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A computational study of the Dougherty model for the prediction of high-spin states in organic chemistry*

Pilar Lafuente[1], **Juan J. Novoa**[1], **Michael J. Bearpark**[2], **Paolo Celani**[2], **Massimo Olivucci**[3], **Michael A. Robb**[3]

[1] Departament de Química Física, Universitat de Barcelona, Martíi Franquès 1, E-08028 Barcelona, Spain
[2] Department of Chemistry, King's College London, Strand, London WC2R 2LS, UK
[3] Dipartimento di Chimica "G. Ciamician", Universitá di Bologna, Via Selmi 2, I-40126 Bologna, Italy

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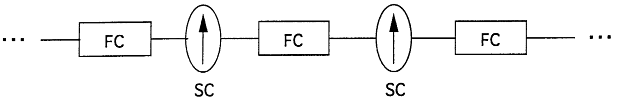
Abstract. The model proposed by Dougherty for the design of high-spin organic systems has been studied from a quantitative point of view using a Heisenberg Hamiltonian formalism. This analysis leads to a decomposition of the phenomenological coupling parameter, J, into contributions from individual active orbital sites and a decomposition of the spin multiplicity into terms from the ferromagnetic coupling unit and the spin-containing units. An analysis of the origin of quintet stability has been carried out for four molecular systems with quintet ground states that have previously been synthesized by Dougherty and by Adam. The results indicate that the ferromagnetic coupling unit plays the dominant role in determining high-spin stability as suggested by Dougherty and gives some insights that may be useful in the rational design of high-spin systems.

Key words: Ferromagnetic coupling – Heisenberg Hamiltonians – CASSCF

1 Introduction

In the design of large organic molecules with high-spin states, Dougherty [1, 2] has proposed a conceptual model (founded on the pioneering work of Itoh [3a]) based on "linking" basic building units as shown in Scheme 1. (Other examples of structures with large spin states and similar mechanism are the polycarbenes, compounds with one-centred interactions placed in delocalized, planar π-systems [3b–e].) The high-spin state in these systems is stabilized by the presence of a ferromagnetic coupling (FC) unit which couples spin-containing (SC) units with high-spin ground states.



Scheme 1

The simplest situation is a single SC-FC-SC system. In the systems studied by Dougherty et al. [2] (and those recently synthesized by Adam et al. [4]), the SC units are triplets (as isolated molecules) coupled via the FC unit. In this case, Dougherty proposes to model [2] the interaction of two triplets, considering a phenomenological Hamiltonian of the form

$$\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2 \tag{1}$$

where $\hat{S}_1$ and $\hat{S}_2$ are the spin operators for the SC units and J is the coupling parameter (or effective exchange integral). In his model, Dougherty associates J in Eq. (1) with the FC unit alone so that the coupling parameter is denoted J_{FC}. The energy gap between the low-spin (LS) coupling and high-spin (HS) coupling states is then expressed as:

$$\Delta E^{\mathrm{S-HS}} = -2J_{\mathrm{FC}}\left(\langle\hat{S}_1 \cdot \hat{S}_2\rangle^{\mathrm{LS}} - \langle\hat{S}_1 \cdot \hat{S}_2\rangle^{\mathrm{HS}}\right) \tag{2}$$

In Eq. (2), $\langle\hat{S}_1 \cdot \hat{S}_2\rangle$ is the expectation value of the product of the total spin operators for each SC unit, and is given as

$$\langle\hat{S}_1 \cdot \hat{S}_2\rangle = \tfrac{1}{2}[s_{12}(s_{12}+1) - s_1(s_1+1) - s_2(s_2+1)] \tag{3}$$

where s_1 and s_2 are the spins of SC_1 and SC_2, respectively, and s_{12} is the vector sum of s_1 and s_2. The energy level diagram for two interacting triplets [2] is given in Fig. 1, from which it can be seen that the sign of J_{FC} determines the multiplicity of the ground state of the molecule. The sign of J_{FC}, in turn, depends on the nature of the FC unit. With this model, Dougherty was able to correlate observed high-spin organic systems with the occurrence of FC units that had triplet ground states as isolated molecules.

In this paper we have two objectives. Firstly, in the Dougherty model [2], no attempt was made to understand why a triplet FC unit yields a $J_{\mathrm{FC}} > 0$. Accordingly, we shall give a theoretical prescription for the

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Correspondence to: M.A. Robb

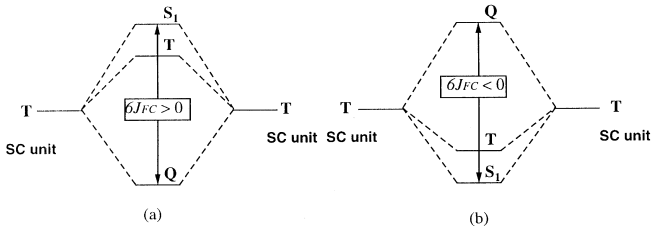


Fig. 1a,b. Energy level diagram for two interacting triplets [eigenvalues of the Hamiltonian in Eq. (1): **a** quintet ground state $J_{\mathrm{FC}} > 0$. **b** singlet ground state $J_{\mathrm{FC}} < 0$

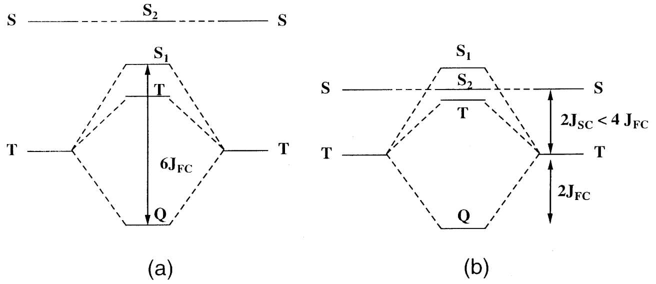


Fig. 2a,b. Energy level diagram including the singlet state S_2 arising from coupling of two singlet states in the SC unit and singlet state S_1 arising from coupling of two triplet states in the SC unit. **a** Lower singlet state is S_1 obtained from the interaction of two triplets in the SC unit. **b** Lower singlet state is S_2 obtained from the interaction of two singlets in the SC unit. In this case, the energy gap between the quintet and the first singlet is given by two contributions: J_{FC} and J_{SC} (if $2J_{\mathrm{SC}} < 4J_{\mathrm{FC}}$)

computation of J and the computation of the spin of the FC unit in the molecule itself. Secondly, Dougherty assumes that the low-spin state arises from the coupling of the triplet states of the SC units to a singlet, as it is shown in Fig. 1. However, this assumption needs to be tested. In fact there are two possibilities, as shown in Fig. 2. The singlet state can also arise from the interaction of the two singlet SC units, when the energy gap between the triplet and the singlet of the SC is small. In this case, the magnitude and sign of J_{SC}, the coupling inside the SC unit, can have a role to play in the value of J. For this case, Dougherty proposed the Hamiltonian [5]:

$$\hat{H} = -2J_{\mathrm{A}}\hat{S}_2 \cdot \hat{S}_3 - J_{\mathrm{B}}\left[\left(\hat{S}_2 + \hat{S}_3\right) \cdot \left(\hat{S}_1 + \hat{S}_4\right)\right] \tag{4}$$

where J_{A} represents the spin-polarization mechanism (related to J_{FC}) and J_{B} characterizes the superexchange mechanism (in relation with J_{SC}). The numbers 1–4 refer to the radical centres of the molecule. Dougherty pointed out that both J_{A} and J_{B} must be positive to a Q ground state result. Of course, in the Dougherty model, the values of J_{FC} and J_{SC} are assumed to be characteristic of the isolated FC and SC units. In Fig. 2b we are assuming that S_1 and S_2 do not interact strongly so that the problem can be represented with two parameters. It remains to be demonstrated that these concepts retain their validity in the supermolecule itself. As we shall subsequently show, we can find examples where the spin multiplicity is determined by J_{FC} and others where J_{SC} plays an important role.

2 Theoretical development

Our objective is to cast the phenomenological Hamiltonian given in Eq. 2 into a form where the parameters can be obtained from ab initio or semi-empirical computations. This is easily accomplished by using valence bond (VB) methods via a Heisenberg Hamiltonian. We can write a general Heisenberg Hamiltonian as:

$$\hat{H}_S = Q - \sum_{ij} J_{ij}\left(2\hat{s}_i \cdot \hat{s}_j + \frac{1}{2}\hat{I}_{ij}\right) \tag{5}$$

where the $\hat{s}_i$ is the spin operator associated with site i, $\hat{I}_{ij}$ is the identity spin operator, the parameter Q is the Coulomb energy (a reference energy zero) and J_{ij} is the exchange energy between the spin-orbitals i, j [6]. This Hamiltonian corresponds to a model with empirical parameters J_{ij} that correlates chemical binding effects with spin coupling (although there is no real coupling between the electron spins). The Heisenberg Hamiltonian given in Eq. (5) can be understood as an effective Hamiltonian computed from an exact full configuration interaction (CI) Hamiltonian using a model space of neutral VB determinants formed from n electrons in n atomic orbitals [7]. We have shown elsewhere [8] that one can derive Q and J_{ij} from CASSCF computations via an effective Hamiltonian formalism. In this case, one can use a localized atomic orbital basis and these orbitals can be identified with sites i and j. Thus Eq. (5) can be rewritten in a second quantized form as:

$$\begin{aligned}\hat{H}_S = Q - \sum_{ij}^{N} J_{ij}\big\langle i(1)j(2)\big|\hat{s}_i \cdot \hat{s}_j \\ + \tfrac{1}{4}\hat{I}(1,2)\big|i(1)j(2)\big\rangle a_i^{+} a_j^{+} a_j a_i\end{aligned} \tag{6}$$

As discussed previously [8a], this operator connects configurations with the same space part which differ only in the spin contribution. Any full CI Hamiltonian can be projected onto such a space and a subset of the eigenvalues can be reproduced exactly [8b].

We must now relate the formalism embodied in Eqs. (5) or (6) with Eqs. (1) and (2) that are used in the Dougherty model. It is convenient to introduce exchange density matrix elements P_{ij} (see [8a]) defined by

$$P_{ij} = \left\langle -\left(2\hat{s}_i \cdot \hat{s}_j + \tfrac{1}{2}\hat{I}_{ij}\right)\right\rangle \tag{7}$$

The expectation value of the Hamiltonian in Eq. (6) is thus given as:

$$\left\langle \hat{H}_S \right\rangle = Q + \sum_{ij} J_{ij} P_{ij} \tag{8}$$

The analogue of Eq. (2) then becomes

$$\Delta E^{\mathrm{LS-HS}} = \sum_{ij} J_{ij} \Delta P_{ij}^{\mathrm{LS-HS}} \tag{9}$$

where $\Delta P_{ij}^{\mathrm{LS-HS}}$ is just the difference in the matrix elements P_{ij} for the low- and high-spin states. Notice that the summations in Eq. (9) run over all active sites i and j. Thus J_{SC} and J_{FC} are associated with partial summations (over orbitals in the SC and FC units) of $J_{ij}\Delta P_{ij}^{\mathrm{LS-HS}}$. Further, we have [9]

$$S(S+1) = -\frac{n(n-4)}{4} - \sum_{ij}^{n} P_{ij} \tag{10}$$

for n electrons and n orbitals. Thus, by examining partial summations of the P_{ij} we can partition the total spin into FC and SC fragments. We now explore a possible decomposition of Eqs. (9) and (10) that yields an understanding of the Dougherty model. However, in order to understand the motivation for such a decomposition we first briefly indicate the physical interpretation of J_{ij} and P_{ij}.

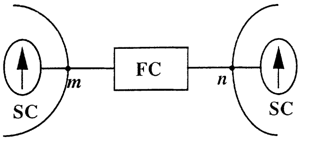
The P_{ij} parameters indicate the nature of the spin coupling between sites i and j. With a single-configuration perfectly paired VB wavefunction (Rumer functions [10]): $P_{ij} = -1$ when the electrons have parallel spins (ferromagnetic coupling) and $P_{ij} = 1$ when they are singlet coupled (antiferromagnetic coupling). However, the computed P_{ij} values differ from the "ideal" values because of configuration interaction.

The exchange parameter J_{ij} in Eq. (9) is interpreted in terms of the electron distribution as the Heitler-London exchange

$$J_{ij} = [ij|ij] + 2s_{ij}\langle i|h|j\rangle \tag{11}$$

where $[ij|ij]$ is the two-electron repulsion integral whose value is very small and always positive, s_{ij} is the overlap and $\langle i|h|j\rangle$ is the one-electron integral (dominated by nuclear electron attraction). The magnitude of parameter J_{ij} is normally dominated by the one-electron term, which is always negative. However, if the overlap between the i, j orbitals is zero, then the J_{ij} will be small and positive.

We now discuss the decomposition of Eqs. (9) and (10) that yield an understanding of the Dougherty model. The basis of our decomposition is given in Scheme 2. There are two common atoms shared by the SC and FC units: the C atom that belongs to $SC_1$and FC is labelled m, and atom n belongs both SC_2 and FC. We now write



Scheme 2

$$\begin{aligned}\Delta E^{\mathrm{LS-HS}} &= \sum_{ij} J_{ij}\Delta P_{ij} \\ &= \Delta E^{\mathrm{SC_1}} + \Delta E^{\mathrm{SC_2}} + \Delta E^{\mathrm{FC}} \\ &\quad + \Delta E^{\mathrm{SC_1-SC_2}} + \Delta E^{\mathrm{SC_1-FC}} + \Delta E^{\mathrm{FC-SC_2}} r\end{aligned} \tag{12}$$

where

$$\Delta E^{\mathrm{SC_1}} = \sum_{i,j\in \mathrm{SC_1}}^{\mathrm{SC_1}} J_{ij}\Delta P_{ij},$$

$$\Delta E^{\mathrm{SC_2}} = \sum_{i,j\in \mathrm{SC_2}}^{\mathrm{SC_2}} J_{ij}\Delta P_{ij},$$

$$\Delta E^{\mathrm{FC}} = \sum_{i,j\in \mathrm{FC}}^{\mathrm{FC}} J_{ij}\Delta P_{ij},$$

$$\Delta E^{\mathrm{SC_1-SC_2}} = \sum_{\substack{i\in \mathrm{SC_1}\\ j\in \mathrm{SC_2}}}^{\mathrm{SC_1+SC_2}} J_{ij}\Delta P_{ij} - J_{mn}\Delta P_{mn},$$

$$\Delta E^{\mathrm{SC_1-FC}} = \sum_{\substack{i\in \mathrm{SC_1}, i\neq m\\ j\in \mathrm{FC}, j\neq m,n}}^{\mathrm{SC_1+FC}} J_{ij}\Delta P_{ij},$$

$$\Delta E^{\mathrm{FC-SC_2}} = \sum_{\substack{i\in \mathrm{SC_2}, i\neq n\\ j\in \mathrm{FC}, j\neq m,n}}^{\mathrm{SC_2+FC}} J_{ij}\Delta P_{ij} \;. \tag{13}$$

We have included the coupling between the electrons placed in the common atoms m, n in the terms $\Delta E^{\mathrm{SC_1}}$, $\Delta E^{\mathrm{SC_2}}$ and ΔE^{FC} so it must be excluded from $\Delta E^{\mathrm{SC_1-SC_2}}$. For a similar reason we need the summation restrictions in the definition of $\Delta E^{\mathrm{SC_1-FC}}$ and $\Delta E^{\mathrm{FC-SC_2}}$.

Some qualitative simplifications are obvious from the outset. The value of J_{ij} as defined in Eq. (11) has a simple geometrical dependence on the distance between the electrons considered. Thus the main contributions to J_{ij} involve interactions between nearest-neighbour i, j electrons. Accordingly, $\Delta E^{\mathrm{SC_1-SC_2}}$, $\Delta E^{\mathrm{SC_1-FC}}$ and $\Delta E^{\mathrm{FC-SC_2}}$ should be negligible, since the orbitals i, j are never nearest-neighbours because the link sites are included in $\Delta E^{\mathrm{SC_1}}$, $\Delta E^{\mathrm{SC_2}}$ and ΔE^{FC}. Thus the important energetic contributions are contained in the intra-unit quantities $\Delta E^{\mathrm{SC_1}}$, $\Delta E^{\mathrm{SC_2}}$ and ΔE^{FC}.

We can now relate the effective parameter J used in the phenomenological Hamiltonian in Eq. (1) with the expressions in Eq. (13). The energy gap in Eq. (2) must be compared with the simplified expression $\Delta E^{\mathrm{LS-HS}} = \Delta E^{\mathrm{SC_1}} + \Delta E^{\mathrm{SC_2}} + \Delta E^{\mathrm{FC}}$ from Eqs. (12) and (13). In the case shown in Fig. 2a, the energy gap between the singlet $S_1$and the quintet is expressed as $\Delta E^{\mathrm{S_1-Q}} = 6J_{\mathrm{FC}}$ [from Eqs. (1) and (3) with $s_1 = s_2 = 1$ for two interacting triplets] and the coupling parameter is characteristic of the FC unit:

$$6J_{\mathrm{FC}} = \sum_{ij}^{\mathrm{SC_1}} J_{ij}\Delta P_{ij}^{\mathrm{S_1-Q}} + \sum_{ij}^{\mathrm{FC}} J_{ij}\Delta P_{ij}^{\mathrm{S_1-Q}} + \sum_{ij}^{\mathrm{SC_2}} J_{ij}\Delta P_{ij}^{\mathrm{S_1-Q}} \tag{14}$$

On the other hand, in the case shown in Fig. 2b there are two important contributions to the energy gap between the quintet and the singlet S_2 (which, in this case, is lower in energy than S_1). First of all, there is the stabilization of the quintet via the FC unit [$E_{\mathrm{Q}} = -2J_{\mathrm{FC}}$, the energy of the quintet obtained from two interacting triplets via Eqs. (1) and (3)]. Then, there is the destabilization of the singlet in the SC unit via the $J_{\mathrm{SC}}(\Delta E^{\mathrm{S_2-T}} = 2J_{\mathrm{SC}})$. Thus we have

$$\begin{aligned}2J_{\mathrm{SC}} - 2J_{\mathrm{FC}} &= \sum_{ij}^{\mathrm{SC_1}} J_{ij}\Delta P_{ij}^{\mathrm{S_2-Q}} + \sum_{ij}^{\mathrm{FC}} J_{ij}\Delta P_{ij}^{\mathrm{S_2-Q}} \\ &\quad + \sum_{ij}^{\mathrm{SC_2}} J_{ij}\Delta P_{ij}^{\mathrm{S_2-Q}}\end{aligned} \tag{15}$$

The corresponding analysis of the multiplicity of the fragments can be carried our by decomposing the summation $\sum_{ij}^{n} P_{ij}$ in Eq. (10) using the same summation restrictions as in Eq. (13) to give

$$P^{\mathrm{SC}_1} = \sum_{i,j\in \mathrm{SC}_1}^{\mathrm{SC}_1} P_{ij} \tag{16}$$

and the other analogously defined terms. From this, we can define

$$[S(S+1)]^{\mathrm{SC}} = -\frac{n^{\mathrm{SC}}(n^{\mathrm{SC}}-4)}{4} - P^{\mathrm{SC}} \tag{17}$$

and

$$[S(S+1)]^{\mathrm{FC}} = -\frac{n^{\mathrm{FC}}(n^{\mathrm{FC}}-4)}{4} - P^{\mathrm{FC}} \tag{18}$$

where n^{SC} and n^{FC} are the number of electrons in the SC and FC units, respectively.

3 Computational details

Our objective in this work is to rationalize the Dougherty model via the computation of Eq. (9). We have used the CASSCF algorithm to calibrate the molecular mechanics valence bond (MMVB) results. The computation of the J_{ij}, however, is not simple for more than two-electron systems. In the CASSCF framework, these can be computed via an effective Hamiltonian approach [11], but this is restricted to small active spaces. As discussed elsewhere [8], the J_{ij} parameters in MMVB were obtained from CASSCF computations. However, only the $2s_{ij}\langle i|h|j\rangle$ contribution is well represented in this approach. Thus we shall be content with a discussion of the $\Delta P_{ij}^{\mathrm{LS-HS}}$ since these can be extracted routinely from any CI-based method.

The P_{ij} matrix can be obtained from a CASSCF computation where the active orbitals have been localized. Alternatively, they arise naturally in the MMVB method that can be used with very large active spaces (24 electrons). MMVB [8] is a hybrid method that uses a MM2 potential [12] to describe the inert molecule σ-bonded framework and an effective Heisenberg [7] Hamiltonian parametrized against CASSCF computations to represent electrons on sp^2/sp^3 carbon atoms which are involved in π-conjugation.

The method for computation of the P_{ij} matrix from a CASSCF computation deserves a brief mention. For practical purposes, the Eq. (6) can be rewritten [8a] in terms of the standard generators $\hat{E}_{ij}^{\sigma\sigma} = a_{i\sigma}^{+}a_{j\sigma}$ of the unitary group U(n) in the form where $\sigma = \alpha, \beta$

$$\hat{H}_S = Q + \sum_{i,j}^{M} J_{ij}\tfrac{1}{2}\left(\hat{E}_{ij}^{\alpha\alpha}\hat{E}_{ji}^{\beta\beta} + \hat{E}_{ij}^{\beta\beta}\hat{E}_{ji}^{\alpha\alpha} + \left[\hat{E}_{ij}^{\alpha\alpha}\hat{E}_{ji}^{\alpha\alpha} - \hat{E}_{ii}^{\alpha\alpha}\right] + \left[\hat{E}_{ij}^{\beta\beta}\hat{E}_{ji}^{\beta\beta} - \hat{E}_{ii}^{\beta\beta}\right]\right) \tag{19}$$

Equation (19) forms the basis of a quantum chemistry implementation of Eq. (6) since the P_{ij} are just the expectation values of the bilinear forms in Eq. (19).

The Heisenberg Hamiltonian implemented in MMVB corresponds to Eq. (6) and Eq. (19) and acts on a basis set of neutral many-electron VB states constructed from active orbitals which are singly occupied. The P_{ij} elements are obtained from the CI vectors of the MMVB [8a] and provide the spin matrix element of the interaction of i, j sites.

The SC-FC-SC systems chosen for our study of the high-spin radicals are the ones synthesized by Dougherty (Fig. 3, structures 2 and 3 [1, 2] and structure 4 [5]) and Adam [4] (Fig. 3, structure 5), which have been shown experimentally to be quintets in the ground state. Structure 1 has been studied to compare the P_{ij} computed from CASSCF versus MMVB. All the geometries of the systems in Fig. 3 have been optimized with the MMVB method.

4 Results and discussion

We shall begin our discussion with structure 1 (Fig. 3). Here we have carried out computations both at the MMVB level and at the CASSCF level. The computations serve both to orient the reader with a simple example and to calibrate the MMVB results.

We begin with a comparison of MMVB and CASCF. In order to calibrate the MMVB method, an 8-orbital 8-electron CASSCF (C p^{π} orbitals on unsaturated sites) in the 6–31g(d) basis has been used. The starting point was a UHF/6–31g(d) optimized geometry and the natural orbitals from this computation were used to define the starting CASSCF active space [13, 14]. The optimized quintet geometry is shown in Fig. 4a (for both

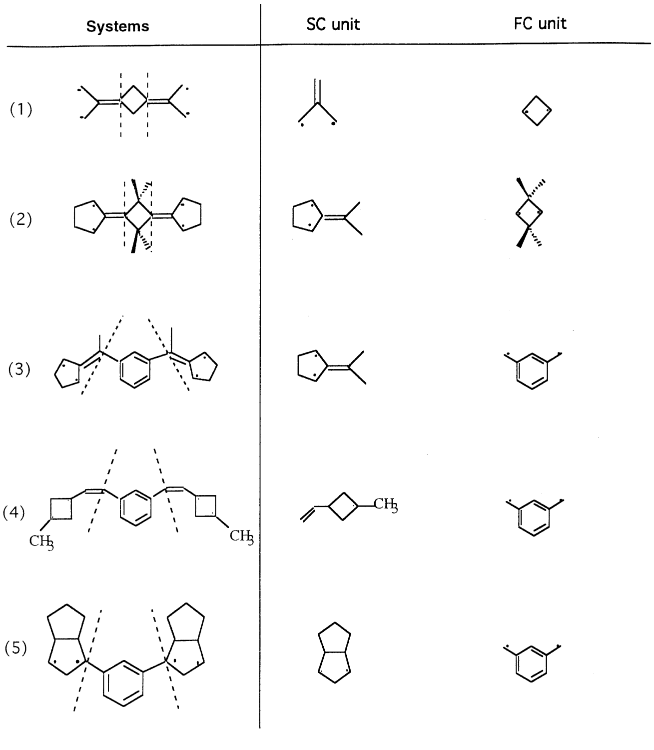


Fig. 3. Structures 1–5 and the corresponding SC and FC units

MMVB and UHF), while the significant $\Delta P_{ij}^{\mathrm{S-Q}}$ (i,j neighbour atoms) are collected in Fig. 4b. The $\Delta P_{ij}^{\mathrm{S-Q}}$ for MMVB and CASSCF are in qualitative agreement.

Now let us discuss the physical interpretation. The computed $\Delta P_{ij}^{\mathrm{S-Q}}$ are all small except for the 1–2 interaction in the FC unit (i.e. the interaction between centres 1 and 2 of the FC unit in Fig. 4b), as expected, for both MMVB and CASSCF. Thus ΔE^{FC} controls the spin multiplicity, in agreement with the Dougherty model. The CASSCF singlet-quintet splitting is 0.60 kcal mol^{-1}. In this simple model where the FC unit has only two active orbitals, the value of J_{FC} is given as

$$\Delta E^{\mathrm{S-Q}} = 6J_{\mathrm{FC}} = 2J_{12}\Delta P^{\mathrm{S-Q}} \tag{20}$$

The value of J_{12} obtained from a CASSCF computation on the isolated FC unit is 0.38 kcal mol^{-1}, which when combined with the computed ΔP_{12} gives a singlet quintet splitting of 0.63 kcal mol^{-1}. Thus both MMVB and CASSCF are in qualitative agreement and the Dougherty model seems to hold nicely. Now notice that J_{12} is positive. The orbitals $i,j = 1,2$ are non-overlapping; thus the J_{ij} corresponds to the two-electron repulsion integral [first term in Eq. (11)], which is always positive. Since $\Delta P_{ij} > 0$, the product of ΔP_{ij} and J_{ij} is positive, which yields the quintet stability.

However, this observation masks a subtlety that is not usually considered in discussing the Dougherty model. In fact $P_{12}^{\mathrm{S/Q}} = 0.086/-0.774$ at the CASSCF level and $P_{12}^{\mathrm{S/Q}} = 0.384/-0.778$ at the MMVB level. However, for two isolated electrons, $P_{ij} = -1$ for the triplet and $P_{ij} = 1$ for the singlet. Thus in the quintet state the FC unit is a triplet approximately ($P_{ij} < 0$), while in the singlet state it is nearly a singlet ($P_{ij} > 0$). The quintet state is only preferred because $\Delta P_{ij} > 0$. Thus, the spin coupling in the FC unit is different for quintet and singlet states and it is, therefore, the triplet preference of the FC unit *in the supermolecule* that gives rise to quintet stability. Thus, the suggestion of Dougherty appears to have quantitative validity. As we shall now show, this observation appears to be general for systems with an energy level diagram of the form given in Fig. 2a.

We now turn to a general discussion of the results obtained for structures 2–5 in Fig. 3. We begin with a discussion of the decomposition of $\sum_{ij}^{n} P_{ij}$ into P^{SC_1}, P^{SC_2} and P^{FC}, which permits the computation of $[S(S+1)]^{\mathrm{SC}}$ and $[S(S+1)]^{\mathrm{FC}}$ for the individual subunits via Eqs. (17) and (18). The values of the spin multiplicity, $2S+1$, obtained in this fashion are collected in Table 1. The results indicate an assignment (indicated in bold) of structures 1–3 into a class where the FC unit changes multiplicity (from a triplet to the average of a

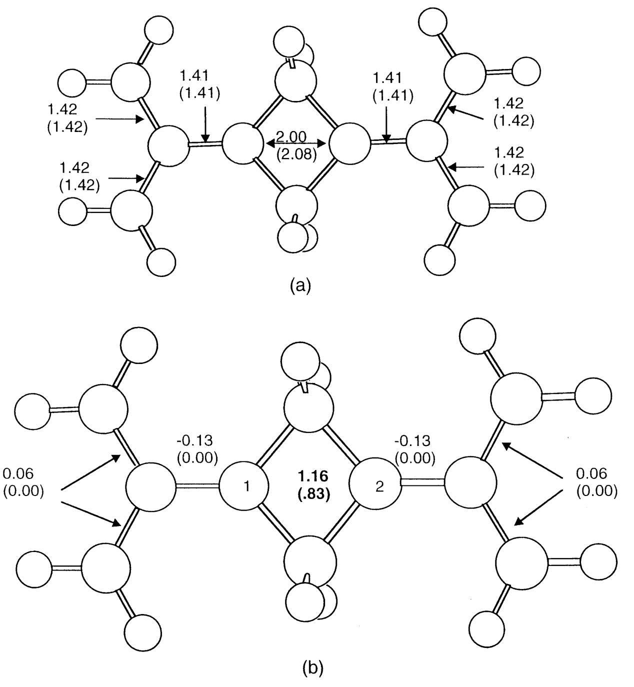


Fig. 4a,b. Geometry and ΔP_{ij} values for structure 1 (Fig. 3). **a** C—C distances for the active neighbour atoms, optimized for the quintet state in MMVB and CAS (in parentheses). **b** ΔP_{ij} values for the nearest-neighbour active atoms in MMVB and CAS (in parentheses)

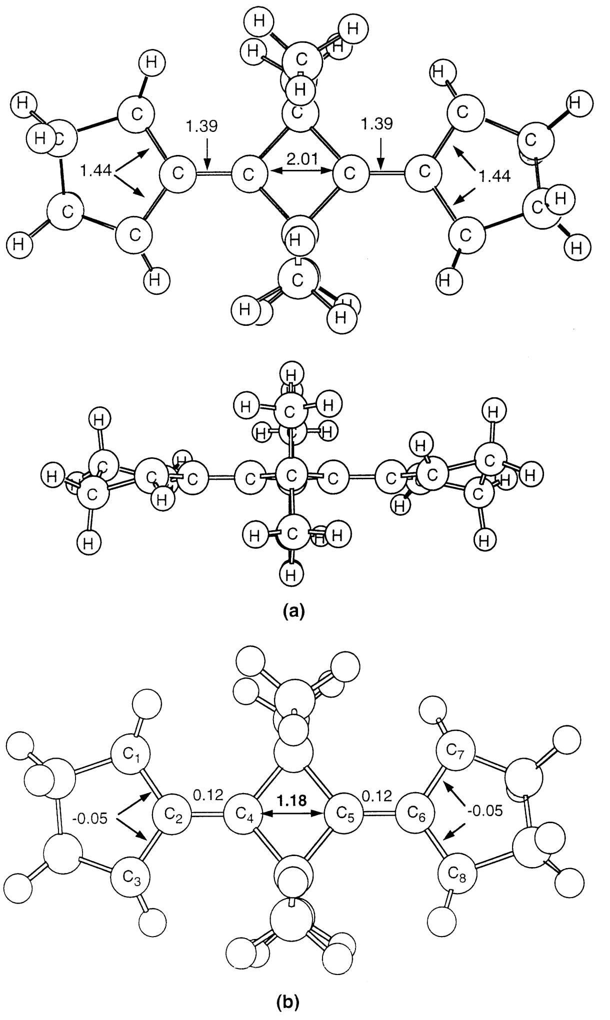


Fig. 5a,b. Geometry and ΔP_{ij} values for structure 2 (Fig. 3). **a** C—C distances for the active neighbour atoms, optimized for the quintet state in MMVB. **b** ΔP_{ij} values for the neighbour active atoms (1–8) in MMVB

singlet and triplet) between the quintet and singlet states while the spin multiplicity of the SC units remain unchanged. Thus the energy level diagram corresponds to Fig. 2a. We shall refer to this class as *FC controlling* (structures 2 and 3). In contrast, structures 4 and 5 belong to the class corresponding to the energy level diagram shown in Fig. 2b and we shall refer to these systems as *SC controlling*. Here the FC unit has the same multiplicity (a triplet) between the quintet and singlet states while the spin multiplicity of the SC units changes from a triplet to the average of a singlet and triplet between the quintet and singlet states.

Now let us turn our discussion to ΔE^{SC_1}, ΔE^{SC_2} and ΔE^{FC}. We focus on ΔP_{ij}^{FC} and ΔP_{ij}^{SC}, remembering that for non-overlapping orbitals J_{ij} will be positive and ΔP_{ij} will be positive to obtain quintet stability, but for overlapping orbitals (nearest neighbours) J_{ij} will be negative and ΔP_{ij} will be negative. The optimized geometries (for the quintet state) together with the significant ΔP_{ij} are collected in Figs. 5–8 for structures 2–5 (Fig. 3).

For the FC controlling class, structures 2 and 3 differ mainly in the nature of the FC unit. Structure 2 has an FC unit with two non-overlapping orbitals, similar to structure 1. However, the FC unit in structure 3 is a delocalized system composed of overlapping orbitals. Thus the nearest-neighbour J_{ij} must be negative. Accordingly, high-spin preference in the FC unit will be associated with negative values for both J_{ij} and ΔP_{ij} in the dominant contributions.

The results for structure 2 (Fig. 5) are similar to structure 1. The ΔP_{ij}^{SC} for the SC units are very small; therefore this system is FC controlling. The value of $\Delta P_{4,5}^{FC}$ is large and positive (see Fig. 5 for centre numbering), consistent with the case of non-overlapping orbitals 4 and 5. Structure 3 has a different FC unit and corresponds to a delocalized FC unit. The results for structure 3 are collected in Fig. 6, in which the centre numbering is shown. Here again the ΔP_{ij}^{SC} for the SC units are very small. The ΔP_{ij}^{FC} are dominated by the nearest-neighbour contributions and the $\Delta P_{4,5}^{FC}$ and $\Delta P_{7,11}^{FC}$ contributions dominate and are negative. In Fig. 9 we show the individual $P_{4,5}^{FC}$ and $P_{7,11}^{FC}$ contributions as well as the $P_{4,11}^{FC}$ between the unpaired electrons of the FC unit. In the quintet state (Fig. 9b) the $P_{4,11}^{FC}$ value is close to -1 (characteristic of the triplet state of the FC unit), while $P_{4,11}^{FC}$ in the singlet is near zero (characteristic of the fact that the FC unit is an average of singlet and triplet). The individual $P_{4,5}^{FC}$ and $P_{7,11}^{FC}$ contributions for the quintet state are large and positive, leading to the negative values for the $\Delta P_{4,5}^{FC}$ and $\Delta P_{7,11}^{FC}$ contributions. Thus the quintet stabilization by the FC unit is due to the creation of strong singlet coupling across the 4,5 and 7,11 links.

We now turn to structures 4 and 5 (Figs. 7 and 8). We have referred to these structures as SC controlling because the spin multiplicity of the SC units changes. Notice that the dominant ΔP_{ij}^{SC} involve $\Delta P_{1,2}^{SC}$ and $\Delta P_{13.14}^{SC}$ in structure 4 and $\Delta P_{1,2}^{SC}$ and $\Delta P_{9,10}^{SC}$ in structure 5. These ΔP_{ij}^{SC} are positive and are associated with non-overlapping orbitals. However, the quintet stability here must be

Table 1. $(2S+1)$ for SC and FC units

System	SC unit $(2S+1)$ computed from P^{SC}		FC unit $(2S+1)$ computed from P^{FC}	
	Quintet	Singlet	Quintet	Singlet
(1)	3.000	2.985	**2.848**	**1.861**
(2)	3.000	2.987	**2.860**	**1.856**
(3)	2.952	2.904	**2.956**	**1.856**
(4)	**2.900**	**1.596**	2.971	2.867
(5)	**2.886**	**1.933**	3.000	2.989

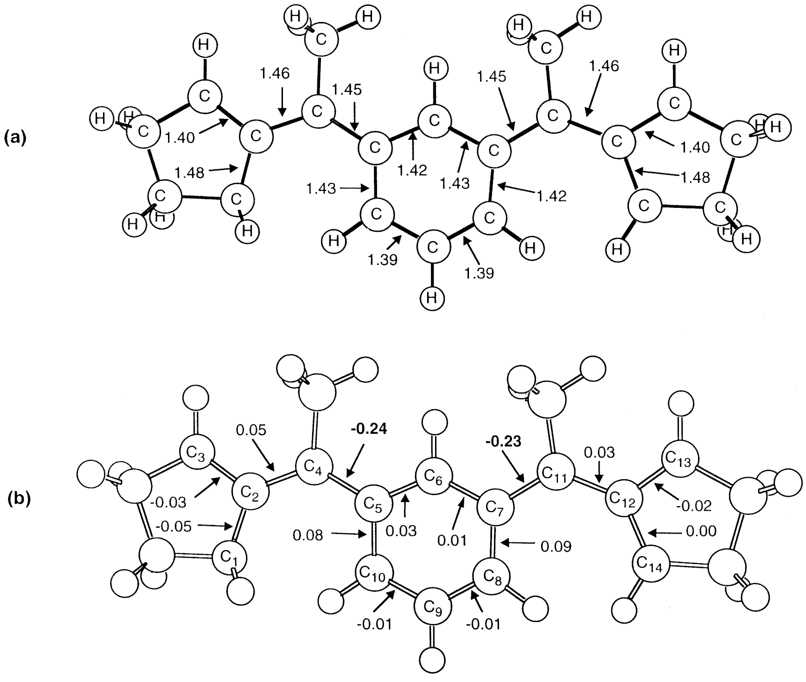
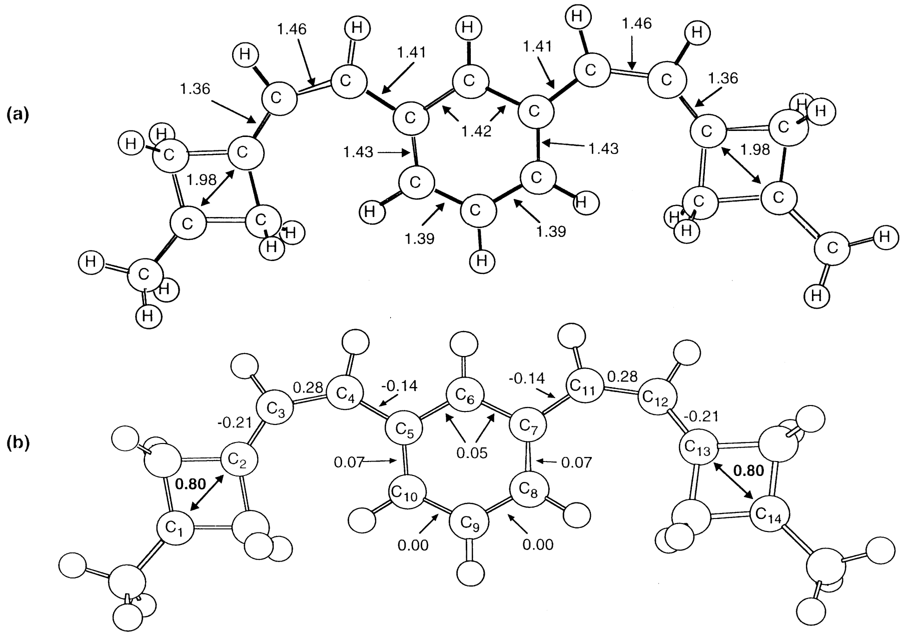


Fig. 6a,b. Geometry and ΔP_{ij} values for structure 3 (Fig. 3). **a** C—C distances for the active neighbour atoms, optimized for the quintet state in MMVB. **b** ΔP_{ij} values for the neighbour active atoms (1–14) in MMVB

Fig. 7a,b. Geometry and ΔP_{ij} values for structure 4 (Fig. 3). **a** C—C distances for the active neighbour atoms, optimized for the quintet state in MMVB. **b** ΔP_{ij} values for the neighbour active atoms (1–14) in MMVB



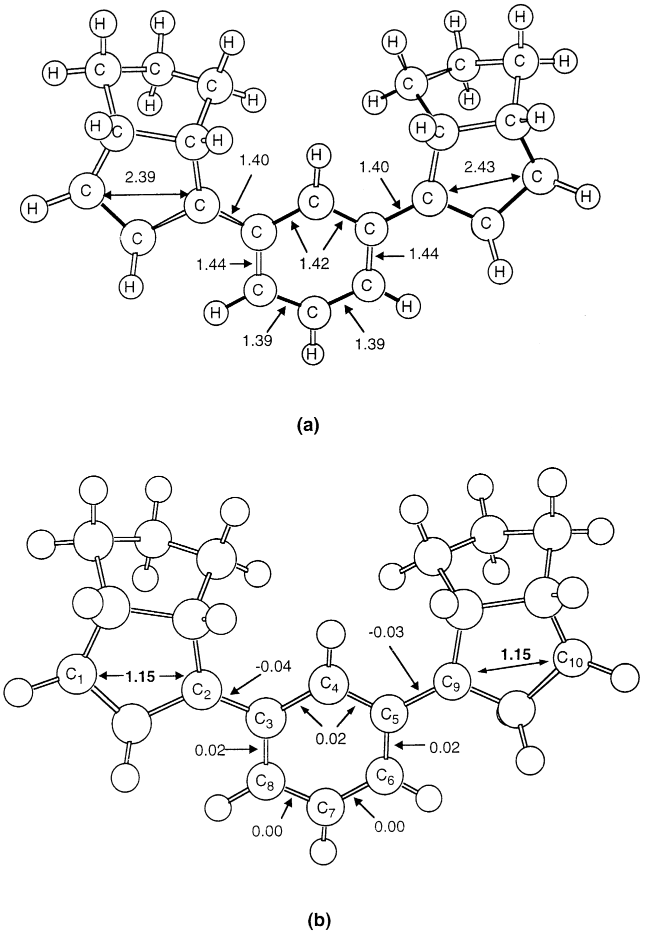


Fig. 8a,b. Geometry and ΔP_{ij} values for structure 5 (Fig. 3). **a** C—C distances for the active neighbour atoms, optimized for the quintet state in MMVB. **b** ΔP_{ij} values for the neighbour active atoms (1–10) in MMVB

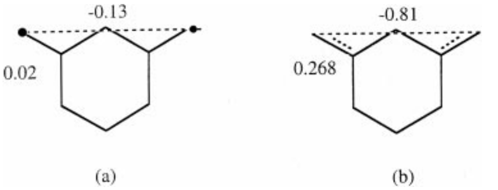


Fig. 9a,b. Computed $P_{4,5}$ and $P_{4,11}$ values in the delocalized FC unit structure contained in structure 3. **a** The singlet state. **b** The quintet state

controlled by both J_{FC} and J_{SC}; thus the quintet singlet splitting is approximately $2J_{\mathrm{SC}} - 2J_{\mathrm{FC}}$. However, it is still the FC unit that controls the quintet singlet stability overall. The value of J_{ij} between the unpaired electrons in the SC units for both structures 5 and 6 will be very small (i.e. orbitals i, j are non-overlapping). Thus J_{ij}^{SC} corresponds to the two-electron repulsion integral [i.e. the first term in Eq. (11), which is always very small and positive]. In contrast, J_{ij}^{FC} are controlled by the nearest-neighbour contributions that are large and negative because the $2s_{ij}\langle i|h|j\rangle$ term dominates, but the $\Delta P_{i,j}^{\mathrm{FC}}$ are very small because the spin of the FC unit does not change. Therefore, it is apparent that the structures should have a much smaller quintet-singlet gap. Thus a successful design strategy for high-spin systems requires both an effective FC unit and an SC unit with a large singlet-triplet splitting.

5 Conclusions

We have examined the model proposed by Dougherty for the design of high-spin systems from a quantitative point of view. It would appear that for FC controlling systems, where the spin multiplicity of the FC unit itself changes from triplet to an average of singlet and triplet (as the total spin multiplicity changes from quintet to singlet), his model may yield a good design strategy. This is particularly true for the case where the FC unit is a delocalized system with a large singlet-triplet gap. However, for localized FC units such as structure 2, this may not always be effective. On the other hand, where the singlet-triplet gap in the SC unit is small (structures 4 and 5), the spin multiplicity of the FC unit hardly changes and the contribution of J_{SC} must be taken into account.

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