The Coloring Problem

Jeremy K. Burdett,[*1] Stephen Lee, and Timothy J. McLarnan

Contribution from the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637. Received May 21, 1984

Abstract: The method of moments is used to treat the general coloring problem of molecular and solid-state lattices. The results are used to illuminate the site preference problem in molecules and solids, the structures of transition-metal alloys, one-dimensional chain systems, and the stable substitution patterns of cyclobutadiene.

I. Introduction

One aspect of structural chemistry of fundamental importance is one which we will call the coloring problem. Consider a fixed molecular or solid-state framework (e.g., a square or the hcp lattice) which is then populated with different sorts of atoms or atom groupings. Such a mapping of vertices to atoms is called a coloring, and the different atoms or units are associated with different colors. We require exactly one atom or atom grouping to lie at each vertex in the framework. In addition we require the coloring to maintain a specific stoichiometry.

Examples of this problem are given in 1–3, the triatomic molecule, the square, and the bcc lattice. Their stoichiometries
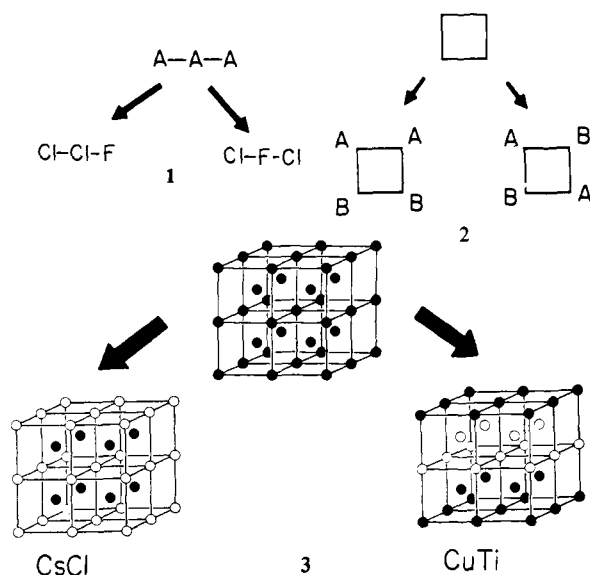
are AB_2, A_2B_2, and AB. There are only two possible colorings for 1 and 2 but an infinite number for the extended solid-state arrays of 3. For a unit cell of finite size, however, the number of possible colorings is finite.[2]

A question which often interests chemists is which coloring has the lowest energy. We begin our analysis in a very general fashion as we wich to describe certain features present in all coloring patterns. We will then apply some of the techniques we have developed in the previous two papers[3,4] in this issue to the problem in general and study two specific problems by using more traditional methods for comparison.

(1) Camille and Henry Dreyfus Teacher–Scholar.
(2) For techniques available for the enumeration of the number of colorings of lattices see: (a) Moore, P. B.; McLarnan, T. J. In "The Structures of Complex Solids"; O'Keeffe, M., Navrotsky, A., Ed.; Academic Press: New York, 1981. (b) Burdett, J. K. Adv. Chem. Phys. 1982, 49, 47. (c) Burdett, J. K.; McLarnan, T. J. J. Chem. Phys. 1981, 75, 5764.
(3) Burdett, J. K.; Lee, S. J. Am. Chem. Soc., first paper of three in this issue.
(4) Burdett, J. K.; Lee, S. J. Am. Chem. Soc., preceding paper in this issue.

II. Moments of Colored Patterns

Within the confines of Hückel theory (see the previous two papers in this issue for our use of this term), the coloring of different sites is basically the use of different α values for the orbitals concerned. We may simplify the problem further by assuming that the interaction matrix elements between the orbitals of the system (the Hückel β's) are independent of the type of atom in the system. (We will lift this restriction later.) Given this assumption, the earliest possible moment that may be different in two structures generated by different colorings is the third moment. Let us see if there are any restrictions on the values of μ_3 for various colorings. The walks are of the type shown in 4.

4
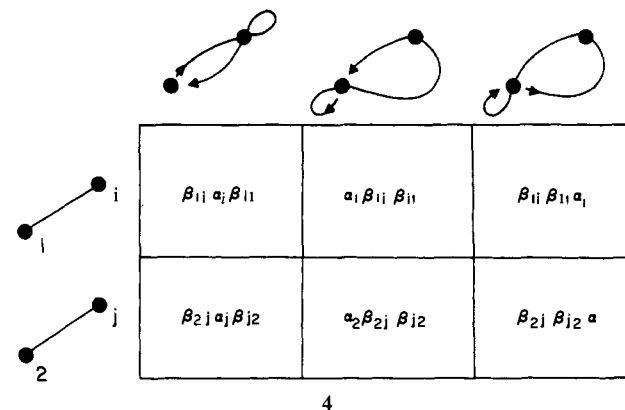
First we need to define an operation which relates two colorings of a system. For example, in the case of the square (cyclobutadiene) system (2), there are two possible A_2B_2 colorings

	vertex			
	1	2	3	4
coloring S	A	A	B	B
coloring T	A	B	A	B

An obvious operation which connects these two colorings is the permutation (23). Thus we define

$$(23)S = T \tag{1}$$

It can be seen that this sort of mapping may be used to relate any two colorings to each other.

Another useful idea is that of a coordination environment which is independent of the types of atoms (colors) involved. Let atom 1 be a vertex in some framework populated by a single orbital. We will define the coordination number c such that

$$c_1 = \sum_{i \neq 1} \beta_{i1}^2 \tag{2}$$

Here i runs over all orbitals in the framework and β_{jk} represents the interaction integral between the jth and kth orbitals. We stressed the relationship between coordination number and the second moment of the energy density of states in the previous paper[4] in this issue.
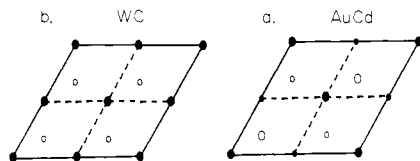
Figure 1. (a) Idealized [8,4] AuCd structure and (b) the [6,6] WC structure, two colorings of the hcp lattice. (The real AuCd structure is a slight orthorhombic distortion of (a), and the WC structure need not be constrained to have an c/a ratio of $(8/3)^{1/2}$. Large circles represent Au and W atoms; small circles are for Cd and C. Filled circles are at height $z = 0$, unfilled circles at height $z = {}^1/_2$.

Proposition 1. Two colorings S and T have identical third moments if there exists a permutation P which only interchanges vertices of identical coordination during $P(S) = T$. [P itself may be written as a product of disjoint cycles $P = p_1p_2p_3\ldots$. Each p_i is made up of vertices with an identical coordination number. p_i and p_j may contain vertices with a different coordination number.]

Proof. S and T have the same number of 3-rings; so by the hypothesis that all β_{ij} are equal, their third moments can differ only because of the contributions of walks of the forms shown in in **4**. The sum of all these contributions will be

$$\sum_{i \neq j} \beta_{ij}^2(\alpha_j + 2\alpha_i) = \sum_{i \neq j} \beta_{ij}^2\alpha_j + 2\sum_{i \neq j} \beta_{ij}^2\alpha_i \qquad (3)$$

If we interchange the meanings of the dummy variables i and j in the first sum and use the fact that $\beta_{ji} = \beta_{ij}$, we can write this as

$$\sum_{i \neq j} \beta_{ij}^2\alpha_i + 2\sum_{i \neq j} \beta_j^2\alpha_j = 3\sum_{i \neq j} \beta_{ij}^2\alpha_i \qquad (4)$$

The coefficient of α_i in this sum is

$$3\sum_j \beta_{ij}^2 \qquad (5)$$

Since the permutation taking S to T takes atom i to a site where the value of this sum is unchanged, the third moments of S and T must be equal.

There are two important examples of colorings for which the above relationship holds. (i) For frameworks in which all the vertices have identical coordination number, all colorings have identical third moments. **2** and **3** are examples of this case. (ii) Let any coloring which does not change under an operation which permutes all of one color for all of another color be called self-complementary. All such self-complementary colorings of a framework have identical third moments. Any self-complementary coloring must have stoichiometry AB, ABC, etc. Furthermore, each type of coordination environment must have the same stoichiometry. Therefore, there always exists a permutation which interchanges only identical coordination number vertices which connects two self-complementary colorings to each other. **2** and **3** are two illustrative examples.

III. Coloring of Lowest Energy

In the previous two papers[3,4] in this issue, we have suggested certain rules by which, from a knowledge of the earliest disparate moments of the energy density of states of two structures, it is easy to determine which variant has the lowest energy. These rules apply especially well to crystals, specifically for the cases we shall study in this paper.

(1) When μ_4 is the dominant moment, then at both low and high band fillings, the structure with the highest μ_4 is most stable (**5**). Near the half-filled band, the structure with the lowest μ_4
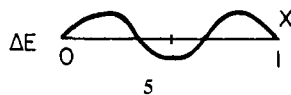
is stable (X is the band filling; empty, $0 \leq X \leq 1$, full). Examples of this case may be found when μ_3 is the same for both colorings

Table I. Known Structures of Transition Metal–Transition Metal Alloys[a]

av no. of s + d electrons	CsCl type	γ-CuTi type	AuCd type
5.5	TcTi, RuSc, ReTi, HfTc		
6.0	RhY, TcV, TaTe, RuZr, RuTi, RhSc, OsZr, OsTi, MnV, IrSc, Hf, Ru, CoSc		
6.5	RuV, PtSc, PdSc, OsV, NiSc, HfRh, CoZr, CoTi, CoHf		
7.0	AuLa, CuY, CuSc, AuY, AuSc, AgY, AgSc, AgLa		PtTi, PdTi
7.5		AgZr, AuHf, AuTi, CuTi, PdTa, AgTi	IrMo, IrW, NbPt, PtV, MoRh
8.0			
8.5	CoFe,[b] FeRh,[b] β-MnPd		
10.5	β-CuPd		

[a] From: Watson, R. E.; Bennett, L. H. *Phys. Rev.* **1978**, *18*, 6439. [b] Magnetic phases.

as we have described in section II above.

(2) When μ_3 is the dominant moment, then at low band fillings, the structure with the highest $|\mu_3|$ is stable. For high band fillings, the structure with the lowest $|\mu_3|$ is stable (**6**). Examples of this
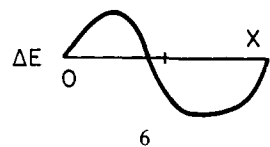
case will be found when the conditions described in section II are not applicable.

The application of these ideas to the coloring problem lead to the following two propositions.

Proposition 2. For those systems in which μ_3 is the dominant moment, $|\mu_3|$ may be maximized by placing the most electronegative atom at the site with the highest coordination number.[5]

Proof. By the proof of proposition 1, the part of the third moment which can vary from one coloring to another is

$$3\sum_{i \neq j} \beta_{ij}^2\alpha_i \qquad (6)$$

This is obviously maximized in absolute value by placing the most electronegative atoms (those with the largest negative α_i) at the sites of highest coordination number.

This is an important result. It suggests that the most stable structure for the heterotrihalide ions XY_2^-, where the "band" is nearly full, is the one where the most electronegative atom lies at the end of the molecule. Thus, for example, we find Br–Br–Cl$^-$ and not Br–Cl–Br$^-$. With fewer electrons, it predicts a changeover

(5) In some cases it may not be clear which atom is more electronegative. For instance let the atoms A and B have the following atomic energy levels.
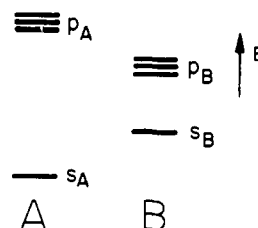
We may resolve this difficulty by noting that eq 31 is linear in α and defining a function, proportional to the electronegativity, as the correctly weighted average of α_s and α_p.

The Coloring Problem
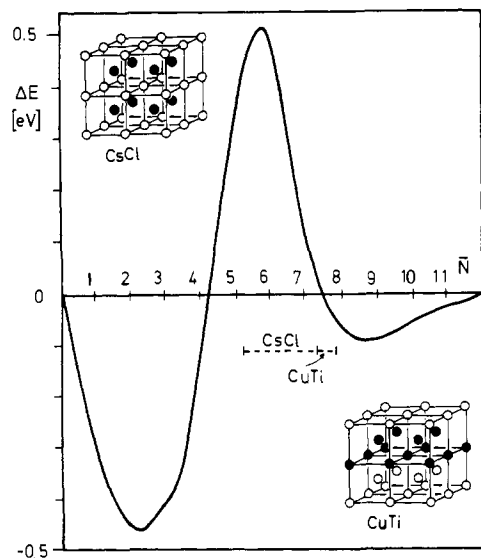
J. Am. Chem. Soc., Vol. 107, No. 11, 1985 3085

Figure 2. Calculated energy difference curve for the [8,0] CsCl and [4,4] CuTi transition-metal alloy structures as a function of the average total number of valence s + d electrons. The dashed lines show the experimentally observed occurrence of examples of the two colorings.

of the stable triatomic isomer to the one with the most electronegative atom in the middle. Thus, for 12 electron Ga_2O, the O atom is two-coordinate. N_2O with four more electrons is found as NNO. We have discussed this triatomic problem by using more traditional ideas elsewhere.[6] In the solid state, similar site reversals are found. It is the electronegative halide ions which occupy the three-coordinate sites in the cadmium halide structures, leaving the metal atoms six-coordinates. In the structure of Cs_2O, which has the anticadmium halide structure, it is the electropositive Cs atoms which occupy the three-coordinate sites. There are many instances of structure–antistructure relationships of this type. Mg_2Si has the antifluorite (CaF_2) structure and Mg_3Bi_2 has the anti-La_2O_3 structure, for example. One particularly intriguing example is the relationship between the structures of the units in realgar, As_4S_4 (**7**) and S_4N_4 (**8**). In As_4S_4, it is the more
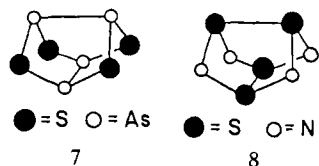
electronegative sulfur atoms which occupy the two-coordinate sites, leaving the arsenic atoms to occupy the three-coordinate sites. In S_4N_4 it is now the more electronegative nitrogen atoms which occupy the two-coordinate sites, leaving the sulfur atoms three-coordinate. In the next proposition the concept of a bipartite framework is useful. A bipartite framework is one which contains no rings of odd length. **1–3**, diamond, and graphite are all bipartite when one considers only first nearest-neighbor interactions. Cubic and hexagonal close packings are not bipartite.[7]

Proposition 3. Let S and T be two AB colorings of a framework such that $\mu_3(S) = \mu_3(T)$ for the reasons given above. In addition, assume that the framework is bipartite. Then that coloring which maximizes nearest-neighbor A–A interactions (and hence maximizes B–B, but minimizes A–B, interactions) is the one with the greater μ_4.

Proof. The fourth moments of two colorings of a bipartite structure can differ only because of the contributions of paths of

(6) Burdett, J. K.; Lawrence, N. J.; Turner, J. J. *Inorg. Chem.* **1984**, *23*, 2419.
(7) In this vein a mineralogist might be tempted to comment that all ionic structures are bipartite or conversely that all bipartite structures are ionic!
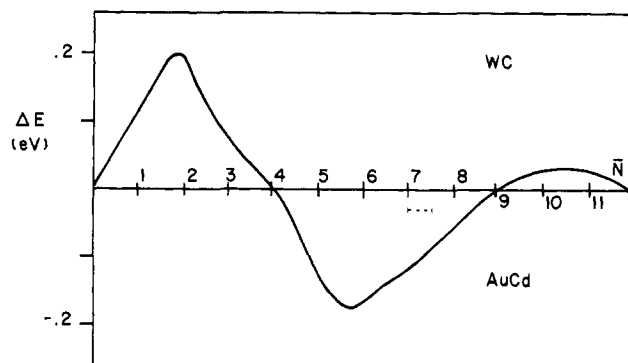

Figure 3. Calculated energy difference curve for the [8,4] AuCd and [6,6] WC transition-metal alloy structures as a function of the average total number of valence s + d electrons. The dashed line shows the experimentally observed occurrence of examples of the AuCd type.

the types shown in **9**. The total contribution of such paths to the fourth moment will be

$$\sum_{i \neq j} \beta_{ij}^2 (3\alpha_i^2 + 2\alpha_i\alpha_j + \alpha_j^2) \qquad (7)$$

Just as in the proof of proposition 1, this can be written as

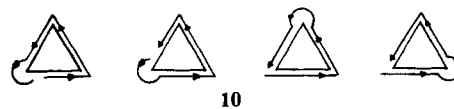$$4 \sum_{i \neq j} \beta_{ij}^2 \alpha_i^2 + 2 \sum_{i \neq j} \beta_{ij}^2 \alpha_i\alpha_j \qquad (8)$$

By the same argument as in proposition 1, the value of the first of these two sums will be the same for S and for T. Thus, the coloring with the largest μ_4 will be the one with the largest value for the second sum. Since all β_{ij} are equal, this means that to maximize μ_4 we must maximize

$$\sum_{i,j \text{ bonded}} \alpha_i\alpha_j \qquad (9)$$

Since S and T have the same number of A atoms and the same number of B atoms, the pattern of bonding in the two can differ only by one or more instances of the replacement of two A–B bonds in one coloring by one A–A and one B–B bond in the other. This changes the sum above by replacing $2\alpha_A\alpha_B$ by $\alpha_A^2 + \alpha_B^2$. Because $\alpha_A^2 + \alpha_B^2 > 2\alpha_A\alpha_B$, this increases the sum and, therefore, increases μ_4. Hence, minimizing the number of A–B interactions maximizes μ_4, as desired.
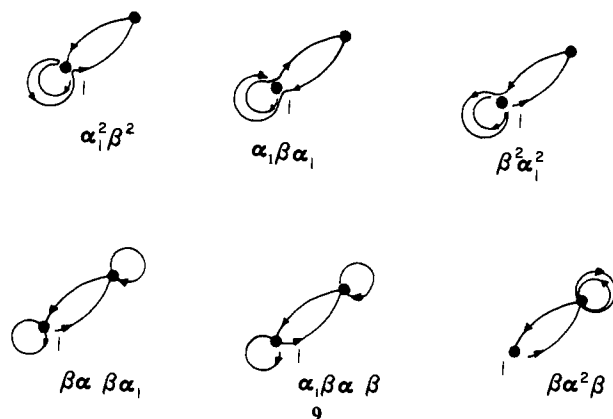
Finally we must consider the case where the third moment of the two colorings satisfies the relation $\mu_3(S) = \mu_3(T)$ and the lattice is not a bipartite one. If the structure of which S and T are colorings is not bipartite, then there is an additional contribution to the fourth moment from paths of the sort shown in **10**. The

Table II. Moments of AABB and ABAB Patterns

ABAB (...ABAB...)[a]

(a) all β equal

$\mu_1 = 2(\alpha_A + \alpha_B)$

$\mu_2 = 2(\alpha_A^2 + \alpha_B^2 + 4\beta^2)$

$\mu_3 = 2(\alpha_A^3 + \alpha_B^3 + 6\beta^2(\alpha_A + \alpha_B))$

$\mu_4{}^a = 2(\alpha_A^4 + \alpha_B^4 + 16[12]\beta^2 + 8\beta^2(\alpha_A^2 + \alpha_B^2) + 8\alpha_A\alpha_B\beta^2)$

(b) all β equal, $\alpha_A = \alpha + \delta$, $\alpha_B = \alpha - \delta$

$\mu_1 = 4\alpha$

$\mu_2 = 2(2\alpha^2 + 2\delta^2 + 4\beta^2)$

$\mu_3 = 2(2\alpha^3 + 12\alpha\beta^2 + 6\alpha\delta^2)$

$\mu_4{}^a = 2(\alpha^4 + 12\alpha^2\delta^2 + 2\delta^4 + 16[12]\beta^2 + 8\beta^2(3\alpha^2 + \delta^2))$

(c) unequal β

$\mu_1 = 2(\alpha_A + \alpha_B)$

$\mu_2 = 2(\alpha_A^2 + \alpha_B^2 + 4\beta_{AB}^2)$

$\mu_3 = 2(\alpha_A^3 + \alpha_B^3 + 6\beta_{AB}^2(\alpha_A + \alpha_B))$

AABB (...AABB)[a]

(d) all β equal

$\mu_1 = 2(\alpha_A + \alpha_B)$

$\mu_2 = 2(\alpha_A^2 + \alpha_B^2 + 4\beta^2)$

$\mu_3 = 2(\alpha_A^3 + \alpha_B^3 + 6\beta^2(\alpha_A + \alpha_B))$

$\mu_4{}^a = 2(\alpha_A^4 + \alpha_B^4 + 16[12]\beta^2 + 10\beta^2(\alpha_A^2 + \alpha_B^2) + 4\alpha_A\alpha_B\beta^2)$

(e) all β equal, $\alpha_A = \alpha + \delta$, $\alpha_B = \alpha - \delta$

$\mu_1 = 4\alpha$

$\mu_2 = 2(2\alpha^2 + 2\delta^2 + 4\beta^2)$

$\mu_3 = 2(2\alpha^3 + 6\alpha\delta^2 + 12\alpha\beta^2)$

$\mu_4{}^a = 2(2\alpha^4 + 12\alpha^2\delta^2 + 2\delta^4 + 16[12]\beta^2 + 8\beta^2(3\alpha^2 + 2\delta^2))$

(f) unequal β

$\mu_1 = 2(\alpha_A + \alpha_B)$

$\mu_2 = 2(\alpha_A^2 + \alpha_B^2 + 2\beta_{AB}^2 + \beta_{AA}^2 + \beta_{BB}^2)$

$\mu_3 = 2(\alpha_A^3 + \alpha_B^3 + 3\beta_{AB}^2(\alpha_A + \alpha_B) + 3(\alpha_A\beta_{AA}^2 + \alpha_B\beta_{BB}^2))$

(g) unequal β[b]

$\Delta\mu_2(ABAB - AABB) \propto -(\alpha_A - \alpha_B)^2$

$\Delta\mu_3(ABAB - AABB) \propto -9(\alpha_A - \alpha_B)(\alpha_A^2 - \alpha_B^2)$

[a] Values for the linear chain in square brackets in μ_4. [b] Assuming $\beta_{ij} \propto (\alpha_i + \alpha_j)$.
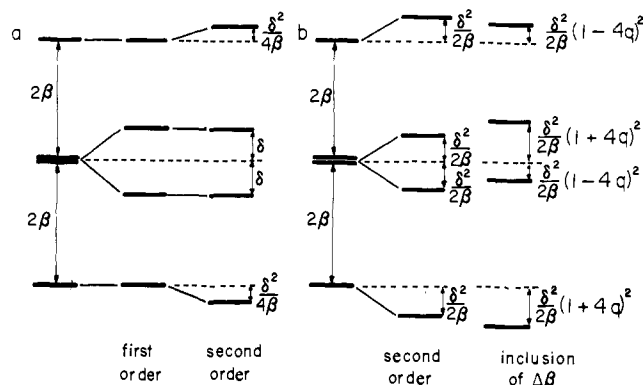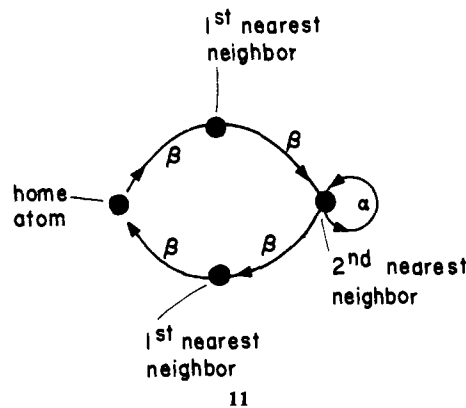

Figure 4. Energy levels of substituted cyclobutadienes obtained via perturbation theory. Shown are the first- and second-order energetic changes (if not zero) and also the shift in the levels of the AABB coloring when the interaction integral is allowed to vary as in eq 15.

Table III. Stabilization Energies of ABAB and AABB Substitution

patterns	ABAB	AABB (no variation in β)	AABB (variation in β)[a]
two electrons[b]	$\delta^2/2\beta$	δ^2/β	$(\delta^2/\beta)(1 + 2q)^2$
four electrons[c]	$(\delta^2/2\beta) + 2\delta$	$2\delta^2/\beta$	$(2\delta^2/\beta)(1 + 4q^2)$
six electrons[d]	$\delta/2\beta$	δ^2/β	$(\delta^2/\beta)(1 - 2q)^2$

[a] As defined in eq 7. [b] AABB always more stable. [c] ABAB more stable assuming perturbation is small. [d] AABB is more stable for $q < 0.146$ or $q > 0.854$. The latter inequality is unlikely since $q \sim S_{ij}$ the i, j overlap integral.

total contribution made by these paths to the fourth moment is

$$\sum_{i,j,k} \beta_{ij}\beta_{jk}\beta_{ki}(2\alpha_i + \alpha_j + \alpha_k) = \beta^3 \sum_{(i,j,k)} 4\alpha_i \qquad (10)$$

where the sums run over all ordered 3-rings (i,j,k) in the structure. This can be rewritten as $4\beta^3\sum N_i\alpha_i$, where N_i is the number of ordered 3-rings at site i. Since S and T are self-complementary, however, they both have equal numbers of A and B atoms in sites with a given value of N_i. As a consequence, paths of the sort shown in **10** make an equal contribution to the fourth moments of S and T. Thus, proposition 3 holds for self-complementary colorings whether or not the underlying structure is bipartite.

An interesting reversal of this result occurs if the two colorings have identical arrangements of first nearest neighbors but differ in the second coordination sphere. In this case there are two competing effects. The second nearest neighbors may be close enough such that the overlap integrals between the second nearest neighbors are significant. (An example of this is in the bcc lattice where second nearest neighbors are only 15% further away than first nearest neighbors.) When this occurs the coloring which maximizes μ_4 is the one with the largest number of *like* second nearest neighbors. The reader may readily show that the two arrangements ...AB*AB*AB... and ...BB*AB*AA..., which have identical nearest-neighbor environments for both atoms, is simply $\beta'^2(\alpha_A - \alpha_B)^2 \geq 0$ where β' is the interaction integral between second nearest neighbors. The latter arrangement is the one with the larger μ_4.

If second nearest neighbors are far away and thus the difference in μ_4 discussed above is small, then one must turn to the higher order moments μ_5 and μ_6. In such cases the walks which need consideration are those which traverse the first nearest neighbors. This is illustrated in **11**.

We note that in certain colorings, μ_5 differences will be zero and μ_6 will become the dominant moment. This parallels our previous discussion of μ_3 vs. μ_4. This parallel exists as the only change which has occurred in the addition of two extra steps. The

only effect of the two steps is to change μ_n into μ_{n+2}. μ_3 becomes μ_5 while μ_4 turns into μ_6.

11

We may use these ideas directly to view the structures of some alloys between two transition metals.

IV. Transition-Metal Alloy Structures

In the previous paper[4] in this issue, we briefly examined some of the crystal structures of the transition elements and referred to the interesting observation that simple Hückel type ideas are able to reproduce the general trend in the variation of the lowest energy crystal structure as the series is traversed.[8] In the case of alloys of the transition metals, little work has been done to date. However several of the structures of known alloys are of particular relevance to this paper. Often what is found for an AB alloy is a simple coloring (in two colors) of structures found for the pure metals. For example, the CsCl and CuTi structures are simply derivative structures of the bcc lattice (**3**). The AuCd and WC

(8) See, for example: (a) Pettifor, D. G. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **1977**, *1*, 305. (b) Pettifor, D. G. In "Physical Metallurgy"; Cahn, R. W., Haasen, P., Ed.; North-Holland Publishing Co.: Amsterdam, 1984.

types (Figure 1) are two colorings of the hcp lattice, and the CuAu and CuPt structures are two colorings of the fcc lattice.

Notice in **3** that the CsCl structure has only AB closest contacts whereas the CuTi structure has AA, AB, and BB contacts. Alternatively, we may regard the bcc structure as the stacking of 4^4 sheets of atoms on top of each other (up c) each sheet shifted $(a + b)/2$ relative to the one below it. In the CsCl structure, the layers are colored ABABAB and in the CuTi structure AABBAA. Examples of both CsCl and CuTi structures as the lowest energy structure at 0 K are found for transition-metal alloys (Table I). Notice the sharp demarcation line between the two structures at (the total number of valence electrons per atom) $N_v \simeq 7.25$. Figure 2 shows the results of an extended Hückel tight-binding calculation for these two structures. (The plot applies to "low-spin", i.e., nonmagnetic alloys.) The calculation is the simplest one we could perform. It included d orbitals only on the two metal atoms. For electron-counting purposes, it is sufficient to realize that of the n s + d valence electrons in the elemental metals, one is essentially present as an s electron. This means that the half-filled band for the elements themselves occurs for the group 6 (chromium) elements.[21] In constructing the abscissa for Figure 2 we have, therefore, "stretched" the range to run from 0 to 12 other than from 0 to 10^9. With the exception of the asymmetry associated with the curve (which we will investigate below in section VI, the general shape of the energy difference function follows the pattern expected. The plot takes the form of **5**, and it is the CsCl structure which is the one preferred at the half-filled point. This is the structure with the smallest number of A–A and B–B interactions. If we describe this structure in terms of the [number of like nearest neighbors, number of unlike nearest neighbors], then the CsCl structure is an [8,0] coloring but the CuTi structure a [4,4] coloring. The CsCl arrangement is therefore the one with the smaller μ_4 and so the favored coloring at the half-filled point. Note that the calculated curve nicely reproduces the observed CsCl → CuTi changeover at $N_v \simeq 7.25$ shown in Table I.

We have also derived[10] the result of Figure 2 by using a more traditional approach. The form of this curve may be obtained by using the energy levels at just two points ($(0,0,0)$ and $(^1/_2, {}^1/_2, {}^1/_2)$) of a tetragonal Brillouin zone corresponding to a four atom unit cell. (A body-centered cubic derivative structure doubled along c). By examining in detail the level shifts of the bcc structure as a result of the two different colorings (much like the cyclo-butadiene problem we show below in section VI), we may also understand the form of this curve.

Figure 3 shows a calculated[9] energy difference curve for the AuCd and WC structures shown in Figure 1. It is strikingly similar to that of Figure 2. For these two structures, there are not easily visualized planes of atoms stacked in a fashion analogous to those in **3**. However, the two colorings are self-complementary and (with the restriction of constant β throughout) will have a zero third moment difference. The AuCd structure is a [8,4] coloring and the WC structure a [6,6] coloring. The former is therefore the structure favored at the half-filled point as confirmed by the numerical calculations shown in Figure 3 and by the experimental observations of examples of this structure type shown in Table I. Notice the shift in the crossing point at high N_v for the AuCd/WC case compared to the CsCl/CuTi system. As described in the two previous papers in this issue, the crossing points in $\Delta\epsilon$ (the stabilization energy as a function of Fermi energy), amenable to simple theoretical interpretation, are often

shifted on moving to ΔE (the stabilization energy as a function of band filling).

The Cu_3Au (**12**) and Al_3Ti (**13**) structures are two colorings of the fcc lattice. The first coordination shell of each structure contains the same number of like atoms, and thus the contribution to μ_4 from first nearest-neighbor interactions is the same for both structures. In fact it has been shown[11] that the first disparate
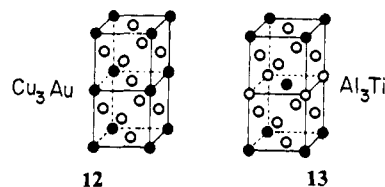
moment is the sixth for these two structures and that it is larger for the Cu_3Au structure with like second nearest neighbors. This leads to an energy difference curve with four crossings, in agreement[12] with structure maps containing experimentally known examples.

V. Stacking Patterns in One-Dimensional Solids

A one-dimensional example involves the stacking of donors (D) and acceptors (A) in integrated stacks.[13] Our model here will be the simplest one could imagine where the energetics of the structures are determined by HOMO–LUMO interactions of the molecules. Two basic possibilities arise for the 1:1 stoichiometry, ...ADAD... and ...AADD.... The former is known for many systems, the latter for only two. For the case where A and D are both closed-shell neutral species, then A^- and D^+ are the radical anion and cation, respectively. Two basic cases immediately arise: (i) the HOMO of D and the LUMO of A have the same symmetry species and may interact in an AD pair of some specified geometry, and (ii) the HOMO of D and the LUMO of A are of different symmetry in all likely stacking geometries and do not interact with each other. Case i is simple and analogous to the simple one-dimensional chain example with one potent orbital per site. With two electrons per AD pair, the band is half full (if the electrons are paired) and the ...ADAD... arrangement predicted. If the interaction between A and D is weak compared to the two-electron terms in the energy, then a high-spin complex may result. In this case, the band will be full of unpaired electrons. Although our approach makes no predictions as to the most stable situation in such a case, note that the Madelung energy is minimized for the ...ADAD... arrangement. Case ii is more interesting. As shown in **14** and **15**, the two orbitals (of symmetry Γ_i and Γ_j) form two bands via interaction with vacant (or full) orbitals on their partner. The result
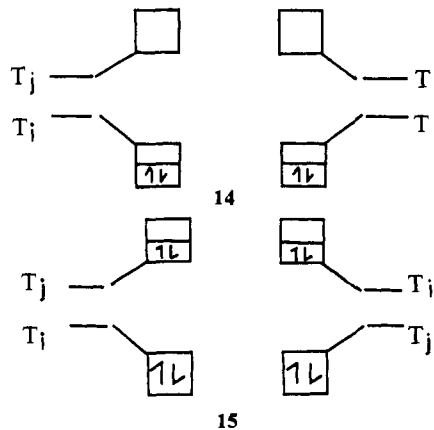
(9) The effect of including s and p orbitals into the calculation is an interesting but complex one. Use of d + s orbitals for the elemental metals themselves leads to a "stretching" of the abscissa of Figure 16 of the previous paper[4] with little change in functional shape. A similar effect occurs in Figures 2 and 3 of this paper if the s orbital is not very diffuse. Use of s, p, and d orbitals in an extended Hückel tight-binding calculation may change this picture depending upon the parameters used. A common feature is loss of the stability field for the ...AABB... pattern at high band fillings and in general significant changes in the predicted structures for $N_v \gtrsim 7$. Some of the problems involved in sorting out this state of affairs are discussed in Burdett, J. K.; McLarnan, T. J. *J. Solid State Chem.* **1984**, *53*, 382.

(10) We have spared the reader the details of this analysis.

(11) Bieber, A.; Ducastelle, F.; Gautier, F.; Treglia, G.; Turchi, P. *Solid State Commun.* **1983**, *45*, 585.

(12) Bieber, A.; Gautier, F. *Solid State Commun.* **1981**, *38*, 1219.

(13) For comprehesive reviews see: "Linear Chain Compounds"; Miller, J. R., Ed.; Plenum Press: New York, 1982–1983, Vols. I–III.

is that the bands of T_j and T_i symmetry are either one-fourth full (in **14**) or three-fourths full (in **15**), two situations which lead to an energetic preference for the ...AADD... structure. This electronic and geometrical arrangement is found[14] in PTZ·Ni(tfd)$_2$. A similiar electronic situation is predicted if one of the species is a radical ion but the other a closed-shell molecule. In this case, the T_i (or T_j) manifold is empty. An example of this situation is found[15] for NBP·TCNQF$_4$.

If the AD system is a triplet and not a singlet for the radical cation and anion case, or a doublet for the case of a single radical species, then these bands become half full of unpaired electrons and the ...ADAD... arrangement is favored. This is the case in[16a] Ni(tfd)$_2$·TTF (radical anion and cation) and[16b] Cu(tfd)$_2$·TTF (radical cation only).
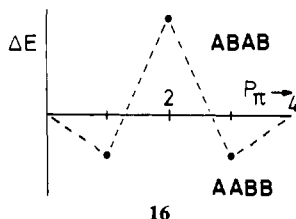
Another possibility arises, of course, if the orbitals on D and A, although of different symmetry, interact because the molecules are stacked in a skewed fashion. In such a case our approach needs to be qualified.

VI. Cyclobutadiene and Changes in Interaction Integrals

These results allow us to comment on an old molecular problem. How may singlet cyclobutadiene (C$_4$H$_4$), predicted to be Jahn–Teller unstable at the square geometry, be stabilized by attaching donor (B) and acceptor (A) groups to give C$_4$A$_2$B$_2$. The effect will be to depress the α values for the carbon orbitals adjacent to A and elevate the α values for the carbon orbitals adjacent to B. As far as the π manifold is concerned, it is simply the coloring problem of **2**. The ABAB isomer, with, from our discussion above, the smaller value of μ_4, is predicted to be more stable than the AABB isomer at the half-filled point, i.e., for C$_4$H$_4$ derivatives itself. Indeed all "push–pull"-substituted cyclobutadienes which have been made to date have this arrangement.[17] This theoretical result was also obtained by using traditional orbital ideas several years ago.[18]

It is instructive to consider the first four moments of these two molecular isomers shown in Table II. (The values for the ... ABAB... and ...AABB... linear chains are similar.) We also show their values relative to the unsubstituted molecule by writing $\alpha_A = \alpha + \delta$ and $\alpha_B = \alpha - \delta$. Notice that the fourth moment of both colorings is increased by this substitution. This is in direct contrast to our discussion in the previous paper[4] in this issue of the Peierls and Jahn–Teller problem, where on distortion μ_4 was reduced in magnitude. In the colorings of **2** the stabilization with respect to the parent appears in second order (Table II).

In a more traditional vein we may simply generate the energy levels of such substituted cyclobutadienes by using perturbation theory. The results are shown in Figure 4 and the stabilization energy as a function of electron count is given in Table III and **19** and is just as expected. One obvious restriction we have placed

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on the entire coloring problem so far is that the interaction integrals are independent of the atoms they join. This is clearly not true, but the simplification of the problem it produced was a useful one. In Figure 4 and Table III we show the effect of changing β during the perturbation. Specifically from the Wolfsberg–Helmholz relationship we have set

$$\beta_{ij} = q(\alpha_i + \alpha_j) \tag{11}$$

where we have assumed q to be constant. (It will in practice be proportional to the ij overlap integral.) The energy levels of the ABAB isomer of Figure 4 remain unchanged when such a modification is included, since all the contacts are AB ones. For AABB, however, some differences appear. As q increases, an interesting effect appears in the energy difference plot of **16**. The high X stability field of the AABB isomer becomes less marked (**17**), and if $q > 0.146$, then it disappears altogether (**18**). For
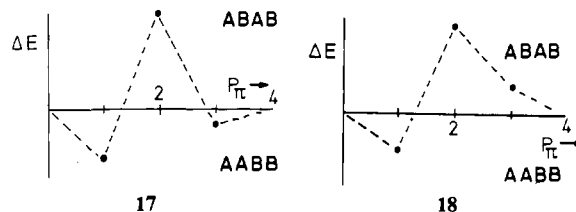
17　　　　　　　　　**18**

the infinite solid this sequence of plots is replaced by a series of smooth curves (**19–21**). We recognize the similarity between
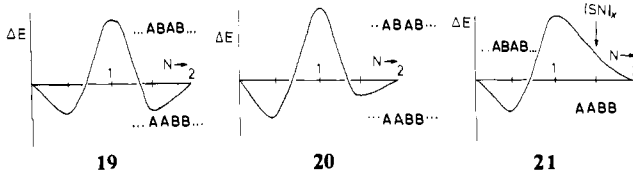
19　　　　　　**20**　　　　　　**21**

20 and the displays of Figures 2 and 3. An example of **21** is found in the structure of the (SN)$_x$ polymer **22**, and its molecular analogue S$_2$N$_2$ (**23**) is an example of **18**. Here the overlap
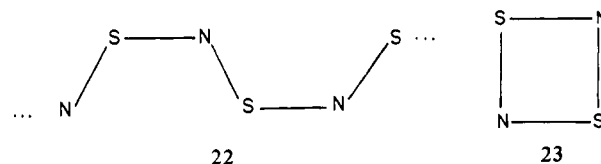
22　　　　　　　　　**23**

between sulfur and nitrogen is large, and so q is expected to be larger than in the transition-metal alloy cases we have just discussed. Calculations on these transition-metal alloy structures show in fact similar behavior when the electronegativity difference between A and B increases.[19]

Examination of Table II shows how this result can be viewed by using the moments approach. Notice how a small change

24

(14) (a) Singhabhandu, A.; Robinson, P. D.; Fang, J. H.; Geiger, W. E. *Inorg. Chem.* **1975**, *14*, 318. (b) PTZ = phenothazine, tfd = *cis*-1,2-bis-(trifluoromethyl)ethylene 1,2-dithiolate.

(15) (a) Metzger, R. M.; Heimer, N. E.; Gundel, D.; Sixl, H.; Harms, R. H.; Keller, H. J.; Nothe, D.; Wehe, D. *J. Chem. Phys.* **1982**, *77*, 6203. (b) NBP = 5-(1-butyl)phenazinium, TCNQF$_4$ = 2,2'-(2,3,5,6-tetrafluoro-2,5-cyclohexadiene-1,4-diylidene)bis(propanedinitrile).

(16) (a) Jacobs, I. S.; Hart, H. R.; Interrante, L. V.; Bray, J. W.; Kasper, J. S.; Watkins, G. D.; Prober, D. E.; Wolf, W. P.; Banner, J. C. *Physica (Amsterdam)* **1977**, *B+C 86–88*, 1. (b) Kasper, J. S.; Moncton, D. E. *Phys. Rev. B: Condens. Matter* **1979**, *B20*, 2341. (c) TTF = tetrathiafulvalene.
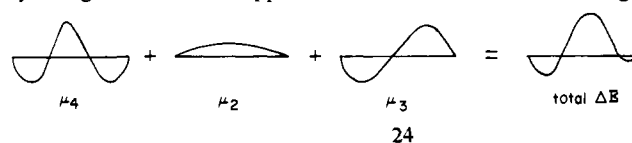
(17) See, for example: Gompper, R.; Seybold, G. *Angew. Chem.* **1968**, *80*, 804.

(18) Hoffmann, R. *Chem. Commun.* **1979**, 240.

(19) The crossover at $q = 0.146$ is suggestive of a difference in structure stability maps in the transition metal as opposed to main group element coloring problems. Recalling the Wolfsberg–Helmholz approximation $q = S_{ij}(K/2)$ where $K = 1.75$, the crossover at the three-fourths filled mark comes at $S_{ij} = 0.167$. Overlap integrals between transition-metal d orbitals are smaller than this (for example, $S_\sigma(dd) = 0.111$ and $S_\pi(dd) = 0.77$ where the Fe atoms are held 2.44 Å apart). Conversely overlap integrals between orbitals located on main group elements often are larger than 0.167 (for example, C with an exponent of 1.625 for its Slater p orbitals has $S_\sigma(pp) = 0.331$ and $S_\pi(pp) = 0.144$ where the C atoms are held 1.40 Å apart).

(20) Whangbo, M.-H.; Hoffmann, R.; Woodward, R. B. *Proc. R. Soc. London, Ser. A* **1979**, *A366*, 23.

(21) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Raman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

appears in the second moment difference if the β_{ij} are not all set equal and also a more sizeable change in the third moment. **24** shows how the μ_4 difference curve needs to be modified as a result.

Appendix

Details of Numerical Calculations. The plots of Figures 2 and 3 were obtained via an extended Hückel based tight-binding method.[8] The parameters for the two metals were single-ζ Slater

d orbitals with an exponent of 2.10 for both atoms and Coulomb integrals of 9.1 and 11.1 eV. A total of 40 symmetry inequivalent k points were used for a primitive tetragonal unit cell (bcc derivative structure doubled along c). The validity of the plots of **17** and **20** for S_2N_2 and the $(SN)_x$ polymer was checked by performing calculations on the observed structures by using the geometrical and orbital parameters of ref 20 and then reversing the S and N sites. The new structure has shorter S–S distances and longer N–N distances than might be expected for a molecule or solid of this type. We did not allow these to relax however, since we have little faith in the ability of extended Hückel calculations to correctly mimic the energetic changes associated with bond length variations.

Registry No. Cyclobutadiene, 1120-53-2.

When Does Electronic Delocalization Become a Driving Force of Molecular Shape and Stability? The "Aromatic" Sextet
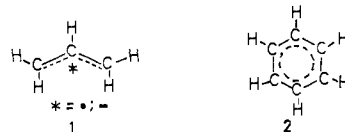
Sason S. Shaik*[1] and Philippe C. Hiberty*

Contribution from the Laboratoire de Chimie Théorique, associated with the CNRS-U.A. 506, Bât. 490, Université de Paris-Sud, 91405 Orsay Cedex, France. Received September 21, 1984

Abstract: The conceptual grasp of electronic *delocalization vs. localization* is reexamined computationally by using "aromatic" 6-electron 6-center (X_6) model species as archetypal systems. It is shown that the character and weights of the resonance structures, which contribute to the "aromatic" sextet, *yield no differentiating information regarding the stabilities or geometries of the X_6 species.* A qualitative model is utilized to understand the physical basis behind the quantitative results. It is shown that the X_6 systems must *"pay a price" for electronic reorganization, while undergoing delocalization.* The "price" depends on the identity of X in X_6. Thus, whenever the X–X two-electron bond is strong (e.g., H–H), the price for electronic reorganization is too high. Such systems (e.g., H_6) will prefer a geometry that *prohibits* delocalization of the electronic sextet. Among these systems is the suspended π system, $Li_6(\pi)$, that lacks a σ skeleton and shows no propensity for π delocalization. Only in a few cases will the price of electronic reorganization be low enough to afford delocalization of the electronic sextet. Such systems possess weak X–X two-electron bonds and will consequently tend to cluster in a regular hexagonal X_6 structure—where electronic delocalization takes place. In view of these trends, a question mark is cast over the propensity of the π system of benzene to remain delocalized without the buttressing effect of the σ framework.

The concepts of resonance theory and electronic delocalization occupy prime places in our conceptual thinking and chemical education.[2] Owing to their very nature, concepts must occasionally be examined. Following this philosophy of reexamination, it was recently proposed[3,4] that electronic delocalization is neither the driving force nor the root cause of the geometric features of "resonating" systems such as **1** and **2**, etc.[5] Rather, it was

suggested that electronic delocalization, in many organic species, *is forced*, and the "resonating" π systems may well be unstable transition states trapped in a stiff σ framework.[3,4]

Since such propositions constitute antitheses to current ways of *thinking and teaching*, we have decided to initiate a quantitative study which is directed at two aims. The specific aim is to in-

(1) Permanent address: Department of Chemistry, Ben-Gurion University, Beer Sheva 84105, Israel.

(2) (a) Resonance theory is summarized in many textbooks. The following is a casual selection showing the importance of the concept in different branches of chemical education. Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960. Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; Harper and Row Publishers: New York, 1976. Levine, I. N. "Quantum Chemistry"; Allyn and Bacon, Inc.: Boston, 1965. Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Interscience Publishers: New York, 1966. (b) The concept of delocalization is common to resonance theory and MO theory. Although the concept is differently formulated, it occupies an important status in both theories. (c) The concept of "aromaticity" is thought to originate in the seminal works of Kekulé and Couper. See: Kekulé, A. *Bull. Soc. Chim. Fr.* 1865, *3*, 98. Couper, A. *C. R. Hebd. Seances Acad Sci.* 1858, *46*, 1157. See also: Wotiz, J. H.; Rudofsky, S. *Chem. Br.* 1984, 720.

(3) Epiotis, N. D. *Nouv. J. Chim.* 1984, *8*, 11. Epiotis, N. D. *Lecture Notes Chem.* 1983, *34*, 358-371. Epiotis, N. D. *Pure Appl. Chem.* 1983, *55*, 229.

(4) Shaik, S. S.; Bar. R. *Nouv. J. Chim.* 1984, *8*, 411.

(5) (a) Similar ideas based on Hückel theory with a variable β were expressed in the following: Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc. London, Ser. A* 1959, *A251*, 172. Salem, L. "The Molecular Orbital Theory of Conjugated Systems"; W. A. Benjamin, Inc.: Reading, MA, 1972, pp 103-106 and 494-505. (b) Electronic delocalization was shown not to be an important driving force in certain allyl-radical-type species: Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* 1984, *106*, 2513. Feller, D.; Huyser, E. S.; Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* 1983, *105*, 1459. Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* 1983, *105*, 3347. Explanations were couched in terms of second-order Jahn–Teller effect and in terms of resonance theory. (c) Localization in some polyenic radicals was found by VB computations to prevail. See: Said, M.; Malrieu, J. P.; Bach, M.-A.G. *J. Am. Chem. Soc.* 1984, *106*, 571.