}-\bar{1}2\bar{3}4\rangle \quad (9)$$

where H is the Hamiltonian of the system. It is seen to be a sum of terms

$$E(^3(L-R)) = 2Q - 2H_{\text{cyclic}} \quad (10)$$

where $Q = \langle 1\bar{2}3\bar{4}|H|1\bar{2}3\bar{4}\rangle$ is the Coulomb integral and $H_{\text{cyclic}} = \langle 1\bar{2}3\bar{4}|H|\bar{1}2\bar{3}4\rangle$.

The energy of the ground singlet state of square CB (which is a transition state) is given by[25,20]

$$E(^1(L-R)) = 2Q - 2H_{\text{cyclic}} + \sum_i K_{ii+1} + \text{higher exchange terms} \quad (11)$$

The exchange terms are of two kinds,[26,27] one-electron terms of the form $2S_{i,i+1}\langle i|h|i+1\rangle$, representing the attractive interaction between two nuclei and the electronic charge between them, and two-electron terms of the form $\langle i,i+1|g|i+1,i\rangle$ representing the repulsive interaction between two electron clouds. The former completely outweighs the latter, as well as the higher exchange terms involving nonadjacent electrons. Comparison of eq 10 and eq 11 shows that the singlet state is more stable than the triplet, *due to the attractive exchange terms*. This turns out to be a general property of the even parity systems, both singlet and triplet are stabilized by resonance interactions and the cyclic terms. However, *there is always an extra exchange stabilization of the singlet*.

We now turn to the general case. The L wave function is

$$^1|L\rangle = (1\bar{2}-\bar{1}2)(3\bar{4}-\bar{3}4)\ldots(2n-1\overline{2n}-\overline{2n-1}2n) = (1-p_{1,2})(1-p_{3,4})\ldots(1-p_{2n-1,2n})\mathbf{M} \quad (12)$$

where $\mathbf{M} = |1\bar{2}3\bar{4}\ldots 2n-1\overline{2n}|$ and $p_{i,j}$ the permutation operator exchanging the i and j electrons.

Therefore,

$$^1|L\rangle = \{I - \sum_{i=0}^{n-1} p_{2i+1,2i+2} + \sum_{i=0,j>i}^{n-3} p_{2i+1,2i+2}p_{2j+1,2j+2} - \ldots + p_{1,2}p_{3,4}\ldots p_{2n-1,2n}\}\mathbf{M} \quad (13)$$

where I is the identity permutation operator, the first summation is over two-electron permutations, the second over four, etc., and the last is the cyclic permutation. Let us denote by $\mathbf{W}$ the determinant obtained by permuting the spins of all electron pairs

$$\mathbf{W} = p_{1,2}p_{3,4}\ldots p_{2n-1,2n}\mathbf{M} = \bar{1}2\bar{3}4\ldots\overline{2n-1}2n \quad (14)$$

This allows a more compact and symmetric representation of $|L\rangle$, in which the maximum number of permutations is $n/2$ rather than n.

$$^1|L\rangle = \{I - \sum_{i=0}^{n-1} p_{2i+1,2i+2} + \sum_{i=0,j>1}^{n-3} p_{2i+1,2i+2}p_{2j+1,2j+2} - \ldots + (-1)^{n/2}\sum_{i<j\ldots<k} p_{2i+1,2i+2}p_{2j+1,2j+2}\cdots p_{2k+1,2k+2}\}(\mathbf{M}+\mathbf{W}) \quad (15)$$

The last term contains all ordered permutations that exchange $n/2$ electron pairs, starting from either $\mathbf{M}$ or $\mathbf{W}$. The symmetric form is possible since there is an even number of electron pairs so that the same permutations may be written either by starting from $\mathbf{M}$ or backward from $\mathbf{W}$. Thus, in a system with $2n$ electron pairs, we have $p_{1,2}\mathbf{M} = p_{3,4}p_{5,6}\ldots p_{2n-1,2n}\mathbf{W}$, $p_{1,2}p_{3,4}\mathbf{M} = p_{5,6}\ldots p_{2n-1,2n}\mathbf{W}$, etc.

A similar expression can be written for $|\mathrm{R}\rangle$

$$^1|R\rangle = (1\overline{2n}-\bar{1}2n)(2\mathrm{n}-1\overline{2n-2}-\overline{2n-1}2n-2)\ldots(3\bar{2}-\bar{3}2) = -(1-p_{1,2n})(1-p_{2n-1,2n-2})\ldots(1-p_{3,2})\mathbf{M} \quad (16)$$

This is possible since in the cyclic molecule atom 1 is connected to both atom 2 and atom $2n$. In this case, the permutation cycles are in the opposite sense to those used for the L structure (note the sign change[20]). R also may be expressed as a combination of $\mathbf{M}$ and $\mathbf{W}$:

$$^1|R\rangle = -\{I - \sum_{i=0}^{n(2n+1=1)} p_{2i+1,2i} + \sum_{i=0,j>i}^{n-2} p_{2i+1,2i}p_{2j+1,2j} - \ldots + (-1)^{n/2}\sum_{i<j<\ldots<k} p_{2i+1,2i}p_{2j+1,2j}\cdots p_{2k+1,2k}\}(\mathbf{M}+\mathbf{W}) \quad (17)$$

leading to

$$^1|L-R\rangle = \{2I - \sum_{i=1} p_{i,i+1} + \sum_{i=1,j>i} p_{i,i+1}p_{j,j+1} - \ldots + (-1)^{n/2}\sum_{i<j<\ldots<k} p_{i,i+1}p_{j,j+1}\cdots p_{k,k+1}\}(\mathbf{M}+\mathbf{W}) \quad (18)$$

For the triplet state, a typical VB structure has the form

$$^3|L_{12}\rangle = (1\bar{2}+\bar{1}2)(3\bar{4}-\bar{3}4)\ldots(2n-1\overline{2n}-\overline{2n-1}2n) = (1+p_{1,2})(1-p_{3,4})\ldots(1-p_{2n-1,2n})\mathbf{M} \quad (19)$$

in which the bond between atoms 1 and 2 was replaced by two electrons with parallel spin. We wish to cast this expression in a form similar to that of the singlet function. It is noted that the only difference between eq 12 and eq 19 is the plus sign in the first term. This means that whereas all n pairwise permutations appearing in the expression for the singlet L have the same sign, in the triplet function L_{12}, one will have the opposite sign. Since we wish to compare the singlet and triplet combinations, it is convenient to preserve the form of eq 13 by keeping the same number of pairwise permutations, (n in this case, thus having an extra permutation instead of one less), adding two permutations with the opposite sign to bring the total number back to the correct one. To keep the number of permutations down, we again write them out using the two cyclic permutations $\mathbf{M}$ and $\mathbf{W}$, obtaining

$$^3|L_{12}\rangle = -\{I + 2p_{12} - \sum_{i=0}^{n-1} p_{2i+1,2i+2} - 2p_{12}\sum_{i=0}^{n-1} p_{2i+1,2i+2} + \sum_{i=0,j>i}^{n-3} p_{2i+1,2i+2}p_{2j+1,2j+2} - \ldots + (-1)^{n/2}\sum_{i<j<k\ldots<n/2} p_{2i+1,2i+2}p_{2j+1,2j+2}\cdots p_{2k+1,2k+2}\}(\mathbf{M}-\mathbf{W}) \quad (20)$$

A similar expression can be written for all other $^3|\mathrm{L}\rangle$ triplet functions ($^3L_{34}$, ... $^3L_{2n-1,2n}$) and for the $^3|R\rangle$ functions ($^3R_{1,2n}$, $^3R_{2n-1,2n-2}$ ... $^3R_{32}$). Altogether, in a $4n$-electron system, there are $4n$ terms such as this (not all independent).

It will be convenient to use a shorthand notation, denoting the sum of all permutations exchanging one pair of electrons going clockwise around the ring by P_1, those exchanging two pairs by P_2, etc. There are $2n$ (n even) electron pairs in each of the structures L and R so that a maximum of n pairs can be exchanged. Using the two cyclic permutations $\mathbf{M}$ and $\mathbf{W}$ as the basis, eq 15 may be written as

$$^1|L\rangle = \{I - P_1 + P_2 - \ldots + (-1)^{n/2}(P_{n/2})\}(\mathbf{M}+\mathbf{W}) \quad (21)$$

and eq 17 as

$$^1|R\rangle = \{I - P_1^\circ + \mathrm{P}_2^\circ - \ldots + (-1)^{n/2}(\mathrm{P}_{n/2}^\circ)\}(\mathbf{M}+\mathbf{W}) \quad (22)$$

where P_1° denotes a permutation of i electron pairs going counterclockwise around the ring.

In this notation, the triplet wave functions may be written as the sums

$$^3|L\rangle = \sum_{t=0}^{n-1} {}^3|L_{2t+1,2t+2}\rangle = \left\{I - \frac{n-2}{n}P_1 + \frac{n-4}{n}P_2 - \ldots + \frac{n-n}{n}(P_{n/2})\right\}(\mathbf{M}-\mathbf{W}) \quad (23)$$

(The coefficient of the last permutation ($P_{n/2}$) vanishes; we wrote the expression explicitly to emphasize the form similarity to the singlet state function (eq 18)). Note that in the triplet, $\mathbf{M}$

and **W** appear with opposite signs, whereas in the singlet functions, they have the same sign. Also, the number of permutations is smaller for the triplet than for the singlet. For instance, the number of pairwise permutations is P_1 for the singlet and only $((n-2)/n)P_1$ for the triplet.

The triplet of the *R* structure can be written likewise as

$$^3|R\rangle = \sum_{t=0}^{n-1} {}^3|R_{2t+1,2t+2}\rangle = \left\{I - \frac{n-2}{n}P_1^\circ + \frac{n-4}{n}P_2^\circ - \ldots + \frac{n-n}{n}(P_{n/2}^\circ)\right\}(\mathbf{M}-\mathbf{W}) \quad (24)$$

The complete singlet wave function is therefore of the form

$$^1|L-R\rangle = N_s\{2I - (P_1 + P_1^\circ) + (P_2 + P_2^\circ) - \ldots (P_{n/2} + P_{n/2}^\circ)\}(\mathbf{M}+\mathbf{W}) \quad (25)$$

The triplet wave function is

$$^3|L-R\rangle = N_T\left\{2I - \frac{n-2}{n}(P_1 + P_1^\circ) + \frac{n-4}{n}(P_2 + P_2^\circ) - \ldots\right\}(\mathbf{M}-\mathbf{W}) \quad (26)$$

(N_S and N_T are normalization constants).

3. The Relative Energies of the Lowest Lying Singlet and Triplet States of an Even Parity Cyclic System

Equations 25 and 26 may be used to estimate the relative energies of the states $^1|L-R\rangle$ and $^3|L-R\rangle$. It was shown recently that the singlet (even though it is a transition state) is the ground state of this system.[20] By Hund's rule, the triplet state would be expected to have a lower energy. This would indeed be the case if the energies were determined solely by the leading term in eqs 25 and 26, namely the first term, as shown next

3.a. Contribution of the Identity Permutation. Under these conditions, the wave functions of the singlet and the triplet states are expressed as $\mathbf{M}+\mathbf{W}$ and $\mathbf{M}-\mathbf{W}$, respectively. The energies, apart from a normalization factor, are then, since $H_{\mathbf{MM}} = H_{\mathbf{WW}}$,

$$E(\mathrm{S}) = \langle L-R|H|L-R\rangle = \langle \mathbf{M}+\mathbf{W}|H|\mathbf{M}+\mathbf{W}\rangle = 2H_{\mathbf{MM}} + 2H_{\mathbf{MW}} \quad (27)$$

$$E(\mathrm{T}) = \langle {}^3(L-R)|H|{}^3(L-R)\rangle = \langle \mathbf{M}-\mathbf{W}|H|\mathbf{M}-\mathbf{W}\rangle = 2H_{\mathbf{MM}} - 2H_{\mathbf{MW}} \quad (28)$$

A typical matrix element of $H_{\mathbf{MW}}$ is of the form $\langle 1\bar{2}3\bar{4} \ldots 2n-12n|H|\bar{1}2\bar{3}4 \ldots \overline{2n-12n}\rangle$. The molecular Hamiltonian is written as $H = T + V$, where V, the interaction potential, contains terms involving interaction between the electrons and the nuclei ($V_{en} = -(Ze^2/R_{Ji})$, where Z is the charge on the Jth nucleus, and R_{Ji} is the distance between it and electron i, and between two electrons ($V_{ee} = e^2/r_{ki}$), with r_{ki} being the distance between the electrons i and k. These terms lead to two contributions to the exchange integral $H_{\mathbf{MW}}$.[26,27] The one-electron term, due to the attractive interaction between the electron in orbitals i and $i+1$ and the nuclei:

$$h_{i,i+1}(I) = \langle 1\bar{2}3\bar{4} \ldots i\overline{i+1} \ldots 2n-1\overline{2n}|Ze^2/R_{Ji}|\bar{1}2\bar{3}4 \ldots \bar{i}i+1 \ldots \overline{2n-12n}\rangle = S_{12}S_{23}S_{34} \ldots \langle ii+1\,|Ze^2/R_{Ji}|i+1\bar{\imath}\rangle \ldots S_{2n-2,2n-1}S_{2n-1,2n} = -2S_{12}S_{34} \ldots h_{i,i+1}S_{i,i+1} \ldots S_{2n-2,2n-1}S_{2n-1,2n} \quad (h_{i,j}S_{i,j} \neq 0 \text{ for } j = i \pm 1) \quad (29)$$

Here S_{ij} is the overlap integral between the (nonorthogonal) orbitals i and j. The sign change in the second to last line of eq 29 is due to the permutation of the electrons between orbitals i and $i+1$. Since $h_{i,i+1}$ represents an attractive interaction, its sign is negative, so that $h_{i,i+1}(I)$ provides a positive contribution to $H_{\mathbf{MW}}$.

The two-electron term is the usual exchange integral of the form

$$g_{ij}(I) = \langle 1\bar{2}3\bar{4} \ldots i\overline{i+1} \ldots 2n-1\overline{2n}|e^2/r_{ij}|\bar{1}2\bar{3}4 \ldots ii+1 \ldots \overline{2n-12n}\rangle = S_{12}S_{23}S_{34} \ldots \langle i\overline{i+1}\,|e^2/R_{ii+1}|\bar{\imath}i+1\rangle \ldots S_{2n-2,2n-1}S_{2n-1,2n} = S_{12}S_{34} \ldots g_{i,i+1}S_{i,i+1} \ldots S_{2n-2,2n-1}S_{2n-1,2n} \quad (30)$$

This term represents repulsive interaction (between two electron clouds) and is much smaller than the one-electron term so that $h_i(I)$ determines the sign of the combined effect of the two terms.

The upshot of this discussion is that as long as we consider only the contribution of the identity operators in eqs 25 and 26, the triplet state is lower in energy than the singlet, as predicted by Hund's rule.

3.b. Contribution of the Two-Electron Permutation Term $P_1+P_1^\circ$. Within the electron-pairing model, apart from the contribution of the identity permutation, the largest contribution to the stabilization energy of the system is due, by eqs 25 and 26, to terms such as $\langle I(\mathbf{M}+\mathbf{W})|H|(P_1+P_1^\circ)(\mathbf{M}+\mathbf{W})\rangle$, where $P_1+P_1^\circ$ exchanges one electron pair. For the singlet state, this term is of the form

$$\langle I(\mathbf{M}+\mathbf{W})|H|(P_1+P_1^\circ)(\mathbf{M}+\mathbf{W})\rangle \quad (31)$$

and for the triplet, a similar expression (except that the $\mathbf{M}-\mathbf{W}$ replaces $\mathbf{M}+\mathbf{W}$) is multiplied by $(n-2)/n$, see eqs 23 and 24.

To estimate the effect of these exchange terms, we note that the contribution of cross integrals such as $\langle \mathbf{M}|H|P_1\mathbf{W}\rangle$ may be neglected by comparison with the homogeneous ones such as $\langle \mathbf{M}|H|P_1\mathbf{M}\rangle$. This may be seen by considering the following typical terms.

For $\langle \mathbf{M}|H|P_1\mathbf{W}\rangle$ we have

$$\langle 1\bar{2}3\bar{4} \ldots i\overline{i+1} \ldots 2n-1\overline{2n}|H|P_1\bar{1}2\bar{3}4 \ldots \bar{i}i+1 \ldots \overline{2n-12n}\rangle = \langle 1\bar{2}3\bar{4} \ldots i\overline{i+1} \ldots 2n-1\overline{2n}|H|1\bar{2}\bar{3}4 \ldots \bar{i}i+1 \ldots \overline{2n-12n}\rangle = 1 \cdot \langle 3\bar{4} \ldots i\overline{i+1} \ldots 2n-1\overline{2n}|H|\bar{3}4 \ldots \bar{i}i+1 \ldots \overline{2n-12n}\rangle \quad (32)$$

This matrix element involves the interaction between two nonneighboring orbitals (3 and $2n$ in this case), which are neglected throughout the present paper, being much smaller than the interactions between neighboring orbitals.

A similar procedure for $\langle \mathbf{M}|H|P_1\mathbf{M}\rangle$ leads to

$$\langle 1\bar{2}3\bar{4} \ldots i\overline{i+1} \ldots 2n-1\overline{2n}|H|P_1\bar{1}2\bar{3}4 \ldots i\overline{i+1} \ldots 2n-1\overline{2n}\rangle = \langle 1\bar{2}3\bar{4} \ldots i\overline{i+1} \ldots 2n-1\overline{2n}|H|\bar{1}23\bar{4} \ldots i\overline{i+1} \ldots 2n-1\overline{2n}\rangle \quad (33)$$

which, by arguments similar to those used in the previous

subsection, leads to n terms of the form

$$h_i(P_1) = 2h_{ii+1}S_{i,i+1} + g_{ij} \quad (34)$$

Again the two-electron terms g_{ij} are much smaller than the one-electron ones so that, although they represent repulsive interaction, the combined effect of $h_i(P_1)$ is attractive. Note that this term is in general larger than the corresponding $h_i(I)$ (eq 29), which contains the product of a large number of overlap integrals (all smaller than unity).

With the neglect of the cross terms, we can estimate the energy difference between S_0 and T_1 as follows.

The energy difference between the singlet and the triplet is:

$$\Delta E(\mathrm{S-T}) = (2/n)\cdot\langle I(\mathbf{M})|H|(P_1+P_1^{\circ})(\mathbf{M})\rangle + (2/n)\cdot \langle I(\mathbf{W})|H|(P_1+P_1^{\circ})(\mathbf{W})\rangle = (2/n)\cdot 4\langle I(\mathbf{M})|H|P_1\mathbf{M}\rangle = (8/n)nh_{ii+1}S_{i,i+1} = 8h_{ii+1}S_{i,i+1} = 8h_i(P_1) \quad (35)$$

(n is the number of P_1 permutations, each contributing the same value).

The sign may be determined by the same arguments as presented in section 3.a, taking into account of the fact that h_i is negative and that each permutation changes the sign of the determinant. It is found that the singlet state is the more stable one. This result was obtained by Goddard and Voter in the special case of CB.[12] Therefore, their conclusion, namely "the dynamic spin polarization correlation effect is merely the static spin-pairing of bond orbitals impicit in resonating VB wave functions"; is actually applicable to all antiaromatic systems.

The following three comments are in order.

1. The stabilization of the singlet with respect to the triplet due to the P_1 contribution vastly outweighs the stabilization of the triplet due to the identity term. The latter is (eq 29)

$$h_{i,i+1}(I) = -2S_{12}S_{34}\ldots h_{i,i+1}S_{i,i+1}\ldots S_{2n-2,2n-1}S_{2n-1,2n}$$

which can be seen to be much smaller than $h_i(P_1) = h_{ii+1}S_{i,i+1}$, as each $S_{i,i+1}$ is less than 1 (a value of 1/4 is a reasonable estimate for cyclic conjugated hydrocarbons).

2. All higher terms, due to P_i, $i > 1$, are much smaller than the first correction, since two permutations lead to interaction terms between nonneighboring orbitals.

3. Summing over all n one-pair permutations, we see that ΔE(S−T) is essentially independent of n, i.e., the ring size. *This result predicts, therefore, that if indeed the one-pair permutation term is the dominant one, the singlet−triplet separation in all antiaromatic compounds will be the same.*

The ground singlet state, formed by the out-of-phase combination of the two Kekulé structures, transforms as a non-totally symmetric irreducible representation of the point group. As noted previously,[20,22] the most symmetric structure is a transition state for reaction along the Kekulé coordinate. The H_4 and H_8 systems were found to be useful model systems to check reactivity patterns; in the absence of other stabilizing effects (such as σ bonding in conjugated cyclic hydrocarbons), the "natural" reaction routes of are found by considering the normal modes. Thus, the Kekulé modes were found to yield two and four molecules from the S_0 state of H_4 and H_8, respectively.

In contrast with the ground state, the T_1 state cannot form dimeric H_2 molecules as the sole products. Two H atoms must be formed: it will dissociate to yield two atomic fragments and one or more molecular ones. The mode responsible for this reaction is the degenerate e_u mode. We have carried out quantum chemical computations on these two model systems, and as shown in the next section, all these predictions were corroborated. Computations were also made on several symmetric cyclic conjugated hydrocarbons, either single ring ones such as CB and C_8H_8 (cyclooctatetraene, COT) or bridged rings such as pentalene and heptalene. We find that all these predictions are indeed borne out by the computations. In the hydrocarbons, the triplet states are not dissociative, apparently due to the restraining σ bonds. However, the frequencies of the e_u modes that lead to reaction in the H_{2n} systems are found to decrease in T_1 compared to S_0 in the hydrocarbon molecules, indicating a decrease of the corresponding force constants.

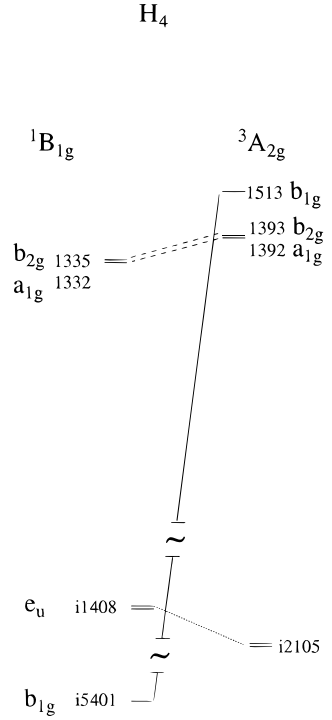

Figure 2. Schematic representation of the correlation between the frequencies calculated for H_4 in the S_0 and the T_1 states. Imaginary frequencies (indicating a transition state) are also shown and correlated. Only in-plane modes are shown.

4. Computational Results

The calculations were performed using the CAS (complete active space) method, with all π electrons and the same number of orbitals. To compare the different molecules on a common basis, the calculations were done with a relatively modest basis set (3-21G), yet these CAS(8,8) calculations (for the cases of COT and pentalene) and CAS(12,12) for heptalene are fairly extensive even with this basis set. Optimization was carried out under a symmetry constraint (D_{4h} symmetry for H_4 and CB, D_{8h} symmetry for H_8 and COT, D_{2h} symmetry for pentalene and heptalene). The geometries were optimized for all molecules in S_0 and in T_1, and vibrational analysis was done for all except heptalene. In S_0, the system is found in a transition state so that one or two of the normal modes have imaginary values. The symmetry constraints were removed or the normal mode analysis. The numerical values of some calculated properties (for instance, the vibrational frequencies) may be changed by using a larger basis set, but the trends, which are the main point of this paper, are not expected to vary.

TABLE 1: Calculated Properties of Some Even Parity Molecular Systems[a]

molecule[b]	CB	COT	pentalene	heptalene	H_4	H_8
ΔE(ST)[c] (eV)	0.55	0.75	0.67	0.67	0.44	0.58
r_{C-C} (Å) (r_{H-H} for H_n)						
1^1B_{1g}	1.459	1.404	1.433, 1.404, 1.509	1.394, 1.399, 1.417, 1.509	1.340	1.100
triplet[d] (min)	1.456	1.403	1.432, 1.405, 1.498	1.394, 1.398, 1.420, 1.501	1.280	1.082

[a] Calculations at the CAS(4,4) level for H_4, CB, at CAS(8,8) for H_8 COT, and pentalene, and at CAS(12,12) for heptalene, all using the GAMESS program suit. The basis set was 6-31G for H_4 and H_8, 4-31G for CB and pentalene, and 3-21G for COT and heptalene. [b] CB, cyclobutadiene; COT, cyclooctatetraene. [c] ΔE(ST) = the energy separation between the symmetric singlet at $\xi = 0$ ($^1B_{1g}$ symmetry) and the first triplet at its optimized geometry ($^3A_{2g}$ symmetry). [d] The symmetry of the first triplet is 1^3A_{2g} in the D_{4h} and D_{8h} point groups and 1^3B_{1g} in the D_{2h} point group.

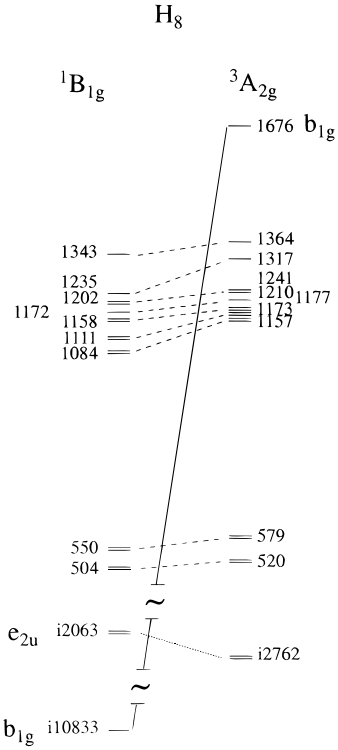

Figure 3. Schematic representation of the correlation between the frequencies calculated for H_8 in the S_0 and the T_1 states. Only in-plane modes are shown.

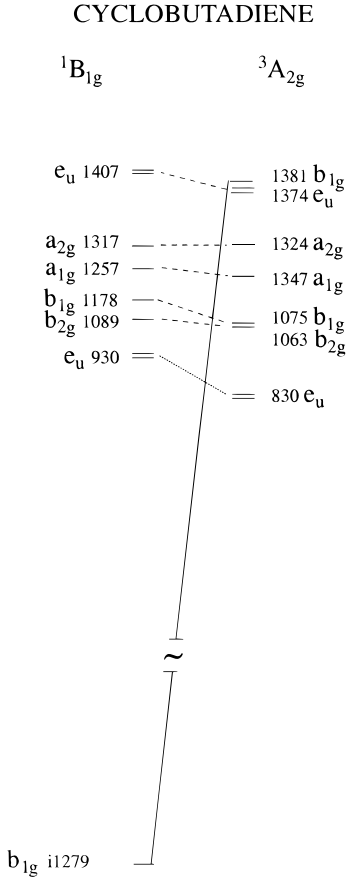

Figure 4. Schematic representation of the correlation between the frequencies (excluding CH stretch modes) calculated for CB in the S_0 and the T_1 states. Only in-plane modes are shown. Note the frequency decrease of the e_u mode in the triplet.

The relative energies of the two singlet twin states and the lowest triplet were previously reported for some of the molecules discussed in this paper.[22] It was found that the ground state transforms in all cases as the non-totally symmetric B_{1g} representation, as predicted by the twin-state model, and the triplet transforms as the A_{2g} representation (D_{4h} or D_{8h} point groups), or B_{1g} (D_{2h} point group). In Table 1 we summarize the computational results for the energies and the geometries of the S_0 (transition state, i.e., most symmetric form) and T_1 states of H_4, H_8, CB, pentalene, COT, and heptalene. It is seen that the equilibrium geometries of the symmetric forms of S_0 and T_1 are very similar for the hydrocarbons, while in the H_{4n} systems, there is a considerable bond contraction upon going from S_0 to T_1. ΔE_{ST} is quite small for all molecules and fairly constant (0.6 ± 0.15) throughout the series. Tables listing the calculated vibrational frequencies of the most symmetric form (transition state) of the lowest singlet and of the lowest triplet are available on request. It was found that the out-of plane vibrational frequencies for both states were essentially the same for a given molecule. The in-plane modes' frequencies (excluding CH stretch modes for the hydrocarbons) are shown in Figures 2−6. The imaginary frequencies are included in order to underline the similar trends found in all systems. The results indicate that in general very little change is found for most in-plane modes. In the H_{4n} species, there is a slight *increase* as the system changes from S_0 to T_1, while in the hydrocarbons the reverse is true. However, two sharp exceptions to that generalization are found for two in-plane modes, the Kekulé mode and an e_u mode leading to formation of two atoms in the case of H_4 and H_8. The frequencies of these vibrational modes were calculated to be imaginary, indicating a transition state. Figure 7 shows schematically the vector displacements of the atoms in the e_u modes of H_4 (or CB) and H_8 (or COT). In the hydrocarbons, dissociation along a similar coordinate is not possible due to the σ structure binding, but we find a distinct *decrease* in the frequency of corresponding vibrations. The change is most drastic in pentalene (from 1172 to 590 cm^{-1}, but is also considerable in COT (1446 to 1263 cm^{-1}) and CB (930 to 830 cm^{-1}), as seen from Figures 4−6.

Discussion

5.a. Energetics and Geometry of the Triplet State. It was shown previously that the ground singlet state of the most symmetric form of even parity systems is necessarily distortive

CYCLOOCTATETRAENE

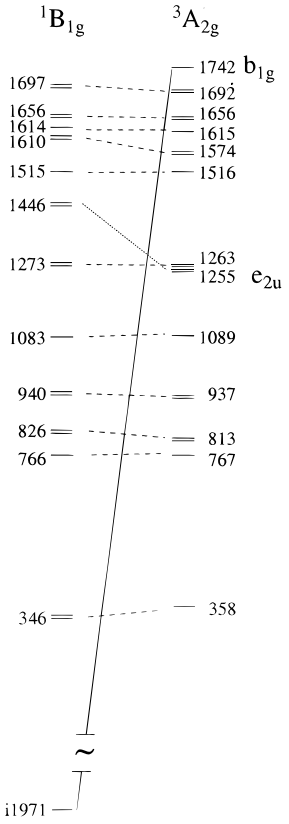

Figure 5. Schematic representation of the correlation between the frequencies (excluding CH stretch modes) calculated for COT in the S_0 and the T_1 states. Only in-plane modes are shown. Note the frequency decrease of the e_u mode in the triplet.

PENTALENE

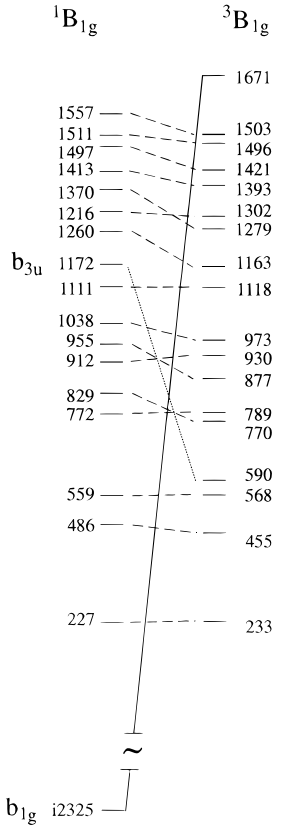

Figure 6. Schematic representation of the correlation between the frequencies (excluding CH stretch modes) calculated for pentalene in the S_0 and the T_1 states. Only in-plane modes are shown. Note the large frequency decrease of the e_u mode in the triplet.

along the Kekulé coordinate.[20] This tendency was ascribed to the fact that there are two "extra" electrons, which resonate with the other pairs but do not pair in the symmetric structure and tend to separate into two doublets or stabilize a distortive structure of bond-alternating nature. In the triplet, the most symmetric form can be maintained, since these two electrons cannot form a bond, losing their distortive power. Therefore, the system is now essentially an odd parity system, with an odd number of electron pairs. Such a system has a characteristic aromatic stabilization so that the lowest lying triplet is expected to have an aromatic character. This was indeed found to be the case by previous MO treatments,[28] but the physical basis, the permutational symmetry of the system leading to strong resonance stabilization between several VB structures (see Figure 1), was not explicitly stated.

The calculations show that the lowest lying triplet state is that due to the most symmetric possible structure. This is not necessarily the case, as comparison with odd parity cyclic (aromatic) systems shows; it is well-known that in those systems the lowest lying triplet is distorted away from the most symmetric structure. Thus, in benzene, the symmetric $^3B_{2u}$ is higher in energy than both distorted $^3B_{1u}$ and $^3E_{1u}$. This trend may be understood by reference to Figure 8. In a triplet state, the two unpaired electrons tend to move apart as far as possible, as requested by the Pauli principle. In benzene, for instance, this is easily achieved by having the two electrons in the para positions and stretching the molecule as shown in Figure 8a. This entails losing a C_3 symmetry axis and keeping the remaining two double bonds equivalent parallel to the new C_2 axis. Using the example of COT (Figure 8c), it is shown that a similar distortion in an even parity system is not possible without a considerable energy increase; lacking an odd parity symmetry axis, one has to destroy an even parity axis, necessarily creating a considerably longer new bond. Such a triplet state is expected to be of higher energy that the symmetric one discussed above. The e_u distortion shown in Figure 8b largely preserves the equilibrium bond lengths of the singlet ground state.

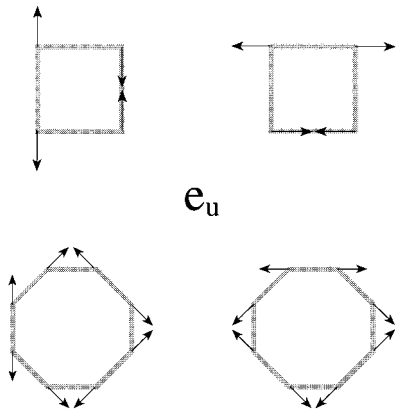

Figure 7. Vector displacements of the e_u modes of H_4 and H_8 in the singlet and triplet states (schematic). Similar displacements are found for the carbon skeleton of CB and COT, respectively.

According to eq 15, the main contribution to the energy difference $\Delta E(S-T)$ between S_0 and T_1 is the exchange integral

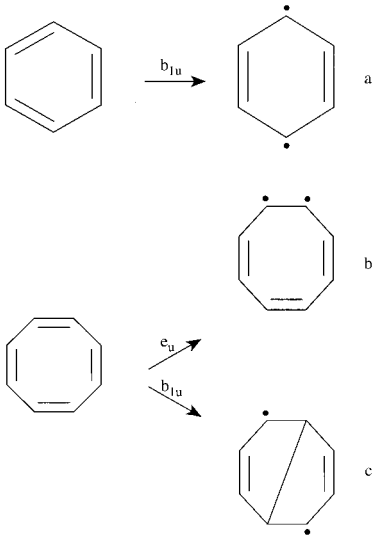

Figure 8. Effect of b_{1u} distortion on the shape of the triplet states of (a) benzene (an odd parity system having a C_3 symmetry axis) and (c) COT (an even parity system that does not). The latter unavoidably involves a large energy destabilzation due to the formtion of a "long" bond. An e_u displacement of COT, in which no excessive bond stretching is required, is shown in (b) for comparison.

$h_i(P_1)$. The computational results confirm the prediction of almost constant ΔE(S−T) for all molecules studied, with an average value of about 0.6 eV.

5.b. Reactivity Patterns of the Triplet State. The A_{2g} triplet states of the antiaromatic molecules have a biradical character, as does the lower lying singlet state. We have shown earlier that the singlet tends to distort along the Kekulé mode;[20] this tendency is completely absent in the low lying triplet. It is found that all triplet states are stable, as shown by the fact that all vibrational frequencies are real. This finding is in accord with the present model. The two nonbonding electrons tend to be spread out over the entire molecular frame. The chemical behavior of the system is revealed in the H_{2n} systems, which are "bare-bones" ones; the stability of the bonds depends solely on the n electron pairs considered in the model. (In the antiaromatic hydrocarbons, the σ CC bonds may counteract their possible pristine effects).

As shown in Figure 2, both the $^1B_{1g}$ and the $^3A_{2g}$ states of H_4 are dissociative. The first dissociates along the Kekulé coordinate forming two H_2 molecules (a b_{1g} mode) and also into one H_2 molecule and two H atoms (an e_u mode). The second dissociates only along the e_u coordinate only. This is a manifestation of the inherent force field of the triplet state; the system tends to form radical centers (doublets). Moreover, the reaction takes place in the plane of the molecule. The reason that the triplet state does not tend to form two new bonds is clear; the two parallel electrons cannot form a single bond. In a larger system (such as H_8), an out-of-plane distortion becomes more likely. However, as Figure 3 shows, the only dissociative mode of the triplet is again an in-plane e_u one.

Since the symmetry properties of the $4n$ electrons in the hydrocarbons are the same as those of the H_{4n} systems, the reaction modes are expected to be of the same symmetry. Indeed, it is found that reaction patterns revealed in the H_{4n} systems are repeated in the even paired cyclic hydrocarbons in both singlet and triplet states. Thus, in COT, the ground-state D_{8h} form distorts first to D_{4h} symmetry along the b_{1g} mode. This forms the bond-alternating structure, which can now bend due to the presence of weaker single CC bonds along the perimeter. In contrast, the triplet state of COT will tend to distort along an e_u mode, just like that of H_8. This is evident from the fact that while the frequencies of all other vibrational modes are essentially equal in the $^1B_{1g}$ and the $^3A_{2g}$ states, this mode's frequency decreases appreciable in the triplet state in comparison with the B_{1g} ground state (from 1446 to 1263 cm^{-1}). Similar frequency decreases were calculated for CB and pentalene for this mode.

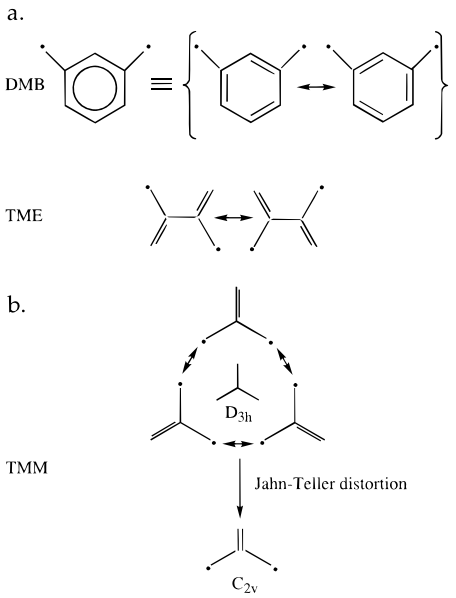

Figure 9. (a) VB structures of DMB and TME radicals; there are two for DMB, but the two nonpaired electrons do not resonate with the ring electrons. In TME, the two electrons are part and parcel of the two resonating structures. Hund's rule holds for DMB but not for TME (see text). (b) VB structures of TMM radicals; there are three for the symmetric form. Since it is genuinely degenerate, having a C_3 symmetry axis, Jahn−Teller (JT) distortion leads to a single C_{2v} structure so that Hund's rule holds.

5.c. Singlet−Triplet Ordering in Other Biradicals. Antiaromatic molecules are one example of biradicals, molecules in which the energy difference between S_0 and T_1 is small. Since spectroscopic transitions between the singlet and triplet systems are very weak and practically unobservable, the energy ordering of these two states has often been a matter of dispute. The electron photodetachment method makes it possible to observe both low lying states in the gas phase and provides a growing database for comparison with theory. For instance, it is found that 1,3-dimethylenebenzene (DMB) has a triplet ground state,[29] while tetramethyleneethane (TME) has a singlet ground state.[18] These results are readily explained within the present model (Figure 9) by noting that in DMB the two nonpaired electrons do not resonate with the others and Hund's rule holds as is well-known for other nondegenerate systems such as atoms and linear molecules (O_2, NCN). In contrast, TME is a genuine two-state system as shown in Figure 9; the two nonpaired electrons are part of the resonating two-state structures, and therefore, our model predicts that the singlet state is of lower energy, in agreement with experiment.

The trimethylenemethane (TMM) biradical is also found to have a triplet ground state;[30] this is explained by noting that TMM has a 3-fold axis, and therefore, a symmetric form would be genuinely degenerate (E_u symmetry). By the Jahn−Teller theorem, it distorts to a C_{2v} symmetry, for which there is only one VB structure, a case in which Hund's rule holds. Thus, the model provides a simple criterion for determining the relative singlet−triplet ordering for any biradical.

Summary

The main result of this paper is that, in all antiaromatic molecules, Hund's rule is not expected to hold; in the most symmetric form the singlet is of lower energy than the triplet. This result, which was previously obtained for CB, is shown here to be of a general nature. It arises from the fact that the system can be represented by two equivalent structures and from permutational symmetry arguments. This result holds for any even parity system, such as perpendicular ethylene and many other biradicals. This theoretical prediction was recently substantiated by photoelectron detachment experiments.

In antiaromatic (even parity cyclic) systems, the ground singlet state of the most symmetric structure has an "extra" electron pair that cannot participate in stabilizing two-electron bonds. It therefore imparts a biradical character to the molecule. Moreover, the singlet system can stabilize by distorting along the Kekulé mode. This stabilization is not possible in the triplet (the parallel spin electron pair cannot form a bond). Therefore, the triplet dissociates into atomic fragments in the case of H_4 and H_8, whereas the singlet dissociates into hydrogen molecules. In the hydrocarbons, the σ frame keeps the triplet bound and the dissociation tendency is expressed in the reduction of the force constant (and frequency) in the corresponding normal modes. Thus, in the even parity conjugated hydrocarbons, the symmetric triplet is bound and, being very close to the singlet ground state, is the lowest lying bound excited state of the system.

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