Computation of an Orbital Isomer of Cyclobutyne

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AM1 molecular orbital calculations of the ring-expansion of cyclopropylidenecarbene **4** and the dehydrogenation of cyclobutene show that this process affords an orbital isomer **1** of cyclobutyne that is the global minimum and reacts in opposition to orbital symmetry predictions.

The question of the smallest cyclic structure into which a triple bond may be incorporated is of long-standing concern,[1] and cyclobutyne **1** is of interest in this context. A paucity of experimental evidence exists for **1**† but the molecule has been the subject of recent theoretical studies predicting it to have a singlet ground state and a barrier to rearrangement high enough to allow its isolation or trapping.[2] Our computational finding that ring-expansion of cyclobutylidenecarbene **2** affords the orbital isomer (lumomer)[3] **3** of cyclopentyne,[4] rather than the classical cycloalkyne, prompted a similar study of the conversion of cyclopropylidenecarbene **4** to cyclobutyne.‡ Whereas our previous calculations predicted cyclopentyne lumomer to be less stable than the classical form,[4a] the current results point to an orbital isomer as the more stable species in the cyclobutyne system.

The ring expansion of **4** to **1** is calculated to be endothermic by some 45.3 kcal mol^{-1} (1 cal = 4.184 J) and to have $\Delta H^{\ddagger}$ 63.3 kcal mol^{-1}, a value significantly higher than that computed for the analogous reaction of **2**.[4a] Examining the molecular orbitals of **1** (see below) indicates that this species is an orbital isomer of classical cyclobutyne. Indeed, the use of several different computational approaches in an effort to locate a potential energy minimum corresponding to the classical cycloalkyne proved unsuccessful, providing in all cases a minimized structure identical to that derived from rearrangement of **4**.[8] Thus, the orbital isomer is the apparent global minimum. This theoretical result is particularly striking because it prompts the conclusion that the orbital isomer is the lowest energy and possibly only form of cyclobutyne.

That **1** is an orbital isomer of classical cyclobutyne is defined by the nature of its molecular orbitals. Analysis of the coefficients and phases of the various eigenvectors calculated for **1** reveals that the HOMO and LUMO correspond to in-plane π- and π*-orbitals of the system and are bonding and antibonding with respect to the triply bound carbon atoms. In this sense, the critical molecular orbitals have symmetries consistent with those expected for classical cyclobutyne. It is only by considering the topologies of these orbitals relative to those of cyclobutene that clues to the unusual nature of **1** are revealed. What is found is that both the HOMO and the LUMO of **1** have topologies corresponding to bonding molecular orbitals of cyclobutene. Thus a molecular orbital in **1** normally expected to be an occupied bonding molecular orbital has become antibonding and therefore unoccupied (Fig. 1).

The aforementioned orbital transpositions are associated with perturbations involving the σ- and in-plane π-orbitals of **1**. Thus, consider the various combinations of in-plane p-orbitals that define the C(1)–C(4) and C(2)–C(3) carbon–carbon bonds of a four-membered ring as depicted in Fig. 1. The resulting σ-type molecular orbitals are expected to have the symmetries and relative energies shown, with the bonding and antibonding orbitals being ψ_1, ψ_2 and ψ_3, ψ_4, respectively. This is precisely the situation existing in cyclobutene, whose molecular orbitals have been calculated and characterized[8] through analysis of the phases and the coefficients of the s, p_x, p_y, and p_z contributions to the appropriate eigenvectors. The situation changes in **1**, however, because both the in-plane π-system and the σ-orbitals ψ_1–ψ_4 are all primarily formed from the set of p_x atomic orbitals. Consequently, the two types of orbitals can have a profound effect upon the energies of each other, and this interaction accounts for the transposition of ψ_2 of cyclobutene, an orbital that is antisymmetrical about the plane bisecting the triple bond, into the LUMO of cyclobutyne. It is this transformation of a bonding into an antibonding molecular orbital that characterizes **1** as an orbital isomer of classical cyclobutyne.

The nature of the classical cyclobutyne, which we are unable to find, and apparently does not exist on the hypersurface, can be assessed by considering the dehydrogenation of cyclobutene, for which the orbital correlation diagram in Fig. 2(*a*) applies. The relevant molecular orbitals in this process are those involved in the bonding of the olefinic hydrogens of cyclobutene. As indicated, this reaction involves the crossing of an occupied and an unoccupied molecular orbital and is therefore forbidden. The two molecular orbitals that cross are of opposite symmetry, resulting in the formation of classical cyclobutyne having a HOMO that is symmetrical and a


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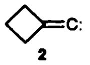
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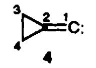

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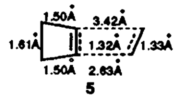

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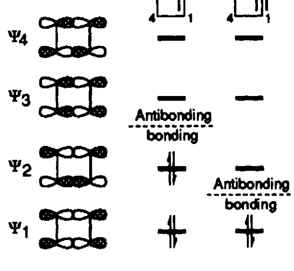

Fig. 1 Linear combinations of in-plane p-atomic orbitals defining C(1)–C(4) and C(2)–C(3) σ-bonds for cyclobutene and **1**

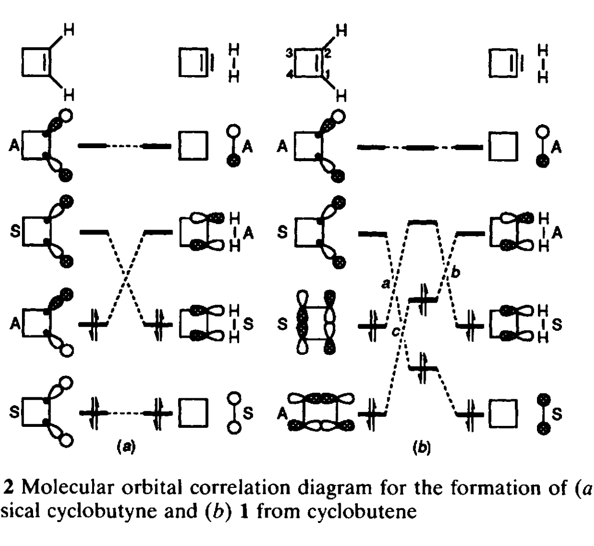

Fig 2 Molecular orbital correlation diagram for the formation of (*a*) classical cyclobutyne and (*b*) **1** from cyclobutene

LUMO that is antisymmetrical with respect to the plane of symmetry bisecting the carbon–carbon triple bond.

The analogous formation of **1** from cyclobutene was studied by molecular orbital calculations, which clearly identified the potential energy surface as that of an allowed reaction. An examination of the relevant molecular orbitals over the course of the reaction provides the orbital correlation diagram shown in Fig. 2(*b*). Thus, the formation of **1** from cyclobutene involves two orbital crossings, denoted by points *a* and *b* (point *c* is not classified as a crossing because the relevant orbitals are occupied, so that no change in orbital populations results), characteristic of an allowed reaction.[9] However, the crossings are different in that the first involves two molecular orbitals of like symmetry whereas the second involves two molecular orbitals of opposite symmetry.

A comparison of the correlation diagrams of Fig. 2 reveals that the difference between classical cyclobutyne and the orbital isomer **1** involves the orbitals from which the in-plane π- and π^*-orbitals of the cycloalkyne result. In the classical species, these orbitals arise from the antibonding and bonding molecular orbitals of the vinylic C–H bonds of cyclobutene. In **1**, the π-type bonding molecular orbital results from a bonding molecular orbital associated primarily with the C(1)–C(2) and C(3)–C(4) σ-bonds in the alkene. The corresponding antibonding orbital also correlates with a bonding molecular orbital of cyclobutene, but one whose primary components are derived from the C(1)–C(4) and C(2)–C(3) σ-bonds. The computed bond order of 0.89 for the C(1)–C(4) and C(2)–C(3) bonds in **1** is significantly less than the bond order of 1.01 calculated for the corresponding bonds in cyclobutene; this result is consistent with the antibonding nature of ψ_2 in **1**.

The fact that **1** has the same overall orbital symmetry of its bonding molecular orbitals as the classical structure raises an important issue. As an orbital isomer of the classical structure, **1** should undergo pericyclic reactions according to the rules of orbital isomerism,[3] yet the symmetry of its bonding molecular orbitals should make the outcome of such reactions amenable to prediction by the rules of orbital symmetry.[10] A unique test of the validity of the two theories is provided by the dichotomy in the predictions they provide for [2 + 2] cycloadditions in this system.

The unimolecular ring-opening of **1** to produce butatriene, conceptually a retro-[2 + 2] cycloaddition, was studied first. The reaction path found by our computations has $\Delta H^{\ddagger}$ 11.9 kcal mol^{-1} and ΔH_r° −107.8 kcal mol^{-1} and is a concerted process characterized by high synchronicity of bond cleavage and formation. Analysis of the geometries of the computed transition state and the optimized structures leading to and from it shows that no rotation of the methylene groups occurs.

By analogy with the electrocyclic reaction of cyclobutene to 1,3-butadiene, the rules of orbital symmetry[10] demand that the concerted electrocyclic conversion of a *cis*-3,4-disubstituted cyclobutyne occur with conrotatory motion to provide a *trans*-1,4-disubstituted butatriene. Such stereorotation is inconsistent with the reaction path computed for ring-opening of **1**. However, the stereochemical outcome is predictable from the theory of orbital isomerism,[3] which states that the allowedness or forbiddenness of a reaction relies only upon whether an orbital crossing occurs and is therefore independent of the path of the reaction. Ring-openings of **1** involving disrotatory motion or no motion at all at C(3) and C(4) are topologically equivalent from the standpoint of this theory, so the conversion of **1** to butatriene matches the stereochemical expectations for an orbital isomer of classical cyclobutyne.

Further evidence that **1** is an orbital isomer whose pericyclic reactions cannot be predicted by the theory of orbital symmetry is found in the computational definition of the potential energy hypersurface for its [2 + 2] cycloaddition reaction with ethylene. The surface is complex but provides for a concerted cycloaddition process having a transition state **5** with $\Delta H^{\ddagger}$ 1.8 kcal mol^{-1} characterized by asynchronous formation of the two new carbon–carbon σ-bonds. The existence of concert is not predicted by consideration of orbital symmetry, but is understandable from the tenets of orbital isomerism. Interestingly, the $\Delta H^{\ddagger}$ calculated for the unimolecular isomerization of **1** to butatriene is sufficiently high relative to that for [2 + 2] cycloaddition to allow experimental observation of bimolecular reactions of **1** so that, in principle, our stereochemical predictions are subject to test.

The identity of the symmetry properties of **1** and classical cyclobutyne, as noted earlier, means that their differences in reactivity cannot be predicted by the rules of orbital symmetry, since both orbital isomers would be expected to react identically. The theory of orbital isomerism, however, clearly establishes the isomeric relationship between these two molecules and therefore allows a prediction as well as a rationalization of their differences in reactivity. The concept of orbital symmetry thus becomes questionable in any case of an orbital isomer whose formation, relative to a classical analogue, is characterized by the transposition of two molecular orbitals of like symmetry. We will continue to search for such exceptions as well as other types of deviations from the Woodward–Hoffmann rules.[10]

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Footnotes

† A preliminary report (K. D. Baumgart and G. Szeimies, *Tetrahedron Lett.* 1984, **25**, 737) has appeared alleging the intermediacy of bicyclo[3.2.0]hept-6-yne, but full details remain to be published.

‡ AM1 methodology with 3 × 3 configuration interaction was used for all computations.[5] Exploration of the potential energy hypersurfaces resulted in transition states that were refined[6] and identified by force constant calculations.[7] Calculated ΔH_f° values for **1**–**4** are 199.8, 129.1, 154.7 and 143.5 kcal mol^{-1}, respectively.

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