On the Bonding in 2,4-Dimethylenecyclobutane-1,3-diyl

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Spin-coupled theory has been applied to the π-electron systems of 2,4-dimethylenecyclobutane-1,3-diyl (DMCBD), of cyclobutadiene, and of 3,4-dimethylenecyclobutene; the descriptions of triplet DMCBD and of cyclobutadiene differ significantly from classical valence bond (VB) theory, and feature triplet coupling of in- and out-of-phase combinations of C(2p$_\pi$) orbitals.

The triplet ground state of 2,4-dimethylenecyclobutane-1,3-diyl (DMCBD), also known as 1,3-dimethylenecyclobutadiene, can be produced by the irradiation of an appropriate diazene precursor.[1] The triplet spin and planar geometry have been confirmed recently using e.s.r. techniques.[2] This molecule, which is yellow–orange with λ_{max} 506 nm (in absorption), is of particular interest as a non-Kekulé isomer of benzene.

We use spin-coupled theory,[3] which represents the modern development of valence bond (VB) theory, to examine the bonding in the π-electron systems of the lowest singlet and triplet states of DMCBD. We compare with the lowest singlet and triplet states of cyclobutadiene, and with the singlet ground state of 3,4-dimethylenecyclobutene.

There have been a number of theoretical studies, at various levels of sophistication, of low-lying states of DMCBD. In particular, Davidson *et al.*[4] have performed complete π-space configuration interaction (CI) calculations in a minimal basis set. They predicted a $^3B_{2u}$ ground state (D_{2h} symmetry), with ^1A_g symmetry for the lowest singlet state, rather than $^1B_{2u}$. A two-configuration SCF description was found to be essential for the ^1A_g state. The planar structure for this state is not a true minimum, but is instead a transition state for the formation of (non-planar) 2,4-dimethylenebicyclo[1.1.0]butane, *via* the development of a long transannular bond.[5—7]

Spin-coupled theory is a sophisticated *ab initio* approach to electronic structure which has now been applied to a very wide range of problems. The calculations in the present work were carried out using the same techniques and the same basis set (triple-zeta plus polarization quality) as in recent studies of the π-electron systems of aromatic molecules[3e,8,9] and of 1,3-dipoles.[10] Our calculations for DMCBD will provide a clear physical picture of the bonding in the π-electron system.

We first carried out a standard restricted Hartree–Fock (RHF) calculation for the lowest triplet state of DMCBD at the partially optimized geometry given by Davidson *et al.*[4] Spin-coupled calculations were then performed explicitly for the π-electron system, which was described by six distinct, non-orthogonal, singly-occupied orbitals. The σ electrons of this molecule were accommodated in the doubly-occupied RHF molecular orbitals (MOs). Bearing in mind that Davidson *et al.*[4] found that the MOs optimized for the $^3B_{2u}$ state gave the best CI description of the ^1A_g state, we chose to use this set of MOs for the σ electrons in all of our calculations on DMCBD.

The π orbitals were fully optimized, in the form of completely general linear combinations of all the basis functions of π symmetry, without any constraints on the overlaps between them or preconceptions as to the degree of localization or delocalization. There are nine allowed ways of coupling together the individual spins of six electrons so as to produce an overall triplet. We optimized the weights of the nine different modes of spin coupling simultaneously with the forms of the six non-orthogonal π orbitals. Analogous calculations were carried out for the π electrons of the lowest singlet state, including all five allowed modes of spin coupling for six electrons with a net spin of zero. It is important to notice that the two states are treated on an equal footing, with just one spatial configuration.

For the $^3B_{2u}$ ground state, the electron correlation taken into account by the spin-coupled calculations gives an improvement over the RHF description of 177 kJ mol^{-1} in the total energy. This state is substantially less stable than the ground state of benzene (by *ca.* 250 kJ mol^{-1}). We find that the lowest singlet state of DMCBD has ^1A_g symmetry, and we estimate a vertical excitation energy of *ca.* 94 kJ mol^{-1} (22 kcal mol^{-1}). Using slightly different planar geometries for the two states, Davidson *et al.*[4] suggested a singlet–triplet splitting of 23.6 kcal mol^{-1}. The calculations of Davidson *et al.*[4] have been extended very recently by Du *et al.*,[11] who used a larger basis set (but smaller than in the present work) and included σ–π correlation. The two sets of calculations produced very similar optimized geometries. Du *et al.* estimate a splitting of 18.2 kcal mol^{-1}.

In order to simplify the discussion of the orbitals in DMCBD, we describe first the preliminary findings from analogous calculations on the lowest singlet and triplet states of cyclobutadiene. For square planar C_4H_4, both spin multiplicities are characterized by orbitals which take the form of in- and out-of-phase combinations of slightly distorted C(2p$_\pi$) functions on opposite corners of the ring. The electrons in each pair are coupled to *triplet* spin. These triplet pairs are then coupled to the overall singlet or triplet spin of the molecule. This appears to be a characteristic feature of anti-aromatic systems.

Distortion of the triplet state of C_4H_4 to rectangular geometry is energetically unfavourable, and the same orbital description pertains. On the other hand, the singlet state, which is lower in energy, becomes more stable at a rectangular geometry. The orbitals change into slightly distorted 2p$_\pi$ functions, localized on each carbon atom. The dominant mode of spin coupling then corresponds to C–C π bonds along the two short sides of the ring.

Analogous spin-coupled calculations at the equilibrium geometry of the $^1A_1$ ground state of 3,4-dimethylenecyclobutene, which is planar (C_{2v} symmetry),[12] result in a description which is very similar to that provided by classical VB theory, except for small distortions of the orbitals.

The spin-coupled orbitals for the $^3B_{2u}$ ground state and for the ^1A_g excited state of DMCBD are shown in Figure 1. For both spin multiplicities, the forms of four of the orbitals, the overlaps between them, and the dominant mode of spin coupling, correspond to two ethylenic π bonds external to the ring. These are very similar to the corresponding units in 3,4-dimethylenecyclobutene. For the singlet state of DMCBD, the two remaining π orbitals, ϕ_1 and ϕ_6 in Figure 1, take the form of localized, slightly distorted C(2p$_\pi$) functions, but for the triplet state we observe in- and out-of-phase combinations, similar to those in cyclobutadiene.

Orbitals ϕ_1 and ϕ_6 in singlet DMCBD have an overlap of only 0.3, with the dominant mode of spin coupling corre-

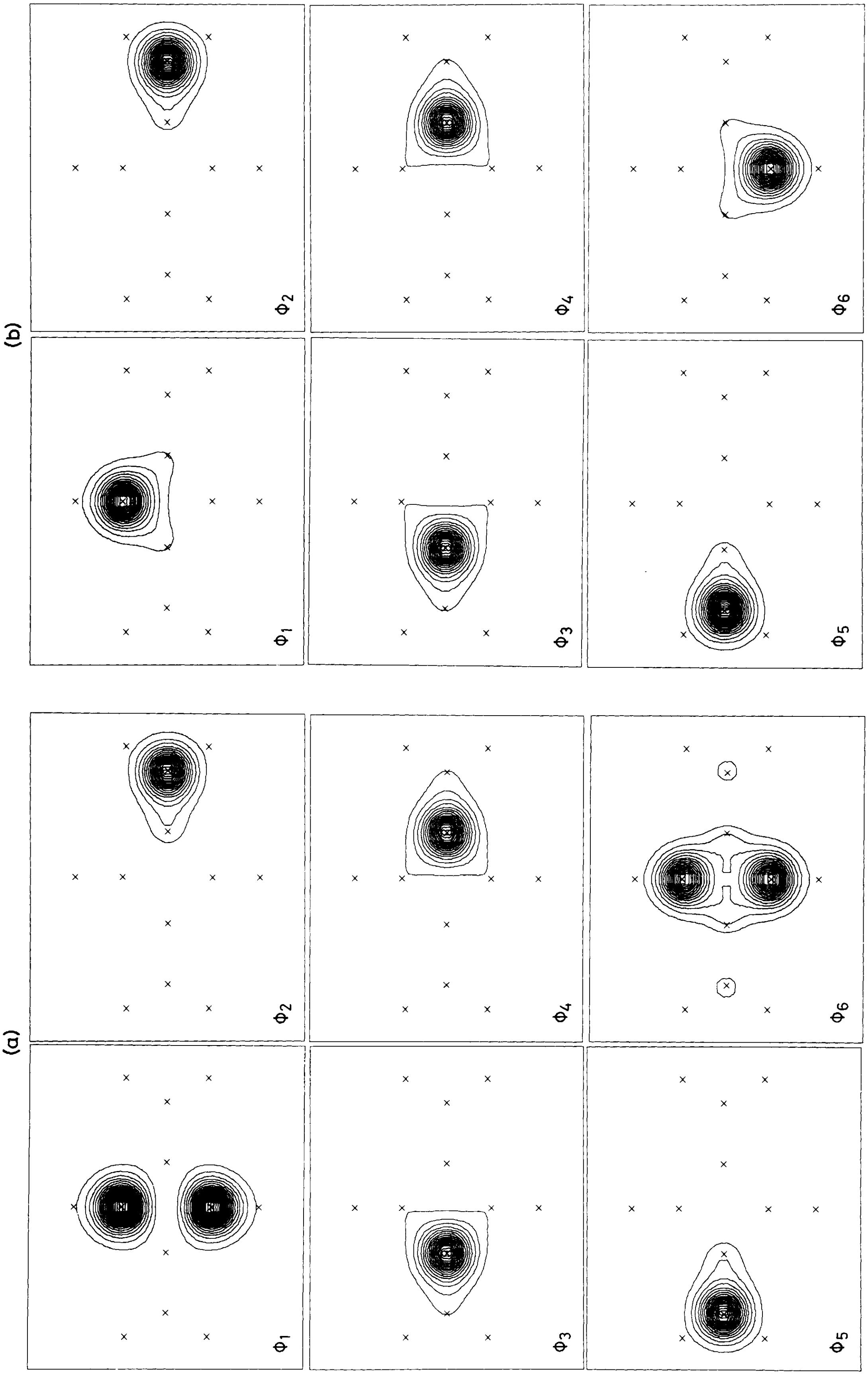

Figure 1. Spin-coupled π orbitals for DMCBD: (a) the $^3B_{2u}$ ground state, and (b) the ^1A_g excited state. We show contours of the square modulus of the orbitals in the plane one unit of atomic distance (*ca.* 53 pm) above the molecular plane. The projected positions of the nuclei are marked with crosses. Note that the numbering of the orbitals is arbitrary.

sponding to pairing these electrons with opposite spin. In order to increase this overlap to a value more typical of a C–C π bond (*ca.* 0.6—0.7), it is clear that the molecule needs to distort from planar geometry. On the other hand, triplet DMCBD, which features the triplet-coupled 'combination orbitals' seen also in C_4H_4, is stable with respect to such distortions. It is important to point out that although the 'combination orbitals' ϕ_1 and ϕ_6 constitute a triplet-coupled pair, there are also small components in the total wavefunction from the other modes of spin coupling. This prevents us from carrying out a linear transformation to localized orbitals. We believe that it is the triplet-coupled pair of 'combination orbitals,' rather than any local 'diradical' character, that is fundamental to the description of triplet DMCBD, and its stability with respect to distortion from planar geometry.

A more detailed account of the consequences of the spin-coupled descriptions of singlet and triplet cyclobutadiene (square and rectangular), of the $^3B_{2u}$ and ^1A_g states of DMCBD, and of the $^1A_1$ ground state of 3,4-dimethylenecyclobutene will appear in due course.[13]

It is easy to envisage a whole series of molecules related to DMCBD by the insertion of further cyclobutadiene rings between the CH_2 groups. Speculation continues as to the spin multiplicity of the ground states of all these $4n + 2$ π-electron systems, and as to the electrical properties of the very long chain molecules.[14] We intend to consider these topics in future work.

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