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Can a Square or Effectively Square Singlet Be the Ground State of Cyclobutadiene?

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Abstract: The question posed in the title can be answered in the affirmative when the important effects of electron repulsion in open-shell systems are considered. Repulsion between the two electrons in the nonbonding MO's of cyclobutadiene is minimized in a square geometry, resulting in a flat curve for rectangular distortion in the lowest singlet state. A flat curve for distortion in this state implies that its stabilization by a pseudo-Jahn-Teller effect is not responsible for dropping its energy below that of the triplet state. It is shown, however, that the singlet can profit by CI from a reduction, unavailable to the triplet, in the repulsion between the nonbonding electrons and those in ψ_1 and that it is this effect that makes the singlet the ground state of cyclobutadiene.

The available experimental evidence strongly indicates that cyclobutadiene has a singlet ground state.[1] It has long been supposed that a singlet ground state for cyclobutadiene is the result of a distortion to a rectangular geometry that drops the energy of this state below that of the triplet, which is expected to have its energy minimum at a square geometry.[2] However, recent ir studies of matrix isolated cyclobutadiene have shown that the geometry of the state observed must be square[3] or effectively square.[4] In this paper MO theory is used to investigate whether, when cognizance is taken of the importance of the effects of electron repulsion in open-shell systems,[7] a square or effectively square singlet can, in fact, be the ground state of cyclobutadiene.

In order that cyclobutadiene have a square (or effectively square) singlet as its ground state, two conditions must be fulfilled: (a) the lowest singlet must have its energy minimum at a square geometry (or the barrier to conversion of one distorted geometry to another must be very small) and (b) the lowest singlet must lie below the triplet. With regard to the first condition, it should be noted that the lowest singlet state of square cyclobutadiene ($^1B_{1g}$) is nondegenerate[2,7a,d] and so is not subject to the consequences of the Jahn-Teller theorem.[8] Although there is a low-lying singlet ($^1A_{1g}$) that can be mixed with $^1B_{1g}$ by a vibration that converts square to rectangular cyclobutadiene,[2] there is no guarantee that this pseudo-Jahn-Teller effect[9] will, in fact, produce any appreciable energy lowering. The reason is that although the distortion does lead to an increase in bonding, it is also accompanied by an increase in electron repulsion. Only in the square geometry of cyclobutadiene (and, more generally, in the most symmetrical geometry of other [4*n*]annulenes)[7a] are the two electrons in the nonbonding MO's confined to different sets of atoms, so that the wave function for these electrons contains no ionic terms.[7b,d] In fact, Snyder has carried out model calculations which show that a rectangular distortion, which causes a decrease in energy of 11.5 kcal/mol for the lowest singlet in a Hückel treatment, results in only a 0.5 kcal/mol energy drop when electron repulsion is included.[10,11]

If, because bonding cannot be maximized while electron repulsion is simultaneously minimized in the lowest singlet, the potential curve for distortion in this state of cyclobutadiene is very flat, then the pseudo-Jahn-Teller effect cannot be responsible for dropping the energy of this state below that of the triplet. When overlap is neglected, the fact that the nonbonding electrons can be confined to different sets of atoms makes the lowest singlet accidentally degenerate with the triplet in square cyclobutadiene.[7a,d,11] However, when the zero differential overlap approximation[12] is not made, scaling the appropriate semiempirical repulsion integrals by the square of the overlap integral allows an estimate of 3 kcal/mol as the amount by which the triplet lies below the singlet in the square geometry.[13] Therefore, if condition (a) is fulfilled, condition (b) can be satisfied only if there exists another effect that drops the energy of the singlet below that of the triplet in the square geometry of cyclobutadiene.

That such an effect does exist is indicated by the ab initio calculation on cyclobutadiene carried out by Buenker and Peyerimhoff.[14] They found that when configuration interaction (CI) is included, the singlet lies below the triplet *at all geometries.*[15] Although these authors carried out extensive (70 × 70) CI, the same result is obtained when just the lowest excited $^1B_{1g}$ and $^3A_{2g}$ configurations are mixed into the lowest singlet and triplet wave functions. Using a standard set of semiempirical parameters,[7d] this mixing is found to stabilize the square singlet by 8 kcal/mol more than it does the triplet, which is sufficient to make the former the ground state at all geometries.

The physical reason for the stabilization of the singlet relative to the triplet by CI is related to the effect on the allyl radical[16] of mixing into $|\psi_1{}^\alpha\psi_1{}^\beta\psi_2{}^\alpha\rangle$ the lowest excited doublet of the same symmetry

$$\Psi = \frac{1}{\sqrt{6}}\left(|\psi_3{}^\alpha\psi_1{}^\beta\psi_2{}^\alpha\rangle - |\psi_1{}^\alpha\psi_3{}^\beta\psi_2{}^\alpha\rangle - 2|\psi_1{}^\alpha\psi_2{}^\beta\psi_3{}^\alpha\rangle\right) \quad (1)$$

The first term in (1), by mixing ψ_3 into ψ_1 with a plus sign, increases the probability of finding the α spin electron in ψ_1 on the terminal carbon atoms. Since this electron has the same spin as that in ψ_2, these two electrons cannot simultaneously appear in the same p orbital. Increasing the probability of finding the former electron on the terminal atoms, to which the latter is confined, decreases the electrostatic repulsion between these two electrons by increasing the probability that they will be found at opposite ends of the molecule rather than on adjacent atoms. The second term in (1) increases the probability of finding the β spin electron in ψ_1 at the central carbon atom. Since this electron is not prohibited from appearing simultaneously in the same p orbital as the α spin electron in ψ_2, decreasing the probability of finding the former at the terminal carbon atoms, where the latter is confined, lowers the one-center repulsion between these two electrons. Together, the first two terms in (1) give rise to the negative spin density observed in the allyl radical.[16] The third term, which differs from the lowest configuration in the orbital assignment of two electrons, decreases the electron repulsion between the electron in ψ_2 and the one of opposite spin in ψ_1 by correlating their motions so that they tend to be at different ends of the molecule.

The lowest singlet and triplet in square cyclobutadiene both place one electron in each of the two nonbonding orbitals, when ψ_2 and ψ_3 are chosen so that they have no atoms in common. In the $m_s = 1$ component of the triplet the electrons in these MO's both have α spin, and the lowest excited triplet that can mix with $|\psi_1{}^\alpha\psi_1{}^\beta\psi_2{}^\alpha\psi_3{}^\alpha\rangle$ is

$$\Psi = \frac{1}{\sqrt{2}}\left(|\psi_1{}^\alpha\psi_3{}^\beta\psi_2{}^\alpha\psi_4{}^\alpha\rangle - |\psi_1{}^\alpha\psi_2{}^\beta\psi_4{}^\alpha\psi_3{}^\alpha\rangle\right) \quad (2)$$

It can be seen that, like the third term in (1), each term in (2) decreases electron repulsion by correlating the motion of the β spin electron in ψ_1 with that of one of the nonbonding electrons. There are no terms in (2) that correspond to the first two in (1), since, unlike the allyl radical, triplet cyclobutadiene has a uniform distribution of unpaired spin at each atom.

The lowest excited singlet that can mix with $^1B_{1g}$ is

$$\begin{aligned}\Psi = \frac{1}{\sqrt{12}}\big(&2|\psi_3{}^\alpha\psi_1{}^\beta\psi_2{}^\alpha\psi_4{}^\beta\rangle - 2|\psi_1{}^\alpha\psi_2{}^\beta\psi_4{}^\alpha\psi_3{}^\beta\rangle + \\ &|\psi_4{}^\alpha\psi_1{}^\beta\psi_2{}^\alpha\psi_3{}^\beta\rangle - |\psi_1{}^\alpha\psi_4{}^\beta\psi_2{}^\alpha\psi_3{}^\beta\rangle - \\ &|\psi_1{}^\alpha\psi_4{}^\beta\psi_2{}^\beta\psi_3{}^\alpha\rangle + |\psi_4{}^\alpha\psi_1{}^\beta\psi_2{}^\beta\psi_3{}^\alpha\rangle\big) \quad (3)\end{aligned}$$

In contrast to (2), (3) contains both types of terms present in (1). The reason is that the lowest $^1B_{1g}$ configuration,

$$\Psi = \frac{1}{\sqrt{2}}\left(|\psi_1{}^\alpha\psi_1{}^\beta\psi_2{}^\alpha\psi_3{}^\beta\rangle - |\psi_1{}^\alpha\psi_1{}^\beta\psi_2{}^\beta\psi_3{}^\alpha\rangle\right) \quad (4)$$

behaves *as if* it had a nonuniform distribution of spin (i.e., α spin at the two atoms spanned by ψ_2 and β spin at those spanned by ψ_3). Although there is, of course, no net spin density at any of the atoms in the $^1B_{1g}$ state of cyclobutadiene, the wave function in (4) does manifest antisymmetry with respect to spin in that, unlike any of the components of the triplet, (4) changes sign on interchange of the spins in ψ_2 and ψ_3. This fact allows (4) to profit by CI from a type of reduction, unavailable to the triplet, in the repulsion between the electrons in the nonbonding MO's and those in ψ_1. Mathematically, this situation is a consequence of the fact that the terms in (3) that are absent from the corresponding expression for the lowest excited $^3A_2$ configuration with $m_s = 0$[17] mix with the first term in (4) via an integral H and with the second via an integral $-H$. In the $m_s = 0$ component of the lowest $^3A_2$ configuration, the minus in (4) is replaced by a plus; consequently, these two integrals sum to zero, hence the absence of the terms that give rise to them from the excited state that is mixed by CI into the $m_s = 0$ component of $^3A_2$.

In summary, unlike the three components of the lowest $^3A_2$ configuration of cyclobutadiene, the lowest $^1B_{1g}$ configuration has a wave function that is antisymmetric to spin interchange between ψ_2 and ψ_3. Consequently, the singlet behaves in CI *as if* it had a nonuniform distribution of spin; and, like the allyl radical, the singlet can thus profit from a decrease in electron repulsion of a type that is unavailable to the triplet. It is this fact that makes the singlet the ground state of cyclobutadiene, even in a square geometry.[18]

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mune[5b] has pointed out, an effectively square geometry for the parent cyclobutadiene in a matrix is not incompatible with the distorted structures found in the crystals of derivatives, provided that the potential surface for distortion is flat. Relatively flat potential surfaces for distortion are known in larger molecules with [4*n*]annulene perimeters, which undergo rapid (on the NMR time scale) oscillation between two equivalent bond-alternated forms with energies of activation on the order of 3–5 kcal/mol.[6]

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(15) An earlier treatment of square cyclobutadiene by Craig[13] also showed that the singlet becomes the ground state when CI is included.

(16) See, for instance, ref 7d, pp 265–271.

(17) The correct expression can be obtained by using the lowering operator on (2). It will then be observed that a detailed interpretation of the effect of CI on improving the $m_s = 0$ component seems different than that for $m_s = 1$, as is often the case in triplet states. Although the mixings of the excited configurations into the lowest ones appear to be very different for the $m_s = 1$ and 0 components of the triplet, they of course have the same effect and result in wave functions that have identical energies.

(18) Note Added in Proof. M. J. S. Dewar and H. W. Kollmar, *J. Amer. Chem. Soc.*, **97**, 2933 (1975), have, in contrast to previous results from the Dewar group,[11] found square singlet cyclobutadiene to lie 13 kcal/mol above the triplet. Since, as discussed above, any calculation of the NDO type, in which the zero differential overlap approximation is made, must perforce lead to an accidental degeneracy between the singlet and triplet in the square geometry, this latest result is obviously spurious. It arises from the fact, apparently pointed out by a referee of the Dewar communication (see footnote 19 therein), that in order to obtain the $^1B_{1g}$ state of the square molecule, CI must be included between the two electronic configurations appropriate for describing the two possible rectangularly distorted cyclobutadienes. Dewar's failure to include this minimal CI results in an overestimation of the energy of the square singlet by $\frac{1}{4}(\gamma_{11} - 2\gamma_{12} + \gamma_{13})$. Using Dewar's formula for calculating electron repulsion integrals, the overestimation of the energy of the square singlet in his recent calculation is computed to be 13 kcal/mol. This fact, taken together with the discussion above of the additional stabilization of the singlet relative to the triplet by inclusion of further CI, renders improbable Dewar's assertion that the triplet lies below the singlet in a square geometry. Thus, even if the triplet should ultimately be shown by experiment to be the state observed in the matrix by ir, Dewar's explanation, that this state is metastable because it has a lower energy at its equilibrium square geometry than the singlet ground state, appears highly unlikely.

Ethylene Formation in Carbon Atom Reactions. Mechanism and Isotope Effects[1]

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Abstract: Energetic carbon-11 atoms were allowed to react with specifically deuterated hydrocarbons containing completely deuterated methyl or methylene groups and with mixtures of protonated and perdeuterated hydrocarbons. The doubly labeled ethylenes (^{11}C and D) formed in this process were radio gas chromatographically analyzed. The failure to observe carbon-11 labeled $C_2H_2D_2$ in any of these systems suggests that a mechanism including C_2 formation, e.g., by "high-energy stripping", and subsequent hydrogen abstraction does not significantly contribute to ethylene-^{11}C production. The ratios $^{11}C_2H_3D/^{11}C_2H_4$ and $^{11}C_2D_4/^{11}C_2HD_3$ obtained from reaction in equimolar mixtures of C_2H_6 and C_2D_6 or C_3H_8 and C_3D_8 and in CH_3CD_3 are consistently greater than 1, which provides additional support for the contention that ethylene-^{11}C is formed primarily via methyne insertion into the carbon–hydrogen bonds of methyl groups. The ^{11}C distribution among the various isotopic ethylenes observed in the systems under investigation indicates preferential CD formation and preferred insertion by methyne (^{11}CD or ^{11}CH) into CH_3 relative to CD_3 groups.

The hot-atom chemistry of carbon has been discussed in review articles by Wolf[2] and Wolfgang[3] in which the mechanistic approach to the chemistry of energetic carbon atoms has been documented.

One of the major products formed following the generation of carbon-11 atoms via nuclear processes, such as $^{12}C(p,pn)^{11}C$, $^{14}N(p,\alpha)^{11}C$, $^{12}C(n,2n)^{11}C$, and others, in hydrocarbons is carbon-11 labeled ethylene. Evidence for methyne ($\dot{C}H$:) insertion into C–H bonds of methyl groups being responsible in major part for the production of ethylene-^{11}C from the hydrocarbons was adduced from structure dependence studies and other data by Wolf and Stöcklin.[4-6] An alternative to this mechanism was suggested by MacKay et al.[7a] who proposed that carbon atom insertion into a C–H bond followed by rapid decomposition of the insertion complex produces a vinyl radical, which in turn can abstract a hydrogen from the substrate to give ethylene-^{11}C. MacKay et al.[7b] subsequently suggested that pentene-*1*-^{11}C resulted from methyne-^{11}C reaction in ethylene. The use of ethylene as a substrate, however, precludes the intermediacy of either the vinyl radical or of methyne in forming ethylene-^{11}C. Thus it is not directly relevant to the results reported in this paper.

Double label techniques will be described which have