On the nature of bonding in the photochemical addition of two ethylenes: C-C bond formation in the excited state?

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In this work, the 2s+2s (face-to-face) prototypical example of a photochemical reaction has been re-examined to characterize the evolution of chemical bonding. The analysis of the electron localization function (as an indirect measure of the Pauli principle) along the minimum energy path provides strong evidence in support that CC bond formation occurs not in the excited state but at the ground electronic state after crossing the rhombohedral S_1/S_0 conical intersection.

Introduction

Conical intersections are now well recognized as essential pieces in the rationalization of organic photochemical processes.[1-7] Considerer, for instance, the case of the concerted 2+2 cycloaddition of two ethylenes,[8] a prototypical model (text-book example indeed), described as a *ground-state forbidden/excited-state allowed* process under the magnifying glass of the Woodward-Hoffmann rules based on the conservation of the orbital symmetry.[9] After the work of Robb et al.,[3,6,10] a crossing seam constitute the key photochemical decay channel connecting singlet electronic states S_1/S_0 for the 2s+2s (face to face) cycloaddition.[1, 8, 11, 12] Indeed, it is well recognized that the seam implies other critical points associated with higher energy processes via the 2s+2a (face to edge, ground-state allowed/excited-state forbidden) and the 2a+2a (edge to edge, ground-state forbidden/excited-state allowed) processes.[10] It should be, however, recognized that attention had been primarily focused only on the energetic interplay concerning the involved electronic states.[11, 13, 14, 15, 16] This fact is naturally associated with the fact that energy differences constitute the essential indicator allowing us to understand, to predict and to modulate both the kinetics and thermodynamics for practical chemical process.[17, 18, 19] Although less attention has been put on the study and characterization of bonding nature of the underlying reaction paths, the specificities of changes of electron density or derived quantities involving excited states and conical intersections have been the subject of more recent interests.[20, 21, 22-26] The characterization of the nature of chemical bonding is undoubtedly at the heart of our understanding of any chemical process with several practical just based on the link between the topology and the local description of chemical bonding implications.[18, 27]

In the case of the 2+2 ethylene cycloaddition, it should also be remarked that minimum energy conical intersections (MECI) can be consistently derived from both Valence Bond (VB) analysis and ab-initio CASSCF calculations,[7, 28] enabling indeed the characterization of the branching space vectors that lift the degeneracy as well as the details of the qualitative phase change (i.e., nucleus displacement vectors) associated to the MECI point.[28] It is now well accepted that the most favorable 2s+2s path implies a MECI with rhomboidal configuration (Scheme 1).
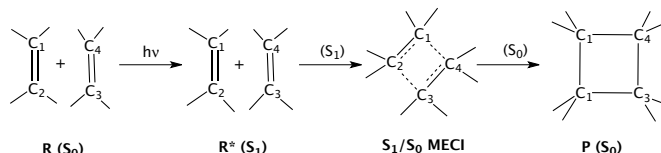
Scheme 1. The currently proposed reaction path for the 2s+2s photochemically induced addition of two ethylenes.[1, 3, 4, 7, 11, 12, 14, 15, 28]

Indeed, the VB analysis evidence the explicit interconnection between the above referenced conical intersections along the seam space, but undoubtedly the bonding situation details remains up to now uncovered,[6, 28, 29] *i.e.,* (i) *how the excitation process changes the bonding pattern of reactants?*, (ii) *where along the path the new C-C bonds are going to be formed?*, (iii) *what is the nature of bonding formation in terms of the changes of the nature of bonding along the path through the S_1/S_0 conical intersection?* In the absence of detailed studies concerning the bonding situation of such a prototypical reaction mechanism, in this work, we aimed to get a complete characterization of the bonding phenomena of the process in the real space.[23, 30] Within such a goal, we resort to the topological analysis of the electron localization function (ELF).[31] In complement to the analysis of other functions as electron density (i.e., QTAIM[32]), within the so-called quantum topological framework of approaches,[20, 22, 23, 26, 33, 34] ELF provides a simple, straightforward connection to the chemical bonding concept,[35, 36] as it can be understood as a local measure of the Pauli repulsion. Hence, ELF has been extensively probed as a valuable tool helping us rationalizing experimental facts in terms of a suitable representation of the elusive but central concept of the *chemical bond*.[37] The usefulness of the ELF to describe bonding is certainly probed and spread several areas of chemistry.[38, 39] The topological analysis of ELF yields a division of molecular space into basins of attractors that enable a convenient association of the electronic molecular structure with chemical concepts inherent to the Lewis-like theory of bonding and related concepts.[36, 40, 41] It is important to emphasize that in such a context, bonding in real space becomes structurally represented in terms of the *shape* of the electron localization pairs and the electron density (i.e., via basin populations). In particular, key bonding events (e.g., bond formation and bond-breaking), as well as the electron rearrangement along any chemical reaction, can be suitably represented by a sequence of *ELF-based molecular configurations (ELF-MG) separated by abrupt changes in the shape of electron pair delocalization*.[39, 42-44] In this work, we

have adopted the well-known notation adopted for describing any chemical transformation.[41, 45-47] It should be mentioned that in the cases chemical bonding in excited states,[22, 23, 26, 48] ELF has been explored only in a few systems,[22, 49] including the dissociation of small diatomics[50] and simple hydrogen/proton transfer.[24, 50] To the best of our knowledge, applications of an ELF-based *bonding evolution theory* [45, 47, 51, 52] to chemical reaction processes involving excited states and conical intersections *have not been previously reported.* In addition, the present work evidence *for the first time* the advantages of the recently discussed methodologies for evaluating ELF in excited states and its evolution along a given path involving a conical intersection.[50]

Computational details

Calculations were performed within the MC-SCF theoretical background using the Gaussian16[53] and ORCA v4.2.1[54] packages of programs. The 2s+2s reaction path was modeled via the Nudged Elastic Band (NEB) approach[55] at the *CASSCF(4,4)/Def2-SVPD* level of theory. Such a path was completely re-optimized at the *NEVPT2(4,4)/Def2-TZVPD* to include suitable dynamical correlation effects. The minimum energy paths (MEPs) calculated in this work contain the evolution of the reacting system in the S_1 excited state towards the MECI, followed by the decay to the S_0 ground state in the direction of the cyclobutane product. The topological analysis of ELF was carried out considering the natural orbitals basis using the Dgrid v5.2[56] and MultiWfn v3.7[57] programs. The identification of the bond breaking/bond formation events along the path was carried out following the analysis of the determinant of the Hessian, as recently discussed.[44] The ELF function was calculated based on the first-order density matrix obtained from MC-SCF calculations, using the expression recently derived within the TD-DFT approach.[50]

Results and discussion

The chosen level of theory provides an excellent energetical agreement with the available experimental,[58] and already well-known highest level theoretical[16, 59] characterizations of the ethylene excited state and the 2s+2s reaction path.[1-3, 11, 12, 14] Henceforth, we will concentrate our discussion only on the new insights concerning the ELF representation of bonding, whereas geometrical parameters enabling reproducing this study are reported as ESI.


(a)

(b)
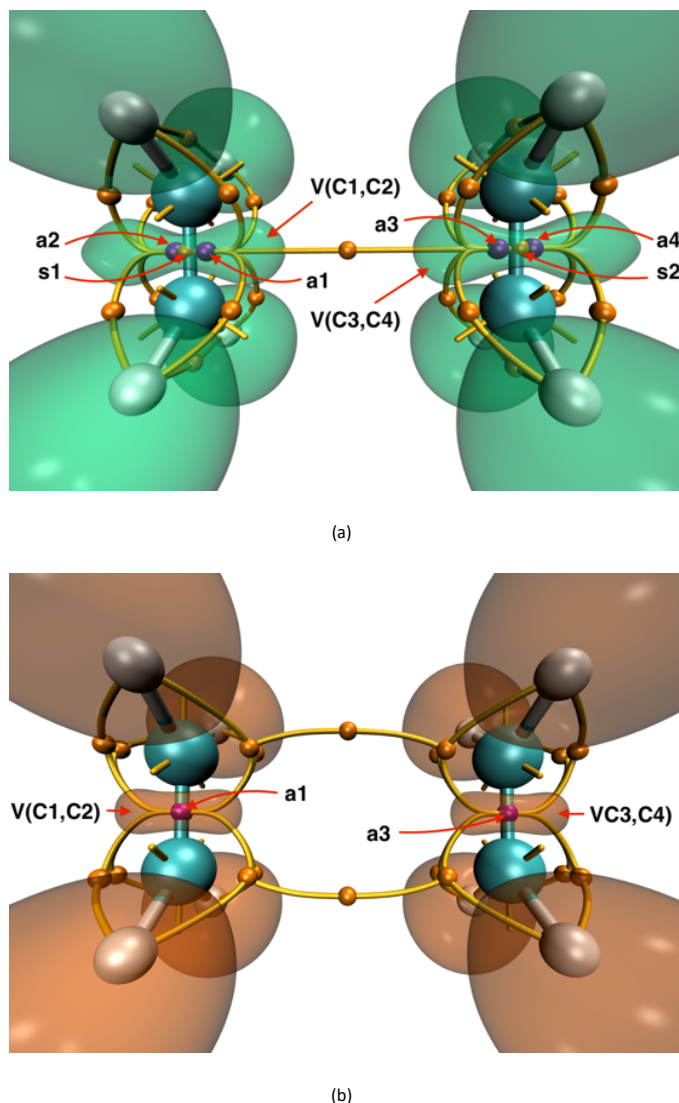
Figure 1. ELF molecular graph over (including gradient paths) and ELF isosurface (0.792) for the ground state R (panel a, **I**) and the excited state R* (panel b, **ELF-MG-II**). Purple and orange dots, respectively, represent some of the maxima and saddles of ELF at this configuration. Upon excitation, leading changes in the ELF topology are localized in the spatial region associated with the C=C region in both ethylenes.

A direct comparison between the ELF topologies of the ground state **R** and the excited state **R*** in the Frank-Condon region, *i.e.*, (d_{C1-C4}=3.80Å, $A_{C2-C1-C4}$=89.96°), is valuable enough to evidence main changes of electron pair localization upon excitation (see Figure 1).

Results allow us to evidence that electron localization decreases at the unsaturated CC bonding regions of both ethylenes. The corresponding disynaptic basin populations V(C1, C2) and V(C3, C4) reduces from 3.35e to 2.83e. The spatial reorganization of electron pairs is shown to be displaced to the neighbourhood of the carbon centres. The disynaptic V(C,H) basin populations increase from 2.00 to 2.40e in each ethylene moiety. The ELF molecular graphs reveal that the change in ELF topology can formally be associated with two simultaneous changes in the ELF topology,[45] each located in the double CC bonds region. As

recently emphasized for the Diels-Alder reaction,[44] the sudden changes in the ELF topology can be here also precisely associated to the simplest elementary Thom's universal unfolding.[42, 43, 45] Here, simply we establish that the sudden change in the ELF topology is associated to the annihilation of a maximum (*a*) and a saddle (*s*) in the C=C bonding region (i.e., *a2+s1* in the case of C1C2, and *a2+s4* in the case of C3C4) as revealed in Figure 1. Note that the ELF maxima *a1* and *a3* become the only attractors for the disynaptic basins at the **R*** configuration on the S_1 electronic state. Correspondingly, and from a purely interpretative chemical point of view, we emphasize that the onset of the evolution of the system along the face-to-face path involving a conical intersection become then naturally associated with the activation of the carbon centre regions over the S_1 excited surface as a consequence of electron density depletion from the CC double bond region. We have found five further critical variations of the ELF topology along the entire path connecting the **R*** and **P** configurations. Scheme 2 summarizes, in terms of a Lewis-like representation, the sequence of different ELF-MG for the whole process. The excitation process separates the configurations corresponding to the reactant ground state (i.e., ELF-MG **I**) and those that start the evolution along the S_1 electronic state (i.e., ELF-MG **II**). After that, the system evolves on the excited state towards the MECI point.
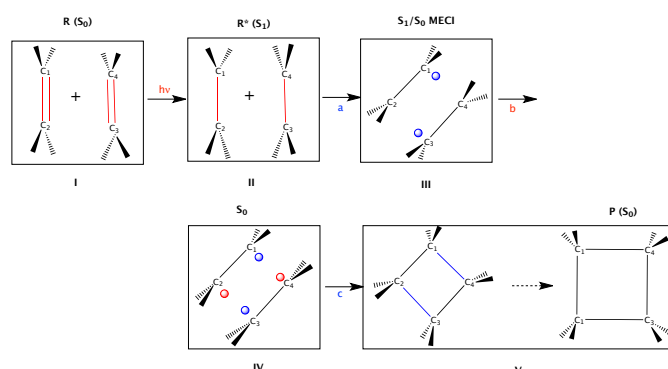
Scheme 2. ELF-based Lewis-like representations for the photochemically induced addition path of two ethylenes in terms of the **ELF-MG (I-V)** sequence along the lowest 2s+2s photoinduced cycloaddition path.

Evolution of the ELF topology at the S_1 excited state. Along the lowest energy path corresponding to the S_1 electronic state, the reaction carbon centre experiences a net deformation from a rectangular geometry to a rhomboidal configuration.[28] The bonding events along this path can now be traced back to the occurrence of two concurrent abrupt changes in the ELF topology. These changes occur at the excited configuration *a* (d_{C1-C4}=2.53Å, $A_{C2-C1-C4}$=78.53°), is determined by the appearance of pairs of maxima and saddle points in the vicinity of the C1 centre (i.e., *a5* and *s3*) as well as for the C3 centre (i.e., *a6* and *s4*) as revealed in Figure 3. These changes separate the ELF-MG-2 and ELF-MG-3 set of configurations along the path. In terms of bonding chemical events, the changes in ELF topology are simply associated with the delocalization of electron pairs in

the neighbourhood of the C1 and C3 carbon centres as the systems evolve through the MECI point.
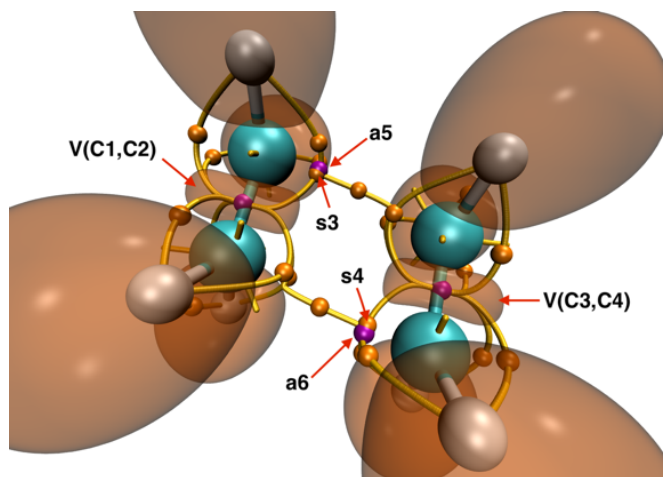
Figure 3. ELF molecular graph and ELF isosurface (0.792) for a configuration point within the **ELF-MG-III** on the S1 surface. Purple and orange dots, respectively, represent some of the maxima and saddles of ELF at this configuration. The S_1/S_0 MECI for the 2s+2s photochemically induced ethylene cycloaddition belongs to such an ELF-MG set of structures.

The non-bonding V(C1) and V(C3) basins increase their electronic population up to 0.32e each, whereas the population of the disynaptic V(C1, C2) and V(C3, C4) basins decreases up to 2.59e each. It is thus clear that upon the evolution of the rhomboidal configuration in the S_1 excited state, migration of pairing density toward the C1 and C3 centres occurs due to the partial reduction of the CC bonds. At the MECI configuration (i.e., d_{C1-C4}=2.17Å, $A_{C2-C1-C4}$=70.60°), which belongs to the ELF-MG-III, the V(C1) and V(C3) monosynaptic basins decrease their population dramatically up to values of 0.05e each. The basin population V(C1, C2) and V(C3, C4) increases to 2.77e. Based on ELF analysis, the high electron fluctuation features the MECI. No evidence for new CC bonding at the S_1 surface has been found. Therefore, we propose a negative answer to the title question: *the new C-C bonds along the 2s+2s reaction path via the rhombohedral MECI do not occur in the S_1 excited state*.

The tools here applied to help us to compressively visualize how chemical processes evolve on both electronic states, of complementary value to modern tools to describe chemical bonding in excited states,[23, 26, 34] and certainly broadening the arsenal of traditional concepts applied to describe the photochemical induced cycloaddition processes.[2, 5, 6, 9, 28]

(a)

(b)

(c)
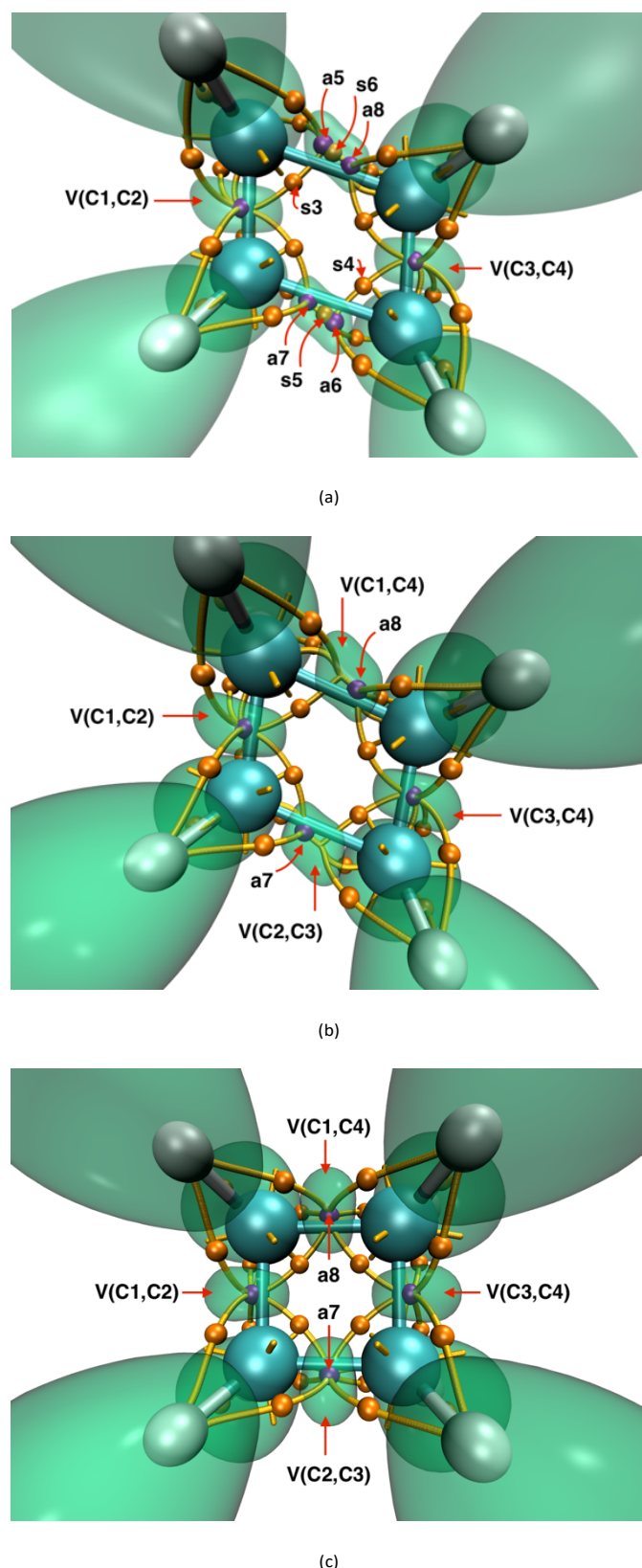
Figure 4. ELF molecular graph and ELF isosurface (0.792) for configuration points within the **ELF-MG-IV** (panel a) and the **ELF-MG-V** (panels b and c), both located on the S_0 electronic state. Purple and orange dots, respectively, represent some of the maxima and saddles of ELF at this configuration.

Evolution of the ELF topology along the S_0 ground state. The configurations in the close neighbourhood to the MECI on the S_0 surface exhibit the same ELF topology corresponding to the ELF-MG-III (See Scheme 2). After that, in the subsequent evolution towards the cyclobutane species (**P**), another two simultaneous changes in the ELF topology occur at the configuration (d_{C1-C4}=1.96Å, $A_{C2-C1-C4}$=73.31°) (see Figure 4a) responsible for the appearance of the attractors (*a5* and *a8*) and saddles (*s3* and *s6*) defining the monosynaptic V(C1) and V(C3) basins. These ELF topological changes separate the set of configurations associated with the ELF-MG-III and ELF-MG-II. Henceforth, the four monosynaptic basins related to the attractors *a5, a6, a7,* and *a8,* increase their electron populations up to 0.64e each. Such a pattern of electron pair localization is accompanied by decreasing the V(C1, C2) and V(C3, C4) basin populations up to 2.05e each. Thus, it became clear that *the stage for the onset of the new CC bond formation is localized on the S_0 surface* and corresponds to the ELF-MG-IV. The following key ELF topological changes occur at the configuration point (d_{C1-C4}=1.88Å, $A_{C2-C1-C4}$=75.35°) originated in the vicinity of the C1 and C3 centres (see Figure 4b). These characterize the annihilation of the *a5/s6* and *a6/s5* pairs of critical points, separating the ELF-MG-**IV** (the onset of the new two CC bond formation) from the ELF-MG-**V** (to which **P** belongs) set of configurations on the S_0 surface. After that, the attractors a8 and *a7*, which defines the disynaptic V(C1, C4) and V(C2, C3) basins, are displaced from the vicinity of centres C2 and C4 to the central position between centres C1-C4 and C2-C3, respectively, as the system evolves towards the most stable rectangular conformation of cyclobutane. The ELF electron populations at the basins associated with the four C-C bonds become equalized at the cyclobutane ring product (d_{C1-C4}=1.54Å, $A_{C2-C1-C4}$=89.71°) at the end of the path (see Figure 4c).

Conclusions

In summary, based on the topological analysis of the electron localization function at both excited and ground states for the photoinduced 2s+2s cycloaddition path of two ethylenes, we present here evidence that demonstrates that formation of the new CC bond does not occur indeed in the S1 excited state. *To the best of our knowledge, this work constitutes the first finding in such a context concerning a ground-state forbidden/excited-state allowed prototypical reaction system*. The sequence of ELF-MG configurations for the reaction path has been fully characterized. Results confirm that C-C bonding is only possible *after* the systems evolve from the rhombohedral conical intersection MECI to the S_0 electronic state. We propose this prediction a challenge to be further tested from other theoretical methodologies.[20, 22, 23, 25, 26, 30, 34] Certainly, a defying quest from the experimental point of view.[18, 19, 60] Regarding a more subtle formal detail, our findings also confirm recent conclusions that bonding events in asymmetric electronic interactions as the thermal 4s+2s Diels-Alder reaction[44] and the photochemically induced 2s+2s cycloaddition of two ethylenes

via MECI can be rationalized in terms of the simplest Thom's universal unfolding.[43-45] The most favorable 2s+2s (face to face) reaction mode involving a rhomboidal conical intersection S_1/S_0 can be represented through the sequence of six abrupt variations in the shape of the electron pair distribution (as characterized by the ELF topology), defining five clear ELF-MG sets of configurations. A simplified representation of such an "evolution of the bonding nature" can be observed in terms of the Lewis-like picture represented in Scheme 2. The current results strongly invite us to re-examine the commonly accepted rationalization of photochemically induced reaction mechanisms. Our groups are currently working to determine if the observed features constitute a general signature in the realm of pericyclic reactions.[44, 50, 52]

Author Contributions

E.C: project supervision, conceptualization; data analysis, manuscript writing; C.G, L. A-H, M.D-N: data analysis, calculations, reaction path characterization; P.P, C.C: project supervision. All authors reviewed, discussed, edited, and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

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