# Two-State Model of Antiaromaticity: The Low Lying Singlet States

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Aromatic and antiaromatic compounds are resonance hybrids of two cyclic covalent Kekulé structures. In both, two combinations can be formed, an in-phase and an out-of-phase one. In aromatic compounds having an odd number of conjugated double bonds, the in-phase combination is the ground state and the out-of-phase one is an excited state. In antiaromatic compounds, having an even number of conjugated electron pairs, the situation is reversed; the ground state is formed by the *out-of-phase combination*. This causes the ground state of these molecules to be a non-totally symmetric one, which in turn means that it has a biradical character. Moreover, the out-of-phase combination is necessarily unstable, being a transition state between the two bond-alternating Kekulé structures. By comparison to noncyclic biradicals such as perpendicular olefins, the antiaromatic cyclic structures are strongly stabilized, reducing the activation barrier from around 50−60 kcal/mol to around 3−5 kcal/mol. Therefore, the bond-alternating structures are easily interconverted at ambient temperatures and in the process acquire biradical character, making them highly reactive and difficult to synthesize. The in-phase combination of the two Kekulé structures is a strongly stabilized totally symmetric excited state which has a similar geometry to that of the ground transition state.

## 1. Introduction

The term “antiaromatic” is applied to cyclic hydrocarbon compounds having an even number of double bonds that alternate with single bonds. These compounds, having $4n$ $\pi$ electrons have captured the imagination of organic chemists over the years because of their apparent similarity to the stable aromatic ($4n + 2$ $\pi$ electrons) systems. They have repeatedly resisted synthesis, but eventually several were prepared. Rather than having a highly symmetric structure, however, they were generally found to be distorted. The most common distortion is bond length alternation, as in linear polyenes. Two equivalent distorted structures are found, with the symmetric form being a transition state between them. By comparison to polyolefins, they are invariably highly reactive or unstable and therefore difficult to handle. Therefore, only few definitive structure determinations are available for the parent molecules.[1] Substitution by bulky groups, such as *tert*-butyl, appears to stabilize them, leading to solid structural data for a few compounds. The highly reactive character of the experimentally observed molecules is somewhat surprising; it is known that aromatic molecules tend to be symmetric, and theory contrasts them with their symmetric antiaromatic counterparts. These structures are known to be distortive. The distortion is supposed to stabilize them; why then do they not become as stable as open regular bond-alternating olefins once they are distorted? Apparently, instability is somehow retained despite the distortion. An interesting feature common to many is a very broad electronic absorption spectrum,[2] extending from the UV to the visible and in some cases (*s*-indacene derivatives[3]) to the near IR.

Early on, molecular orbital (MO) theory of monocyclic antiaromatic compounds, based on a simple perfect polygon model,[4−6] was used to show that the systems are expected to have a biradical nature. In these models, the highest occupied MO is degenerate, although the ground state is not. Pseudo Jahn−Teller theory was invoked to explain the distortive nature of these systems. However, it was soon shown that MO models using one configuration are unable to reproduce the properties of the symmetric structure, and all modern calculations employ some form of configuration interaction. These calculations have revealed that the (symmetric form) ground states of cyclobutadiene (CB)[7] and cyclooctatetraene (COT)[8] transform as one of the non-totally symmetric irreducible representations (irrep) of the point group. The reaction coordinate, $\xi$, along which one of the distorted structures converts to the other also transforms as the same irrep. Valence bond (VB) calculations reached the same conclusion.[9,10] A characteristic result of these calculations is the existence of a low lying singlet excited state transforming as the totally symmetric irrep and having the geometry of the symmetric form at a rather low energy (1.5−2 eV) above the ground state. Calculations show that this excited state is strongly bound for motion along the reaction coordinate, which becomes a normal vibrational mode with an unusually high frequency. In addition, a very low lying triplet state is calculated to lie at about 0.5 eV above the ground state. Since the ground state is found to have a biradical singlet character, Hund’s rule appears to be violated in this case. This apparent discrepancy was extensively discussed in the literature.[5,8,10,11]

Extending MO theory to polycyclic antiaromatic compounds, such as pentalene and heptalene, leads to more difficulties. In these systems, simple MO theory predicts a closed shell in which all orbitals are nondegenerate and doubly occupied. Therefore the single configuration approximation necessarily predicts a totally symmetric ground state. To account for the fact that it transforms as one of the non-totally symmetric irreps, configuration interaction (CI) must be invoked. Such high level calculations indeed reveal the correct character of the distortive ground state. Nonetheless, calculations assuming a single configuration that attempt to account for the pseudo Jahn−Teller distortion still appear in the literature.[12] *Indeed, MO theory does not explain why CI in this case changes dramatically the*

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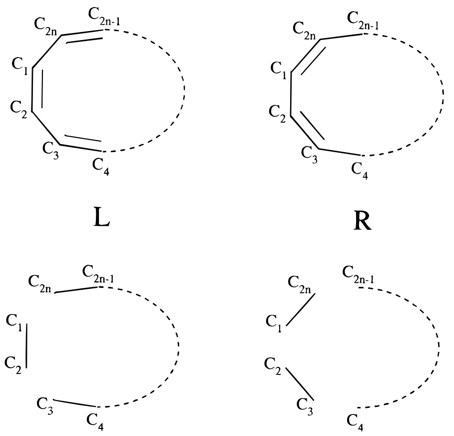


**Figure 1.** Diagram of a cyclic $C_{2n}H_{2n}$ hydrocarbon with alternating bond lengths. The lower scheme shows the spin-pairing pattern for the two possible Kekulé structures.

*symmetry characteristics of these systems*, while, for instance in the case of polycyclic aromatic compounds (such as naphthalene), a single configuration provides the correct result, and CI is used only to achieve better quantitative agreement with experiment.

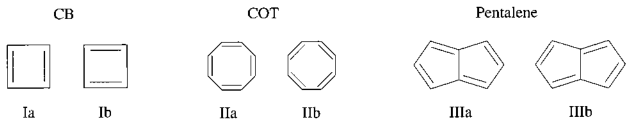
Around 1950, Craig addressed this issue and proposed a criterion for distinguishing between aromatic and antiaromatic compounds. He showed, using MO considerations, that the ground state wave functions of antiaromatic compounds are not totally symmetric. He pictorially explained this result by using Kekulé VB structures but erroneously proposed that the ground state is the in-phase combination of two Kekulé structures and the excited state is the out-of-phase combination. As we showed recently,[13] a simple VB analysis shows that the ground state is formed by the out-of-phase combination and the excited state by an in-phase one. Craig proceeded to propose a criterion that will enable the nonspecialist to decide for any given cyclic molecule whether it is aromatic or antiaromatic. The mathematical basis of this criterion was later developed by Klein,[19] who also discussed its limitations. Unfortunately, it does not always lead to a unambiguous result, as shown by Murrell et al.,[14] where a lucid exposition of Craig's method is given.

In this paper, we propose a very simple and straightforward criterion that can be used without applying complicated calculations. This criterion is based on VB structures that are based on the tendency of electrons to pair in chemical bonds. In particular, we show that all properties of antiaromatic compounds can be accounted for using a model based on the premise that the symmetric form of these $4n$ $\pi$ electron cyclic compounds can be represented by an out-of-phase combination of two Kekulé-type VB structures shown in Figure 1. The in-phase combination forms the excited state mentioned in the previous paragraph. The model was recently presented at length[13b] so that only its basic highlights will be repeated here in Section 2, which also discusses the symmetry properties of the systems. In Section 3, we present computational support for the model, and in Section 4, we discuss the high reactivity of the distorted cyclic antiaromatic hydrocarbons and the related $H_{2n}$ systems and how they are explained by the model. Examples demonstrating the applicability of the criterion based on the model are presented in Section 5.

## 2. Model

We term cyclic conjugated hydrocarbons having $4n + 2$ $\pi$ electrons as odd parity systems and those with $4n$ $\pi$ electrons as even parity ones, denoting the number of $\pi$ electron pairs that can be formed in them. Our model is based on a single premise, the tendency of electrons to pair in chemical bonds. This renowned G. N. Lewis hypothesis[15] has been later supported by extensive quantum mechanical arguments. The model is presented using valence bond (VB) terminology, based on the method developed by Pauling and Wheland.[16,17] It is well-known that classical VB theory cannot account for antiaromaticity, for instance in accounting for Hückel's celebrated $4n + 2$ vs $4n$ rules. The important work of Oosterhoff and co-workers,[18] Klein,[19] and Malrieu[20] extended the theory and provided better insight. A succinct account given by Kuwajima[21] summarizes the current state of the art, but there is still a lack of a clear physical picture of the nature of aromaticity and antiaromaticity.

**SCHEME 1**



We consider a hydrocarbon consisting of one ring (or more, see below) of the general formula $C_{2n}H_{2n}$ ($n \geq 2$) and explore the possibility of forming a symmetric form of this molecule. The basic assumption of the model is that the system will tend to form as many valence electron pairs between the atoms as possible. In the present case, this assumption leads to the formation of $\sigma$ bonds between one carbon atom and one hydrogen atom and between adjacent carbon atoms. These bonds account for the one 1s hydrogen electron and three of the four carbon $2s^2 2p^2$ electrons. The $2n$ remaining valence electrons can form $\pi$ bonds between neighboring carbon atoms or longer bonds between nonadjacent atoms. The latter option leads to higher energy systems and is rejected. As seen from Figure 1, there are two ways of pairing the $\pi$ electrons. Starting with, say, $C_1$, a $C_1C_2$ bond may be formed and, going clockwise, bonds $C_3C_4$, $C_5C_6$, etc., up to $C_{2n-1}C_{2n}$. Alternatively, going counterclockwise from $C_1$, the $C_1C_n$ bond is formed, etc., concluding with the $C_2C_3$ bond. These two options lead to two degenerate structures, which may be written in VB language as the "Kekulé" structures **Ia** and **Ib** shown for cyclobutadiene (CB), **IIa** and **IIb**, shown for cyclooctatetraene (COT), and **IIIa** and **IIIb** for pentalene, see Scheme 1. The model applies also to polycyclic systems, such as pentalene, as long as only two equivalent electron-pairing arrangements are possible.

Since the two electron-pairing arrangements are equivalent, the desired system is likely to be constructed from a linear combination of the two, with equal coefficients. Let the clockwise arrangement be described by a VB function $|L\rangle$ and the counterclockwise one as $|R\rangle$.

The $|L\rangle$ and $|R\rangle$ wave functions are written in the standard fashion:

$$L = \sum_p \epsilon_p P 1(1)2(2) \ldots 2n(2n)\, [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \times [\alpha(3)\beta(4) - \beta(3)\alpha(4)] \ldots [\alpha(2n-1)\beta(2n) - \beta(2n-1) \times \alpha(2n)] \quad (1)$$

$$R = \sum_p \epsilon_p P 1(1)2(2) \ldots 2n(2n)\, [\alpha(1)\beta(2n) - \beta(1)\alpha(2n)] \times [\alpha(2n-1)\beta(2n-2) - \beta(2n-1)\alpha(2n-2)] \ldots [\alpha(3)\beta(2) - \beta(3)\alpha(2)] \quad (2)$$

where the summation is over all $2n!$ permutations $p$ each with parity $\epsilon_p$. We use a short hand notation

$$L = (1\bar{2}-\bar{1}2)(3\bar{4}-\bar{3}4)\ ...\ (2n-1\overline{2n}-\overline{2n-1}2n) \qquad (3)$$

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

$$R = (1\overline{2n}-\bar{1}2n)(2n-1\overline{2n-2}-\overline{2n-1}2n-2)\ ...\ (3\bar{2}-\bar{3}2) \qquad (3')$$

The actual wave function of the system is constructed from the combination of the two VB structures $L$ and $R$. Since we are looking for a symmetric molecule, two combinations are possible, an in-phase one $L + R$, and an out-of-phase one $L - R$. Their energies are given by

$$E^{\pm} = \frac{H_{LL} + H_{RR} \pm 2H_{LR}}{2 \pm 2S_{LR}} \qquad (4)$$

According to eq 4, if $H_{LR} < 0$, the ground state will be the in-phase combination, and the out-of-phase one will be an excited state. On the other hand, if $H_{LR} > 0$, the ground state will be the out-of-phase combination, while the in-phase one, which transforms as the totally symmetric irreducible representation (irrep) of the point group, is an excited state. This conclusion is far reaching, since it means that the electronic wave function of the ground state is nonsymmetric in this case, in contrast with common chemical intuition. We show that when an even number of electron pairs is involved, this is indeed the case so that the ground state is not stable as a symmetric species. In fact, the symmetric species is a transition state, and the stable structure of the molecule is distorted.

This was shown in ref 13b by evaluating the matrix element $H_{LR} = \langle L|H|R\rangle$. In classical VB theory, this term was written as (omitting the normalization constant)

$$H_{LR,\mathrm{CL}} = (-1)^{n-1}2\{Q + K_{12} + K_{23} + ...\ K_{ii+1} + ...\ K_{2n1} + \text{higher exchange integrals}\} \qquad (5)$$

where the Coulomb integral $Q = \langle 1\ \bar{2}\ 3\ \bar{4}\ ...\ 2n-1\ \overline{2n}|H|1\ \bar{2}\ 3\ \bar{4}\ ...\ 2n-1\ \overline{2n}\rangle$ and $K_{ij}$ are exchange integrals containing terms such as $\langle i,i+1|g|i+1,i\rangle + 2S_{i,i+1}\langle i|h|i+1\rangle$.[22] The second term, representing the attractive interaction between two nuclei and the electronic overlap charge between them, is the dominant one and completely outweighs the first repulsive term. $K_{i,i+1}$ therefore has the same sign as the Coulomb integral $Q$. (For the details of the derivation, see the treatment given by Eyring, Walter, and Kimball for the special cases of four- and six-electron systems in Chapter 13 of ref 23).

In eq 5, $H_{LR,\mathrm{CL}}$ is the cross term obtained by classic VB theory,[16] in which only contributions from electron pairwise transposition permutations were considered. In particular, higher permutations, including the cyclic ones, were neglected. Bonding in these systems is due mainly to the exchange integrals $K_{i,i+1}$ between orbitals in the same cycle.[22] Pauling[16] showed that the most important contributions are due to neighboring orbitals, justifying the neglect of the smaller terms in eq 5. His paper does not explicitly mention the contribution of the cyclic permutations, although they are also due to neighboring orbitals.

Within the classical treatment, it was shown[13b] that the sign of the Coulomb integrals is different for odd and even systems. In the former, the Coulomb integrals contribute together $2Q$. While for the latter, the total contribution to the energy is $-2Q$. Since $Q$ is negative, and $H_{LR,\mathrm{CL}}$ for the ground state must have a negative sign, it follows that the ground state for the odd parity systems is the in-phase combination, while for even parity systems, the out-of-phase wave function is the ground state.

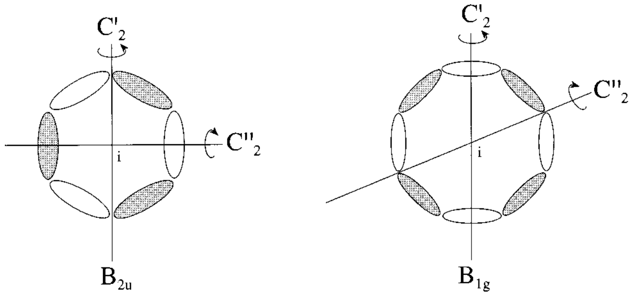


**Figure 2.** Twin state model: the symmetry characteristics of the out-of-phase combination of the two Kekulé structures in even and odd parity cyclic systems. They are represented by six and eight carbon atom rings, respectively. In both systems, the wave function has a node at the location of the carbon atoms. The change of sign is symbolized by the difference shading of the electron density amplitude. The wave function is obviously an ungerade one in the odd systems and a gerade one in the even systems. In the odd systems, the wave function changes sign upon rotation around the $C_2'$ axis running through the atoms and maintains its sign upon rotation around the $C_2''$ axis, which runs through the bond centers. This function therefore transforms as the $B_{2u}$ irrep. In the even parity case, the wave function has $B_{1g}$ symmetry in the usual axis convention.

We suggest that this difference is the basic origin for the characterization of aromaticity and propose a practical definition of an antiaromatic system: *it has a ground state that may be constructed from the out-of-phase combination of two bond-alternating even parity cyclic VB structures (even parity Kekulé structures)*. It will usually transform as one of the non-totally symmetric irreducible representations (irreps) of the relevant point group. This result, which was previously obtained[9,10] for the special cases of cyclobutadiene and cyclooctatetraene, is actually of a general nature. The in-phase combination transforms as the totally symmetric irrep but is an excited state. Thus, the symmetric antiaromatic molecules *always have a nonsymmetric electronic ground state wave function*.

It is recalled that as long ago as 1951, Craig[24] showed that the ground state of square cyclobutadiene, and by implication other even parity molecules, has a ground state that does not transform as the totally symmetric irrep. He showed that this state and the first excited singlet are represented by the in-phase and out-of-phase combinations of two Kekulé structures. Unfortunately, he assigned the ground state to the in-phase combination. In any case, Longuett-Higgins[25] correctly noted that even if the ground state is asymmetric there is no obvious reason why asymmetry would destroy the stability of the molecule. As we have shown, the instability is in fact a fundamental property of this system, arising from the permutational symmetry requirements.

**2.a. Corollary: Symmetry Properties of Aromatic and Antiaromatic Systems.** The in-phase combination of the two Kekulé structures transforms as the totally symmetric irrep. The out-of-phase one transforms as a $b_2$ or $b_{2u}$ one for the odd systems and as a $b_1$ or $b_{1g}$ one for the even ones. This is readily verified by considering each individual case, but the special cases of perfect polygons illustrate the point and provide a justification for the even−odd terminology. In the even paired polygons (having 4, 8, ... sides), the out-of-phase wave function transforms as a gerade or even state as can be verified by inspection of the signs of the wave function (Figure 2). This can be traced to the fact that in this system there are only even-fold axes of rotation. On the other hand, for odd paired polygons (having 6, 10, ... sides and at least one odd-fold axis

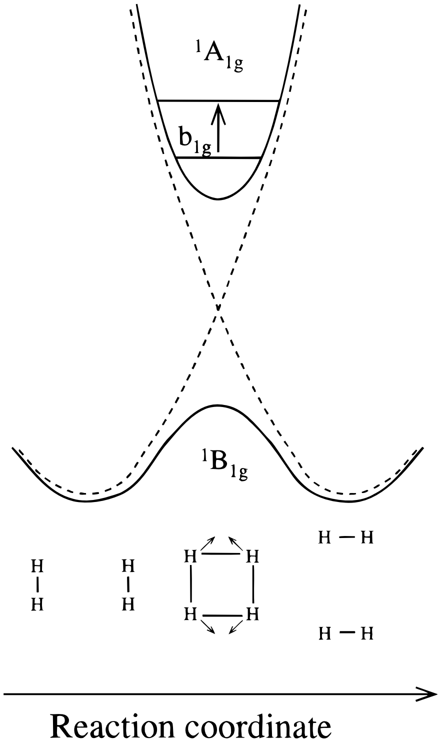


**Figure 3.** Avoided crossing model energy diagram of the $H_2 + H_2$ transposition reaction along the Kekulé reaction mode, $\xi$. The calculated (CAS (4,4), 6-31G) imaginary frequency of the $B_{1g}$ transition state is i5400 cm$^{-1}$, and the exalted $b_{1g}$ frequency in the excited state is 1574 cm$^{-1}$.

of rotation), the out-of-phase wave function is an ungerade one. The same figure shows that the even system belongs to a $B_1$ symmetry type and the odd system belongs to a $B_2$ one.

## 3. Computational Examples

We have used the CAS method[26] to calculate the properties of the ground state and the $1^1A_g$ excited state of three prototype even parity systems, CB, COT, and pentalene. In addition, the properties of the $H_2 + H'_2 \rightarrow HH' + HH'$ system, in which two hydrogen molecules exchange atoms via a square transition state, were calculated. As discussed below, this even parity system is also antiaromatic in the sense used in this paper. In particular, we were interested in the energy gap between the two states as the system moves along the coordinate $\xi$ that transforms the $L$ bond-localized form to the $R$ one. In the ground state (the out-of-phase combination), this mode is a reaction coordinate, having an imaginary frequency at $\xi = 0$, while in the excited state (the in-phase combination), it is a high-frequency vibrational mode (the Kekulé mode). Figure 3 shows the avoided crossing scheme for square $H_4$ and the form of the Kekulé mode. For any even parity molecule, the vector displacements of the atoms in this mode are calculated to be almost identical in the two states, as expected from the model.

Table 1 lists the results for the four molecules. The energy gap is systematically lower for the odd parity molecules compared to the even parity ones, for which it is about 5 eV,[13] and the frequency of the exchanging mode is much larger for the even parity systems than for the odd parity ones. For comparison with possible future experiments, we list also normalized frequencies for the excited states, which were scaled by 0.87 (a value obtained from the experimental result for benzene).

## 4. Discussion

**4.a. General Comments.** The essential parts of the model are the facts that electrons tend to be paired in covalent chemical bonds, that the systems in question have to be considered as two-state systems, and that avoided crossing[27,28] leads to the formation of two twin states. The properties of antiaromatic molecules are essentially due to the even parity of the system. The fact that it was found for conjugated hydrocarbons is not fundamental. Therefore, the conclusion of ref 29a that the antiaromaticity of cyclobutadiene arises from the $\sigma$ frame ring strain may be correct, but is not of a basic nature. Indeed, pentalene is also antiaromatic, while ring strain is practically unimportant. Of more fundamental importance is the fact that any attempt to assign the ground symmetric form of even parity systems to the totally symmetric irrep is bound to fail *as long as this ground state is primarily of covalent nature, as it appears to be in all known hydrocarbons*. (Other systems, such as $(SiH)_n$ molecules, may be mostly ionic and require a different approach).

Since the symmetric form belongs to non-totally symmetric irreps in the ground state, it cannot be represented by a single determinant. This conclusion was arrived at by considering

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

| molecule[b] | CB | COT | pentalene | $H_4$ |
|---|---|---|---|---|
| energy of $1^1B_{1g}$ state (H) | −152.833 64 | −305.894 50 | −304.730 14 | −2.064 91 |
| $\Delta E^c$ (eV) | 2.4 | 1.5 | 3.1 | 4.13 |
| $\Delta E(S-T)^c$ (eV) | 0.55 | 0.75 | 0.67 | 0.44 |
| $r_{C-C}$ (Å) ($r_{H-H}$ for $H_4$) | | | | |
| $1^1B_{1g}$ (TS) | 1.459 | 1.404 | 1.433, 1.404, 1.509[d] | 1.340 |
| $1^3B_{1g}$ or $1^3A_{2g}{}^e$ (min) | 1.456 | 1.403 | 1.432, 1.405, 1.498 | 1.280 |
| $1^1A_{1g}$ (twin, min) | 1.466 | 1.404 | 1.428, 1.405, 1.502 | 1.142 |
| frequency[f] (cm$^{-1}$) | | | | |
| ground state | i1278 | i1970 | i2325 | i5400 |
| twin state, cal[g] | 2098 | 2863 | 2880 | 1574 |
| twin state, nor[g] | 1825 | 2491 | 2506 | 1369 |
| distortion energy[h] (eV) | 0.29 | 0.22 | 0.42 | 6.3 |

[a] Calculations at the CAS(4,4) level for $H_4$ and CB and the CAS(8,8) level for COT and pentalene, all using the GAMESS program suit.[26] The basis set was 6-31G for $H_4$, 4-31G for CB and pentalene, and 3-21G for COT. [b] CB = cyclobutadiene; COT = cyclooctatetraene. [c] $\Delta E$ = the energy gap between the ground state and its twin at the symmetric structure ($\xi = 0$). $\Delta E(S-T)$ = the energy separation between the symmetric singlet at $\xi = 0$ ($^1B_{1g}$ symmetry) and the first triplet at its optimized geometry ($^3B_{1g}$ symmetry). [d] Bond lengths in pentalene, from left to right (see structure **VI**): $R(C_1C_2)$, $R(C_2C_3)$, $R(C_1C_5)$. [e] The ground state of pentalene is of $B_{1g}$ symmetry, and that of the twin is of $A_g$ symmetry. In pentalene and $H_4$ the first excited $A_g$ ($A_{1g}$) state is ionic. The twin is the $2^1A_g$ and $2^1A_{1g}$, respectively. [f] Frequency of the mode exchanging the two Kekulé structures. Imaginary frequencies indicate a reaction coordinate. [g] Cal = calculated; nor = normalized using the scaling factor of 0.87 derived from the experimental value for benzene (1570 cm$^{-1}$). [h] The energy of the transition state above the bond-alternating form of the molecule.

individual cases[9,10,29b] but is shown here to be a fundamental property of even parity systems. As a corollary, their properties cannot be discussed in terms of the frontier orbital approximation, and any conclusions based on properties of the HOMO or LUMO orbitals should be considered with great care.

A direct consequence of the fact that the electronic ground state is nonsymmetric is that not all electrons can be paired within the same molecular orbital. In other words, the system must have at least two unpaired electrons, residing in two different molecular orbitals. This fact is the reason for the biradical character of the symmetric even parity molecules, as also predicted by simple MO models.[5]

It was further shown,[13b] that the symmetric form is an unstable one and will always distort to a less symmetric form. This reduction of the symmetry (for instance, in the case of cyclobutadiene, from $D_{4h}$ to $D_{2h}$) leads to two distinct equivalent structures. All electrons are paired in the ground state of these bond-alternating molecules, which transforms as the totally symmetric irrep of the lower symmetry group.

**4.b. What Causes the High Reactivity of the Distorted Antiaromatics?** Given that the symmetric ground states of the antiaromatic molecules cannot be isolated, since they necessarily distort, one might expect these molecules to become reasonably stable in the bond-alternating form. Rather, many have never been isolated, while the few that were prepared are all known to be highly reactive, much more so than regular polyenes. As mentioned above, antiaromatic molecules have often been discussed in terms of biradical structures; see Chapters 3 and 5 of ref 4. In our model, this property arises from the fact that an odd number of electron pairs tends to stabilize a cyclic system. In an even parity system, there is an "extra" pair, which causes the biradical character of the system. By comparison with open biradicals, such as twisted olefins, this biradical is not localized in a certain part of the molecule and thus is resonance stabilized in the cyclic system, much like the aromatic stabilization of benzene compared to cyclohexatriene.

The twisted form of ethylene and of polyenes in general is a prototype biradical. This form is quite reactive, but its formation from the planar form requires a high energy input, about 60 kcal/mol.[30] This is high enough to guarantee the stability of the molecules at ambient temperatures. Because of the resonance stabilization, the corresponding energy barrier for the cyclic antiaromatic molecules is about an order of magnitude smaller (Table 1). Therefore, the distorted molecules can easily acquire the energy of the labile symmetric form, explaining the high reactivity of these systems. It also explains the difficulty of preparing them; typical barriers for any chemical reaction are larger than the symmetrization barrier. Therefore, during an attempted synthesis, the system finds itself with enough energy to form the symmetric form, which may promptly react with one of the mixture's components. One should also note the presence of another low lying, possibly reactive state, the $^3A_{2g}$ triplet.

As in the case of twisted biradicals, many excited states of ionic character are present, normally at higher energies than the covalent ones. Among them, there is a state that transforms as the totally symmetric irrep, which may mix with the covalent twin totally symmetric state, lowering its energy close to, or even below, the nonsymmetric ground state. In that case, the symmetric form may become more stable than the distorted ones and the molecule will be found to have a symmetric structure. This may be the case for indacene.[3] However, the system remains highly reactive, since the biradical state is still quite low in energy and is readily populated.

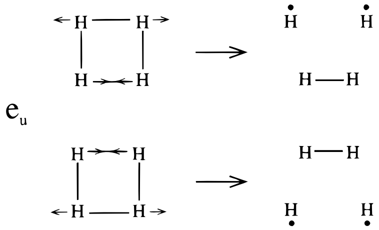


**Figure 4.** Form of the degenerate $e_u$ vibrational mode of $H_4$ leading to dissociation to a hydrogen molecule $H_2$ and two hydrogen atoms.

It is noted in passing that the low barrier helps in making the distorted forms of the antiaromatic molecules highly reactive but is not by itself a sufficient condition for reactivity. Thus, aromatic systems such as semibullvalene[31] are characterized by very low barrier between distorted forms but do not display any biradical character.

**4.c. Other Cyclic Systems.** The essential part of the model is the fact that electrons tend to be paired in chemical bonds. In the $C_{2n}H_{2n}$ system, there are 3 C−C bonds for each carbon atom, creating an asymmetry that leads to the representation of the system by two covalent VB structures. Note that there is no special role for the $\pi$ electrons, except for providing a "marker" that makes the two forms distinguishable. Thus, one can describe the system as containing three types of electron pairs: $\sigma$ pairs between atoms bound also by a $\pi$ pair ($\sigma_\pi$ electrons), $\sigma$ pairs between atoms not bound a $\pi$ pair ($\sigma$ electrons), and $\pi$ pairs ($\pi$ electrons). There are $n$ electron pairs of each type, and the total ground state wave function may be written as the product of the three.

$$\Psi = \psi(\sigma_\pi)^n \psi(\sigma)^n \psi(\pi)^n$$

According to this analysis, each of the $\psi$'s transforms, for an even parity system, as one of the non-totally symmetric irreps. Therefore, $\Psi$ also transforms as the same irrep, and it is immaterial whether the $\sigma$ or $\pi$ electrons are "responsible", in fact, their roles are completely interchangeable.

*4.c.1. $H_{2n}$ Systems.* This discussion may be extended to other systems, having alternating bond types. The simplest is a ring having an even number of hydrogen atoms, such as $H_4$. Its square form may be considered as having one type of electron pairs, those shared as $\sigma$ bonds between two atoms. There are two possible equivalent rectangular arrangements whose in- and out-of-phase combinations constitute a twin pair. Since this is an even system, the ground state should transform as a non-totally symmetric irrep and the excited state as the totally symmetric one. Early studies of this system by Rubinstein and Shavitt[32] and by Michl and co-workers (see ref 33 and also pages 230−238 of ref 34) indicated a pair of covalent states of square symmetry. The ground state is a transition state between the rectangular ones and the excited-state having a deep minimum. According to the present model, the ground state should be repulsive and dissociate into a pair of $H_2$ molecules.

These predictions are fully borne out by quantum chemical calculations on the system, which confirm the analogy with square cyclobutadiene. In particular, the Kekulé vibrational mode, which is the reaction coordinate in the ground state, becomes a high-frequency vibrational mode in the twin, which is, as predicted by the model, a $^1A_{1g}$ state in $D_{4h}$. The degenerate $e_u$ mode is also found to be reactive in the ground state, leading to a hydrogen molecule and two H atoms (Figure 4). This is a clear manifestation of the biradical character of the system, which is "masked" in the multiple bonded hydrocarbon systems.

Here, in the absence of an extra bonding structure (as is the carbon–carbon $\sigma$ structure in the cyclic olefins), the tendency of the system to form two unpaired electrons is revealed in the reaction pattern. It is noted that two degenerate reaction modes are found, in line with the idea that the system has an "extra" electron pair, which is *not* localized in a given bond. From the calculated magnitude of the imaginary frequencies, it is deduced that the driving force for the symmetric molecular dissociation mode is larger than that for the radical one. A similar result is obtained for $H_8$—in the ground state, two imaginary vibrational frequencies are found, the Kekulé mode and two degenerate $e_u$ modes leading to the formation of two hydrogen atoms and three $H_2$ molecules.

The same analysis, when carried out for $H_6$, leads to an aromatic system. The ground-state transforms as $A_{1g}$, and the excited twin as $B_{2u}$, just as in benzene. The latter is calculated to lie at a very high energy, about 10 eV. The ground state is unstable and is a transition state between two systems consisting of three $H_2$ molecules.[35] In contrast with the case of $H_4$, the only imaginary frequency is found for the Kekulé mode, while all other modes, including those that may lead to radical formation, have real frequencies, i.e., are stable vibrations. Thus, there is no indication of a biradical character. This system is similar to that of semi-bullvalene,[31] recently discussed using the "twin-pair" model.

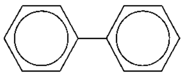
It is noted that the out-of-phase combination, forming the excited state as expected for odd systems, transforms as an ungerade (odd) irrep, again lending support to the odd/even characterization of aromatic and antiaromatic molecules used in this model.

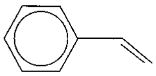
*4.c.2. Other Cyclic Hydrocarbons.* The foregoing discussion traces the properties of antiaromatic molecules to the presence of an odd number of different bond types that alternate around the ring (three for the conjugated hydrocarbons, one for $H_4$) and to the even parity of the system.

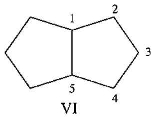
Pentalene and heptalene are bicyclic systems having an even parity, with more than one ring. Their antiaromaticity arises naturally from the twin-state model, since their structures can be represented by a resonance hybrid of two covalent VB structures having an even number of electron pairs. These molecules necessarily have a biradical character.

Since antiaromatic molecules are intrinsically unstable, they tend to avoid the biradical character imposed by symmetry. In the simple $H_{2n}$ model systems discussed in the previous subsection, this was achieved by dissociation into $2n-1$ $H_2$ molecules and a pair of H atoms. In the cyclic conjugated hydrocarbons, this dissociation is prevented by the $\sigma$ CC bond structure and the molecule tends to distort. A third way is open to systems that can be separated into weakly interacting even parity subunits.

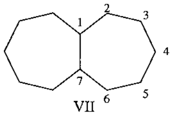
This is the case of molecules, such as biphenyl (**IV**) and styrene (**V**), that formally are even parity systems, having six and four $\pi$ electron pairs, respectively. Therefore, both molecules behave as a substituted benzene, with their ground state being essentially aromatic, and the lowest excited singlet is a twin state having the characteristic exalted frequency of the Kekulé mode.[36] Note that such separation is impossible for the bicyclic systems pentalene (**VI**) and heptalene (**VII**).


IV


V



VI



VII

## 5. A Criterion for Ground State Symmetry and Stability

An application of the ideas of this paper is a simple method for determining the symmetry of the ground state of conjugated cyclic hydrocarbons and therefrom the distortivity of the most symmetric form. The procedure is as follows.

1. Write down all possible covalent VB structures.
2. Choose reference resonating pairs, namely pairs having alternating single and double bonds that can be exchanged by a proper coordinate (these are the *L* and *R* structures; see Figure 1). The *L*, *R* pair with the maximum number of electron pairs (usually the one where bonds alternate along the periphery) will be the one with the maximum resonance stabilization.
3. If there is only *one* pair of resonating VB structures, count the number of electron pairs that resonate in a single structure to determine their parities. If the parity of the number of electron pairs for a given *L*, *R* pair is odd, the system has an aromatic character and the in-phase combination of $L + R$ is the ground state. If the number of electron pairs in the resonating structures is even, the system is antiaromatic and the out-of-phase combination is the ground state, which will necessarily distort to a less symmetric form.
4. If there are several resonating pairs of VB structures, the ground-state character will be determined by the pair with maximum number of electron pairs.
5. When in addition to the resonating pairs there is a single VB structure C (which is necessarily totally symmetric) it will interact with the $L + R$ only. Two cases can be distinguished.

(5a) If the system has odd parity, the combination of $L + R$ with C will yield further stabilization, and the system will remain predominantly aromatic.

(5b) If the system has even parity, the interaction between C and $L + R$ will stabilize this combination to below the $L - R$ energy. The system's characteristics are primarily determined by C, and its nature is recognized as nonaromatic.[37] However, in this case, there will be a low lying excited state with antiaromatic character (e.g., tendency to distort). In addition, there will be a low lying triplet state (see next paper).

6. A system that has only nonpairable VB structures is nonaromatic, neither aromatic nor antiaromatic. The ground state will be totally symmetric; there will be no twin excited state.

A few examples will serve to demonstrate the application of this procedure and compare it with Craig's.

1. For acenaphthylene, Craig's rule yields an aromatic ground state, as shown in Figure 5. Three covalent VB structures may be drawn, as for naphthalene.[27b] The two resonating structures have an odd parity (five electron pairs). Their in-phase combination is therefore the ground state, it is resonantly stabilized by both the classical pairwise exchange interaction and also by the cyclic permutation exchange (see Figure 2 of ref 13b). The third VB structure, C, has the same symmetry as the in-phase combination and combines with it to form the ground state, which has an aromatic character. It is noted that in this case the aromaticity of the system is "diluted" by the nonaromatic character of C, but due to the expected strong resonance stabilization, the contribution of the aromatic component is in general expected to dominate.
2. For aceheptylene, Craig's rule leads to an ambiguous result (Figure 6). The two resonating structures (*R* and *L*) have an even number of electron pairs so that the out-of-phase combina-

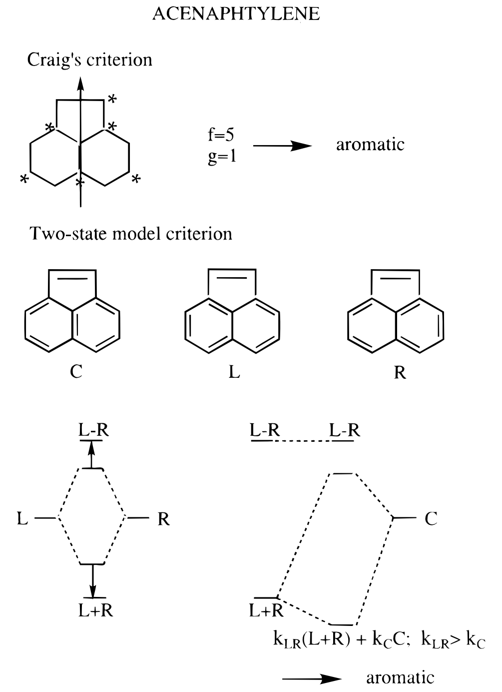


**Figure 5.** Analysis of the electronic character of acenaphthylene using Craig's method and the two-state model; both methods predict an aromatic ground state.

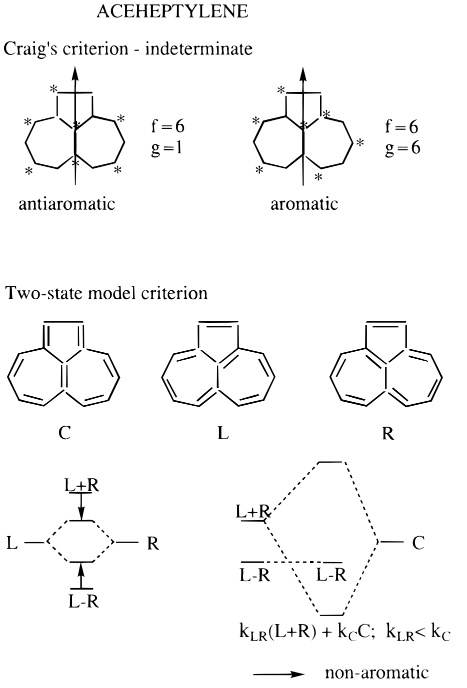


**Figure 6.** Analysis of the electronic character of aceheptylene using Craig's method and the two-state model. The former is ambiguous, the latter predicts a nonaromatic ground state.

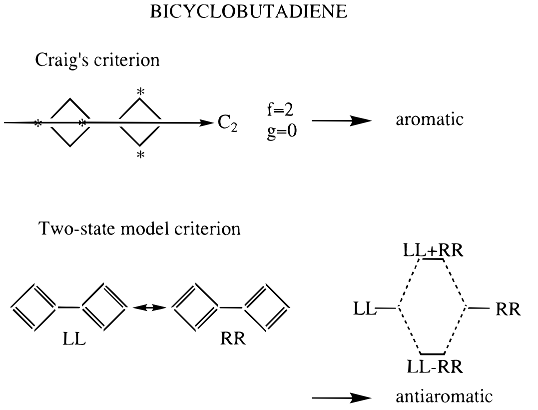


**Figure 7.** Analysis of the electronic character of bicyclobutadiene. Craig's method predicts an aromatic ground state, while the two-state model predicts an antiaromatic one. See text for further details.

tion is lying lower than the in-phase one. Here, the cyclic permutation exchange term operates to destabilize the ground state (Figure 2 of ref 13b) so that the $L - R$ combination will be the lower energy state. However, as the $L + R$ state resonantly interacts with C to form a lower ground state. Since C is expected to be of lower energy than $L + R$, this combination will have some aromatic character but is more appropriately described as a nonaromatic state. Note that the $L - R$ combination is a low lying excited state.

3. For bicyclobutadiene (Figure 7), according to Craig's procedure this system is aromatic. As shown in Figure 7, several VB bond-alternating structures can be written. They may form in-phase and out-of-phase combinations in several different ways ($RR \pm LL$, $RR \pm RL$, etc.), all of which have an even number of resonating electron pairs, as demonstrated in Figure 7 for the *RR*, *LL* pair. Therefore, the system is antiaromatic, as verified by computations.

In this paper, we considered in detail only the cases of cyclic hydrocarbons of the general structure $C_{2n}H_{2n}$. Other resonating systems may be analyzed with the same formalism. The case of butadiene, which is also represented by an out-of-phase combination of two resonance structures, is taken up in a forthcoming paper.[40] Systems such as $C_{4n-1}H_{4n-1}^+$ (such as $C_3H_3^+$ and $C_7H_{71}^+$), having an odd number of electron pairs, can be shown to be aromatic. They are represented by an odd number of resonance structures, making the analysis a bit more complex. The even parity systems $C_{4n+1}H_{4n+1}^+$ (such as $C_5H_5^+$) are antiaromatic. The ground state of the symmetric structure is degenerate (transforms as $E_1'$ in the $D_{5h}$ point group) and Jahn-Teller distorts to a less symmetric structure. The discussion of these interesting systems (see ref 41) is deferred to a separate publication.

## 6. Summary

The model puts aromatic and antiaromatic systems on equal footing; both are cyclic molecules, having an odd number of covalent two-electron bond types alternating around the ring(s). It underlines the importance of *electron pairs* as the fundamental factor determining the properties of cyclic systems, rather than the number of electrons. Thus, the traditional distinction between $4n$ and $4n + 2$ electron system is only a reflection of the difference in parity between them. There is an even number of bonds of each type in the antiaromatic molecules and an odd one in aromatic ones. The bonds can be arranged in two different equivalent structures around the ring(s), and the system can be thought of as a resonance hybrid formed by an equal weight combination of these two structures. The two possible combinations, an in-phase and an out-of phase one, form the ground state and a low lying excited singlet. In the antiaromatic molecules, the out-of-phase combination is the ground state, while in aromatic ones, it is the in-phase one. Since equal weights of the Kekulé structures are used, a symmetric, nonbond-alternating system is obtained in both states for aromatic as well as antiaromatic molecules.

The ground state electronic wave function of the antiaromatic molecules transforms as one of the nontotally symmetric irreps of the group (of $B_1$ or $B_{1g}$ symmetry). It is unstable with respect to motion along the Kekulé mode that interchanges the two original structures; therefore, the system can never be observed in the symmetric form, which is a transition state. This transition state is resonance stabilized so that the activation barrier between the two bond-alternating forms is small, typically 3−5 kcal/mol.[38] The nonsymmetric character of this state imparts it with a biradical character, which is reflected in the system's high reactivity and the difficulty to isolate even the more stable distorted structures. This is also the origin of the paramagnetic properties of the system. These molecules are expected to be thermochromic; on heating, their spectrum should show a red shift.

The in-phase combination of the two bond-alternating structures (the twin state) transforms as the totally symmetric irrep and is a strongly bound excited state in the antiaromatic systems. The reaction coordinate exchanging the two alternating-bond structures transforms as the non-totally symmetric irrep of the ground state and becomes a high-frequency mode on the twin excited state. The ground state, having a biradical nature, could be either a triplet or a singlet. Indeed, there is a low lying bound triplet state of $B_1$ or $B_{1g}$ symmetry close in energy to the ground state but of *higher* energy. The two bound states (the triplet and the twin singlet) are in principle experimentally observable. The singlet is characterized by a very high-frequency $B_1$ (or $B_{1g}$) vibrational mode. A possible way of observing them is by photodetachment of electrons from the planar molecular anion, as shown recently for the triplet state of planar COT.[39] Using a higher photon energy should lead to observation of the singlet as well.

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