A Woodward−Hoffmann Approach to the C_{60} Cluster Opening Leading to Homo[60]fullerenes

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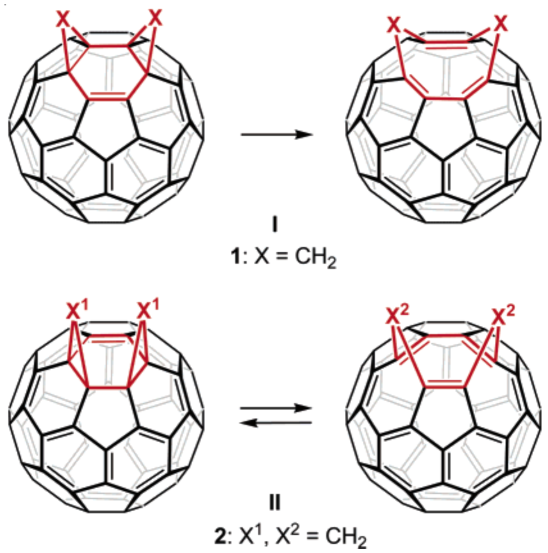
The electrocyclic valence isomerization interconverting bismethano[60]fullerenes **1** and **2** with 1,2,3,6- (type **I**) and 1,2,3,4-addition patterns (type **II**) into the corresponding cluster-opened bismethano-homo[60]fullerenes was investigated computationally with respect to the energy profile and to the retention of molecular orbital symmetry. Whereas for **1** the closed form is unstable and spontaneously isomerizes to the cluster-open adduct, the energy difference between the open and closed isomers of **2** is comparatively small. The B3LYP/6-31G* energy of open **2** is only 1.2 kcal mol^{-1} higher than that of the closed form. Analysis of the frontier orbital symmetries of **1**, **2**, and the [5,6]-bridged methano-homo[60]fullerene **3** showed that during these electrocylic valence isomerizations the orbital symmetry is retained and, as a consequence, a Woodward−Hoffmann-type selection principle is valid.

Much of the exploitation of the chemical reactivity of fullerenes[1] has been aimed at attaching a variety of molecular fragments to the carbon cage in order to produce systems that benefit from the combination of the properties of two moieties, one of which—that is, C_{60}—is an excellent electron acceptor while also being π-electron rich. Complementary to the primary investigation, although by no means less important, has been the goal of selectively opening (and then closing) the cage.[2−4] As early as 1995, an 11-membered orifice was introduced in the cage by Wudl and co-workers and subsequently "healed" to form $C_{59}N$ derivatives.[3a−c] Afterward, versatile methods to form bis-homo[60]fullerenes involving 1,2,3,6-addition patterns were developed by Rubin[2o] and Komatsu[4a−e] and co-workers. In these bis-homo[60]fullerenes **I**, two former [5,6]-bonds within one six-membered ring of the fullerene core are always open, retaining the whole 60-π-electron system of the fullerene core (Scheme 1). Quantum mechanical calculations showed that such opening reactions are energetically favorable.[2e,f,q,3f] It is important to point out that specific bis-homo[60]fullerenes **I** served as very suitable starting materials for subsequent hole enlargement reactions, which formed the basis of the successful encapsulation of small molecules into the fullerene cluster.[3g,4a−e] Next to **I**, a variety of examples for adducts **II** (Scheme 1) where the addends bridge two [6,6]-bonds within one six-membered ring of the fullerene core (1,2,3,4- or cis-1 addition pattern) have been synthesized as well.[2k−n] In such cis-1 adducts, preferably aza-bridges are involved. Interestingly, depending on the nature of the substitutent of the aza-bridge, either closed or cluster-opened bis-homo[60]fullerenes are formed. Indeed, via substituent exchange reactions, the open adduct can be transferred into the closed form and vice versa.[2n] This suggests that the energy difference between open and closed forms of **II** (Scheme 1) is comparatively small, which was supported by semiempirical calculations.[2e,n] In view of the usefulness of these valence isomerization reactions able to open or close the fullerene cage, it is perhaps surprising that it has not been the object of a scrutiny in terms of molecular orbital (MO) symmetry. The difficulty in applying Woodward−Hoffmann and related schemes to fullerenes lies in their structure. Indeed, while functionalization removes the 5-fold degeneracy of the HOMO of C_{60} both in the reactant and in the product, the five higher occupied molecular orbitals remain sufficiently close, and possibly so delocalized over the entire molecule as to make not straightforward the identification of which of them drives the reactivity. Implicitly, for an MO analysis, this would force consideration of the entire π-electron system, a feature that would complicate

SCHEME 1: Two Prototypes of [60]Fullerenes Involving Two X-Bridges within One Six-Membered Ring of the Fullerene Cluster (X = CR^1R^2, NR, O)[a]



[a] **I**: 1,2,3,6-adducts where the methano (CR^1R^2), aza (NR), and oxa (O) brigdes are located at [5,6]-binding Sites. **II**: 1,2,3,6- or cis-1-adducts where the methano (CR^1R^2), aza (NR), and oxa (O) bridges are located at [6,6]-binding sites. For **I**, only the open forms are known. For **II**, the open and closed forms can be interconverted upon variation of the nature of the bridging addend X.

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TABLE 1: Summary of the Calculations for 1 and 2

system	relative energy (kcal mol^{-1})^{a}	first bond length (Å)	second bond length (Å)	imaginary frequency (cm^{-1})
1 S transition state	2.2/0.3	1.76	1.76	869i
2 S transition state	13.9/2.6	1.90	1.90	574i, 288i
2 first **A** transition state	10.1/12.3	2.04	1.60	274i
2 second **A** transition state	12.2/6.2	2.16	1.82	532i
1 closed^{a}	0./0./spontaneous opening	1.61//1.76	1.61/1.76	none
1 open	−53.5/−25.6/spontaneous opening	2.30/2.31	2.30/2.31	none
2 closed^{a}	0./0./0.	1.57//1.61	1.57//1.61	none
2 singly open	10.0/2.5	2.11	1.60	none
2 open	−5.2/9.6/1.2	2.31//2.23	2.31//2.23	none

[a] Each column reports first the AM1 result; after the first slash the value calculated for this geometry at the B3LYP/6-31G* level is given, and after the second slash the value with full B3LYP/6-31G* optimization is given. The energy differences are relative to the closed structures. **2** is more stable than **1** by 17.5/18.2 kcal mol^{-1}.

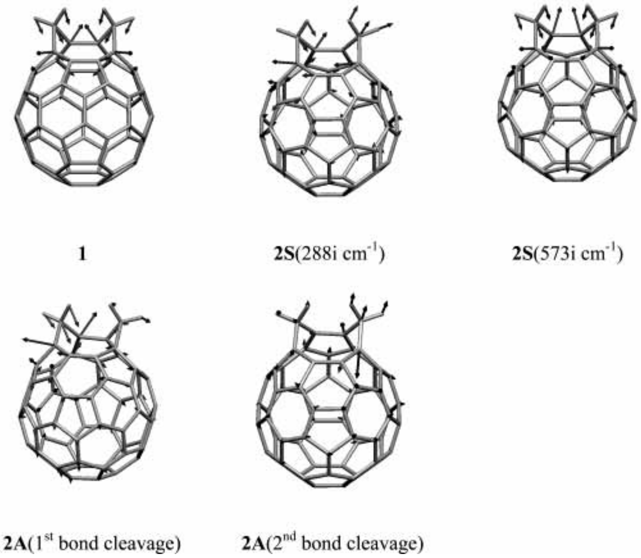
the molecular orbital analysis greatly. In practice, it turns out that, at least in certain regions of the reaction pathway, one can identify a driving MO. Such an MO satisfies the primary condition of being located "mainly" in the reaction region, and the secondary but equally important requisite that the π system outside such region has its shape/symmetry preserved during the reaction. Qualitative analysis of the chemical reactivity of fullerenes has already considered the pyramidalization of the carbon atoms,[5] or the electron density in the form of the free valence index,[6] but has not, so far, drawn heavily from the Woodward−Hoffmann type of approaches.

As model compounds for the theoretical investigation of the valence isomerization of type **I** and **II** adducts we choose **1** and **2**, where the bridges X are $-CH_2-$ groups. This isomerization corresponds to the interconversion of bismethano[60]-fullerenes and bismethano-homo[60]fullerenes. Initially, it was decided to locate the transition states for the opening reaction both in **1** and in **2**. Both synchronous, **S** (simultaneous snapping of the two bonds), and asynchronous, **A** (cleavage of one bond at a time), pathways of opening were initially explored at the semiempirical AM1 level,[7] using the Gaussian98 suite of programs;[8] the stable isomers were then re-optimized at the B3LYP/6-31G* level. The approach is rather similar to that used by Cases et al. in the study of the mechanism of the addition reaction of alkyl azides to [60]fullerene and the subsequent N_2 extrusion to form monoimino-[60]fullerenes.[9]

Table 1 shows some characteristics of the transition states together with those of the minima.

Figure 1 displays the optimized molecular geometries of the transition states, with arrows that indicate the motion associated with the vibration with the imaginary frequency that promotes opening (and closing) of the cage.

For **1**, only the synchronous opening pathway exists. Indeed, the calculation of a grid of points, where one of the two functionalized bonds was elongated and the geometry of the rest of the molecule underwent full geometrical optimization, found spontaneous opening of the other bond at the AM1 level, while the closed isomer is not even stable at the B3LYP/6-31G* level. For **2**, two paths were located. A synchronous one, **2S**, leads to a transition state characterized by two imaginary frequencies and, at slightly higher energy, an asynchronous, two-step pathway. The nonsynchronicity in the bond cleavage of **2A** path destroys the plane of symmetry of the partly open adduct. Two-step pathways have been identified before in Woodward−Hoffmann-forbidden reactions: for instance, for the symmetry-forbidden 2+2 cycloaddition of ethylene plus ethylene.[10] The small difference in energy between the two paths likely makes them equally available to the reaction at room temperature. Because of the lack of symmetry in **2A**, only **2S** will be discussed in the following.


1 **2S**(288i cm^{-1}) **2S**(573i cm^{-1})

2A(1st bond cleavage) **2A**(2nd bond cleavage)

Figure 1. Transition-state structures for **1**, **2S** (288i cm^{-1}), **2S** (573i cm^{-1}), **2A** (first bond cleavage), and **2A** (second bond cleavage). The arrows indicate the motion associated with the vibration with the imaginary frequency that promotes opening (and closing) of the cage.

The exploration of the opening pathways finds that both isomers have rather low barriers. Using transition-state theory, the calculated barriers and vibrational frequencies can be turned into kinetic rates (see, for instance, ref 11) which show that the reactions take place in a millisecond at most. Both reactions can therefore be considered energetically allowed. *But are they symmetry allowed?* The question we ask is whether a fundamental feature of the Woodward−Hoffmann model, that is, "retention of orbital symmetry" during the transformation, holds for these reactions and, rather importantly for a qualitative understanding, whether the analysis of the analysis of the HOMO's coefficients can be limited to the reacting six-membered ring.

Two complementary views are pursued here. In the first, the focus is on the mechanism that forms the σ bonds; in the second, the whole reaction pathway is assessed.

Closing the Ring. The interconversion between the open and closed forms of **1** and **2** proceeds unimolecularly with the reacting double bonds that are part of a single conjugated π-system. The reaction must therefore be regarded as 60 π-electron electrocyclic reactions. Alternatively, one could try to envisage it as a cycloaddition, such as a [2+2+2] or a [4+2]. However, the analysis of the reaction along these lines requires the HOMO of one reactant and the LUMO of the other. Since this is a single conjugated system, the selection of the HOMO for a reactant and of the LUMO for another introduces, at the

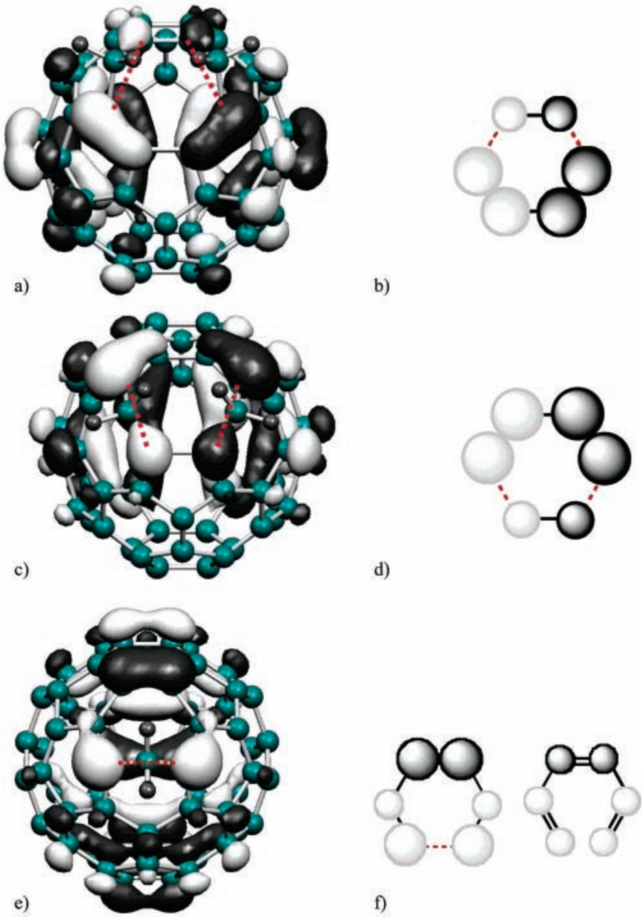


Figure 2. HOMO orbitals at the B3LYP/6-31G* level and the schematic representation of the coefficients of the orbital at the bridged six-membered ring ($X = CH_2$) (only the exohedral part is shown for clarity). The dotted lines give the location of the open trans-annular bonds bridged by methano groups: (a) bisfulleroid **1** and (b) its schematic representation; (c) bisfulleroid **2** and (d) its schematic representation; (e) singly functionalized fulleroid **3** and (f) left, its schematic representation, and right, schematic representation of the HOMO of hexatriene provided for comparison.

very least, an arbitrariness that rules out the possibility of considering the reactions as cycloadditions.

In a thermally allowed electrocyclic reaction, the symmetry of the HOMO of the open species dictates the motion of both the opening and the closure of the newly formed σ bonds. The motion can be conrotatory or disrotatory, depending on whether the π orbital termini next to the σ bond that is formed are oriented parallel (i.e., in-phase) or antiparallel (i.e., out-of-phase) with respect to each other.

The HOMOs of open **1** and **2** are shown in Figure 2. In both cases, the orbital is antisymmetric with respect to the mirror plane of the molecules. The π orbital termini flanking the two σ bonds that form during the cyclization are parallel, or in-phase, with one other.

As a consequence, the motion of the symmetry-allowed cyclization and opening reactions must be disrotatory. Indeed, disrotatory motions of these conversions are the only type consistent with the structure of products and reactants. They are also in line with the calculated motion of the transition states shown in Figure 1.

A similar treatment of the electrocyclic ring opening and closure for the singly [5,6]-bridged methanofullerene $C_{61}H_2$ (**3**) gives the same result. In this case, the HOMO is symmetric with respect to the plane of symmetry (Figure 2). At the same time, the plane of symmetry bisects the σ bond that opens. The consequence is that the motion of the symmetry-allowed 60-π-electron electrocyclic reaction of singly bridged fulleroid must be disrotatory, which, again, is in line with the observed structure of products and reactants. Notice that the local symmetry of the HOMO at the six-membered ring that contains the trans-annular bond resembles that of (*Z*)-hexatriene (see Figure 2), a system that also undergoes a thermally allowed disrotatory cyclization.

TABLE 2: Percentage of Contribution of the HOMOs of the Atomic Orbitals of the Six-Membered Ring Where the Reaction Takes Place[a]

	closed isomers		transition states			open isomers	
	1	**2**	**1**	**2S**	**2A**	**1**	**2**
HOMO	25(S)	3(A)	32(S)	43(A)	43(N/A)	18(A)	48(A)
HOMO-1	5(A)	8(S)	17(A)	20(S)	4(N/A)	7(S)	22(S)
HOMO-2	3(A)	3(A)	5(A)	4(A)	6(N/A)	5(A)	3(A)
HOMO-3	12(S)	14(S)	12(S)	4(A)	5(N/A)	13(A)	7(A)
HOMO-4	11(A)	8(A)	18(A)	15(S)	14(N/A)	16(S)	10(S)

[a] In parentheses, the symmetric, S, or antisymmetric, A, behavior of the MO with respect to the plane, if present, is indicated.

A final remark concerns the opening of a single bond of **2** in the asynchronous mechanism, which is also disrotatory (not-shown).

The Reaction Pathway. The HOMOs of open **1** and **2** give disrotatory ring closure. As mentioned above, functionalization removes the 5-fold degeneracy of the HOMO of C_{60}, but the five higher occupied molecular orbitals remain sufficiently close in energy. It is therefore necessary to ascertain that the remaining four do not play a role in determining the reactivity pattern. The transition state of the reaction is an optimal candidate for the analysis. In fact, as the reaction proceeds, one orbital must become the driving frontier orbital; in other words, it must separate from the other nearly degenerate four orbitals. The MO coefficients confirm this idea. Table 2 shows the percentage of the contribution to the five HOMOs of the atomic orbitals of the ring, together with their symmetry at the minima and the transition states.

Two of the five HOMOs are symmetric, S, and three are antisymmetric, A. The relative ordering changes in the two isomers and along the reaction pathways. Notice that some MOs make very small contributions to the reacting six-membered ring, i.e., are irrelevant for the reaction. However, at the transition states and for the "natural" reactant (closed **1** and open **2**), the HOMO is consistently located mainly at the reacting ring. Above we have seen that, for the open isomers of **1** and **2**, the HOMOs are antisymmetric. Along the reaction pathway, from the closed to the transition state to the open form, the HOMO of **1** is S, S, A, while for **2** it is A, A, A. The variation of the symmetry of the HOMO along the path of **1** implies the presence of energy level crossing during the reaction. Moreover, since the transition-state HOMO has the same symmetry as the closed form (but not the open one), the opening reaction of **1** must have an early transition state. Indeed, AM1 finds that, at the transition state, the lengths of the bonds that open are 1.76 Å for **1** and 1.90 Å for **2**, while the B3LYP/6-31G* geometry optimization finds only the open isomer!

The conclusion of this work is that the cage opening (electrocyclic valence isomerization) for the two types (**I** and **II**) of bismethanofullerenes, as well as for the monoadduct **3**, is symmetry allowed, although there are differences for the two isomers **1** and **2** both in terms of the barriers and in terms of the presence of level crossings. A corollary to these findings is that for **II**, substituents of the bridging moiety able to stabilize the open bonds should be able to form them, since the full geometry optimization at the B3LYP/6-31G* level of open **2** shows that it is only 1.2 kcal mol^{-1} higher than the closed isomer. Qualitatively, the same behavior is expected for type **I** and **II** adducts as well as [5,6]-bridged monoadducts with bridging addends other than CH_2, for example, NR and O, since the nature of the addend has no influence on the symmetry of the frontier orbitals of the fullerene cage. As a consequence, the related valence isomerizations are also symmetry allowed and, as has been demonstrated before,[2n] exhibit related energy profiles.

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