

## Differences in Expected Stability of the Triplet State in Cyclic $\pi$ -Systems Containing $4n$ Electrons

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**Summary** Theoretical considerations indicate that in  $4n$   $\pi$ -electron systems the triplet state in rings of  $4n$  atoms is less stable with respect to the lowest singlet than in the isoelectronic systems consisting of  $4n \pm 1$  or  $4n \pm 2$  atoms.

SIMPLE Hückel theory allows one to predict that molecules containing  $4n$   $\pi$ -electrons in a ring of  $4n$  or  $4n \pm 1$  atoms should be nonaromatic. Furthermore, since two electrons must be distributed between two degenerate orbitals, such molecules should have ground states which are either symmetrical triplets or Jahn-Teller distorted singlets.<sup>1</sup> An SCF-MO calculation predicts<sup>2</sup> and experiments seem to confirm<sup>3</sup> that the latter alternative is preferred in cyclobutadiene. However, in several cyclopentadienyl cations the triplet is either the ground state or very close to it.<sup>4</sup> I present a theoretical demonstration that this difference between isoelectronic  $4n$   $\pi$ -systems in rings of  $4n$  and  $4n \pm 1$  atoms is to be generally expected. Only in the latter is the triplet state expected to show any stability with respect to the lowest singlet.

A planar symmetrical ring of  $m$  atoms belongs to the point group  $D_{mh}$ . If the molecule has  $4n$   $\pi$ -electrons, two electrons must be placed in two orbitals which belong to the degenerate  $E_n^*(m = 4n \pm 1)$  or  $E_{ng}(m = 4n)$  representation of the group. The symmetries of the electronic states so formed may be deduced from the irreducible representations spanned by the direct product  $E_n^* \times E_n^*$  in a ring of  $4n \pm 1$  atoms and  $E_{ng} \times E_{ng}$  in a ring of  $4n$  atoms. The former gives rise to states  $A_1'$ ,  $E_{2n-(1 \mp 1)/2}'$ , and  $A_2'$  in a  $4n \pm 1$  membered ring. The  $A_2'$  state can be shown to be the triplet which lies  $2K_{ij}$  lower than the  ${}^1A_1'$  state and  $K_{ij}$  lower than the pair of degenerate singlet states, where  $\psi_i$  and  $\psi_j$  are the degenerate molecular orbitals and

$$K_{ij} = \int \psi_i^*(1)\psi_j^*(2)(e^2/r_{12})\psi_j(1)\psi_i(2)d\tau \quad (1)$$

In the groups  $D_{mh}$  ( $m = 4n$ ) the direct product  $E_{ng} \times E_{ng}$  spans  $A_{1g}$ ,  $B_{1g}$ ,  $B_{2g}$ , and  $A_{2g}$ . Again  ${}^1A_{1g}$  and  ${}^3A_{2g}$  are split by  $2K_{ij}$ , but the other two singlet states are, in general, no longer degenerate. They are split by  $2K'_{ij}$ , where

$$K'_{ij} = \int \psi_i^*(1)\psi_i^*(2)(e^2/r_{12})\psi_j(1)\psi_j(2)d\tau \quad (2)$$

The fact that group theory shows a degenerate pair of states in rings of  $4n \pm 1$  atoms means that in these systems the symmetry of the degenerate orbitals must cause  $K'_{ij}$  to vanish. However, for rings of  $4n$  atoms symmetry does not cause  $K'_{ij}$  to vanish. In fact, in these systems it can be shown that  $K'_{ij} = K_{ij}$ , if the usual approximation of zero differential overlap is made.<sup>5</sup> This means that within the validity of this approximation,<sup>†</sup> in  $4n$   $\pi$ -electron systems

consisting of  $4n$  atoms, the lowest singlet and triplet have the same energy.<sup>‡</sup>

In order that  $K'_{ij} = K_{ij}$ , comparison of equations (1) and (2) shows that a sufficient condition is

$$\psi_j^*\psi_i = \psi_i^*\psi_j \quad (3)$$

This equality can be demonstrated using two symmetry-related properties of  $\psi_i$  and  $\psi_j$ . The first is that because they are a degenerate pair, they can be written as complex conjugates of each other:

$$\psi_i = \psi_j^* \quad (4)$$

The second is that as two nonbonding molecular orbitals in an alternant hydrocarbon,<sup>6</sup> if  $\psi_i$  is written

$$\psi_i = \sum_k^{2n} C_k \phi_k + \sum_l^{2n} C_l \phi_l \quad (5)$$

where the atomic orbitals have been divided into two sets,  $k$  and  $l$ , which alternate around the ring, then  $\psi_j$  may be written

$$\psi_j = \sum_k^{2n} C_k \phi_k - \sum_l^{2n} C_l \phi_l \quad (6)$$

Substituting (5) and (6) into (4) yields

$$\sum C_k \phi_k + \sum C_l \phi_l = \sum C_k^* \phi_k - \sum C_l^* \phi_l \quad (7)$$

Equating coefficients,

$$C_k = C_k^* \text{ and } C_l = -C_l^* \quad (8)$$

showing that the  $C_k$  must be pure real and the  $C_l$  pure imaginary numbers.

Use of (5), (6), and (8) gives

$$\psi_j^*\psi_i = (\sum C_k \phi_k + \sum C_l \phi_l)^2 \quad (9)$$

$$\psi_i^*\psi_j = (\sum C_k \phi_k - \sum C_l \phi_l)^2 \quad (10)$$

Finally, since zero differential overlap implies

$$\phi_k \phi_l = 0 \quad (11)$$

the cross terms vanish and

$$(\sum C_k \phi_k)^2 + (\sum C_l \phi_l)^2 = (\sum C_k \phi_k)^2 + (-\sum C_l \phi_l)^2 \quad \text{Q.E.D.} \quad (12)$$

The different situations with regard to the energy of the states in  $4n \pm 1$  and  $4n$  systems are summarized in the

<sup>†</sup> When differential overlap is not neglected the triplet falls below the singlet. However, inclusion of extensive configuration interaction has the opposite effect. See ref. 1 for a discussion of the particular case of cyclobutadiene.

<sup>‡</sup> This follows from the fact that all four states have the same coulomb repulsion energy when complex MO's are used. When real MO's are used, obviously  $K'_{ij} = K_{ij}$ , but one must show that the coulomb repulsion energies for the states are the same. The proof is similar to the demonstration that  $K'_{ij} = K_{ij}$  for complex MO's.

Figures.<sup>7</sup> In fully symmetrical rings of  $4n \pm 1$  atoms, the triplet lies lowest. Even if the ground state of the system

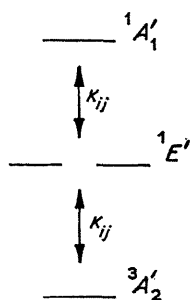


FIGURE 1. State energies of a  $4n \pm 1$  atom ring containing  $4n$   $\pi$ -electrons.

is a distorted singlet, the triplet, once populated, should show some stability if the distortions caused by the molecular vibrations are sufficiently small for the singlet to remain above the triplet and if tunnelling is unimportant. In contrast, even in fully symmetrical rings of  $4n$  atoms the lowest singlet lies very close to the triplet, and a pseudo-Jahn-Teller distortion is capable of further lowering its energy. Therefore, it is predicted that the triplet state

should play a much less important role in rings of  $4n$  atoms than in the isoelectronic  $4n$   $\pi$ -systems of  $4n \pm 1$  atoms.<sup>§</sup>

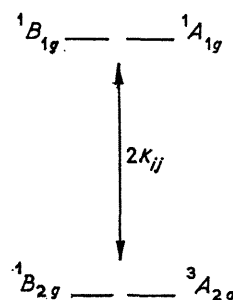


FIGURE 2. State energies of a  $4n$  atom ring containing  $4n$   $\pi$ -electrons.

Group theory shows that rings of  $4n \pm 2$  atoms containing  $4n$  electrons also have a degenerate pair of singlet states. Therefore, they are expected, like the isoelectronic  $4n \pm 1$  atom rings, to have a symmetrical triplet state of some potential stability. Hoiijtink has observed stable triplet states in the dianions of triphenylbenzene and decacyclene.<sup>8</sup>

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§ As ring size increases, the magnitude of  $K_{ij}$  decreases; so the stability of the triplet relative to the undistorted singlet in  $4n \pm 1$  atom rings should be greatest in small systems.

<sup>1</sup> For an excellent discussion and review of the particular case of cyclobutadiene see H. E. Simmons and A. G. Anastassiou, in M. P. Cava and M. J. Mitchell, "Cyclobutadiene," Academic Press, New York, 1967, pp. 368–392.

<sup>2</sup> M. J. S. Dewar and G. L. Gleicher, *J. Amer. Chem. Soc.*, 1965, **87**, 3255.

<sup>3</sup> L. Watts, J. D. Fitzpatrick, and R. Petit, *J. Amer. Chem. Soc.*, 1966, **88**, 624.

<sup>4</sup> R. Breslow, A. W. Change, R. Hill, and E. Wasserman, *J. Amer. Chem. Soc.*, 1967, **89**, 1112.

<sup>5</sup> For a discussion of the zero differential overlap approximation see R. G. Parr, "Quantum Theory of Molecular Electronic Structure," Benjamin, New York, 1963, pp. 50–62.

<sup>6</sup> C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.*, 1940, **36**, 193. For a review of the properties of alternant hydrocarbons see L. Salem, "Molecular Orbital Theory of Conjugated Systems," Benjamin, New York, 1966, pp. 36–43.

<sup>7</sup> For calculations applying the zero differential overlap approximation to specific systems and giving exactly this pattern of energy levels, as of course they must, see H. C. Longuet-Higgins and K. L. McEwen, *J. Chem. Phys.*, 1957, **26**, 719.

<sup>8</sup> R. Jesse, P. Biloen, R. Prins, J. van Voorst, and G. Hoiijtink, *Mol. Phys.*, 1963, **6**, 633.