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Electron Fluctuation in Pericyclic and Pseudopericyclic Reactions

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Since the very beginning pericyclic reactions have presented difficult mechanistic problems. It was not until Woodward and Hoffmann set up their theory of orbital symmetry conservation that the mechanisms of these reactions clearly showed up. A few years after that, Ross et al.^[1] proposed the term “pseudopericyclic” to describe a set of reactions which broke the laws given by Woodward and Hoffmann. So far, the most noticeable work towards a proper characterization of pseudopericyclic reactions has been conducted by Birney and co-workers.^[2–4]

Zhou and Birney^[4] described a pseudopericyclic reaction as a reaction with a low or a nonexistent barrier, with planar transition structure and cyclic overlap disconnections. Although this definition is widely accepted by the chemistry community, these criteria become controversial when trying to classify borderline cases.^[5–11] Some authors have proved the energy barrier to be an ambiguous criterion, since some pseudopericyclic reactions exhibit significant energy barriers.^[6,8] Planarity is also far from being a definitive criterion; some authors reported quite planar pericyclic reactions^[6,8] while other authors found far-from-planar pseudopericyclic mechanisms.^[4] Another popular descriptor to characterize the reaction mechanism is the aromaticity of the transition state (TS). As stated by the Evan's principle,^[12] one would expect pericyclic reactions to have aromatic TSs, unlike pseudopericyclic reactions where the disconnected cyclic overlap prevents aromaticity. However, one has to bear in mind that aromaticity is a multidimensional quantity, that is, different indexes can lead to different conclusions.^[8–10]

In this Communication we study the electron fluctuation of the TS structure for a set of different electrocyclic processes (A–H) by means of the electron localization function (ELF).^[13,14] The electron distribution in the TS will provide enough proof to discern between both mechanisms. In a pericyclic reaction the electron charge is spread among the bonds involved in the rearrangement, and that is the reason for aromatic TSs. Besides, pseudopericyclic reactions are characteristic for electron accumulations and depletions on different atoms, and thus the electron distribution in the TS is far from being uniform for the

bonds involved in the rearrangement. Since ELF accounts for the electron distribution we expect connected (delocalized) pictures of bonds in pericyclic reactions, while pseudopericyclic reactions will give rise to disconnected (localized) pictures.

The following set of reactions,^[15] containing several kinds of processes, serves our purposes: A, B, C, and D are electrocyclic ring closures that have been recently a matter of discussion,^[5–11] E is a cycloaddition of acetylketene to acetone,^[3] F a Claisen rearrangement,^[16] G is an electrocyclic ring opening,^[2] and H the butadiene electrocyclic ring closure (reaction schemes are given in the Supporting Information). Reactions C, F, and H are generally accepted to be pericyclic while D, E, and G have been characterized as pseudopericyclic. On the other hand, A and B are controversial reactions which have been classified as pericyclic or pseudopericyclic by different authors.^[5–11] In particular, these reactions have been recently considered as a borderline case between pericyclic and pseudopericyclic.^[10] Although the ELF pictures are clear enough to elucidate the reaction mechanism (the reader can notice that core basins are clearly visualized due to poor delocalization in pseudopericyclic reactions), fluctuation diagrams are also provided in Figures 1 and 2 to give the preferred electron fluctuation direction and an idea of its magnitude. The electron fluctuation is measured as the relative electron sharing between a given electron pair bond and the adjacent bonds, showing the preferred direction of electron fluctuation (see ref. [11] for the detailed definition). We compare covariance contributions to a given bonding basin coming from adjacent bonding and the lone pair basins^[17] for the clockwise and counterclockwise directions to determine the direction in which the electron fluctuation is larger. When two consecutive bonds fluctuate charge in opposite directions, the atom in between suffers from electron depletion (no arrows pointing to the atom) or electron concentration (both arrows pointing towards the atom), whose magnitude can be deduced from the ratios given above the arrows. The arrows on the figures give the direction of fluctuation with an estimation of its magnitude calculated as the ratio between the fluctuation of the clockwise and counterclockwise directions. This procedure is supported by a recent study on cyclic π -conjugated molecules, where the relative ratio of electron fluctuation on both sides of the bonds in the ring was found to be a good indicator of aromaticity.^[18]

In the TSs of near barrierless reactions, we expect almost no electron density on the sigma bonds that are to be formed, since the TSs of these reactions resemble the reactants. Hence, we focus on the electron distribution of the π bonds that are broken and formed in the TS. The electron organization becomes quite evident from Figures 1 and 2,^[19] and thus, one would characterize reactions A, B, D, E, and G as pseudopericyclic since they exhibit electron depletions and accumulations of fluctuation (cf. diagrams on Figures 1 and 2 where several pairs of arrows point towards or depart from the same atom), breaking the cyclic uniform electron distribution expected in a pericyclic process. On the other hand reactions C, F, and H exhibit a cyclic electron distribution without electron depletions

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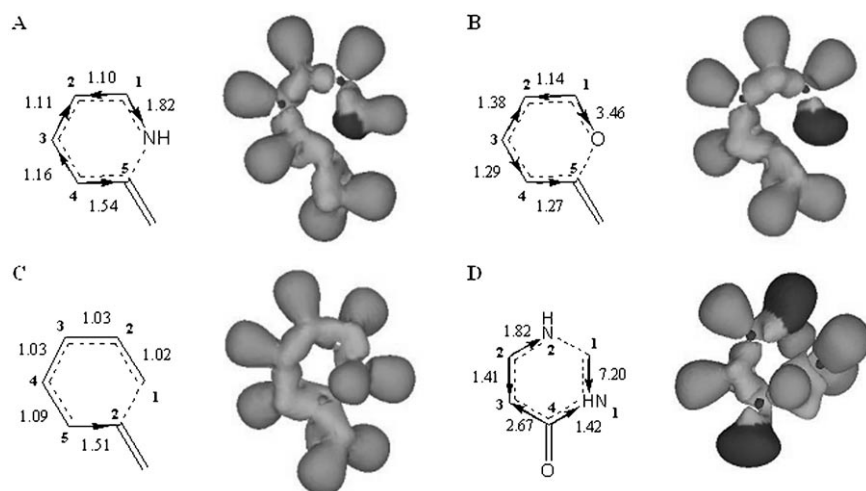


Figure 1. Scheme of the transition-state structures together with relative electron fluctuation magnitudes and ELF = 0.60 pictures for reactions A–D.

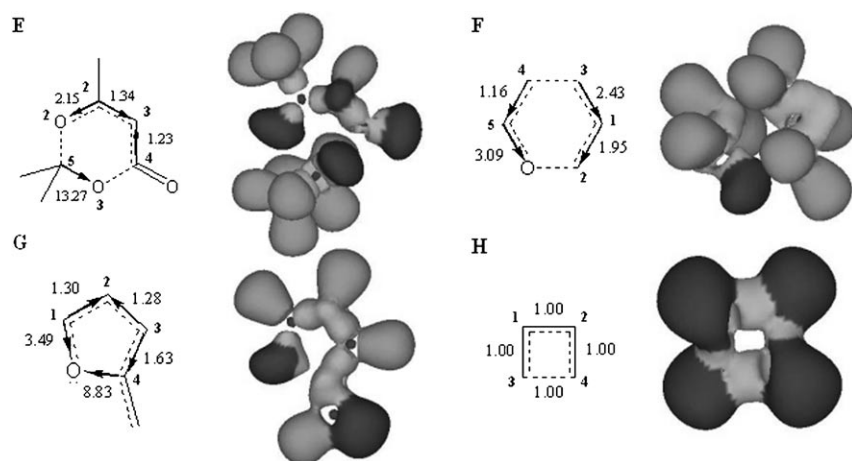


Figure 2. Scheme of the transition-state structures together with relative electron fluctuation magnitudes and ELF = 0.60 pictures for reactions E–H.

or accumulations of fluctuation for bonds involved in the π -electron rearrangement, and therefore they are pericyclic.

Various criteria are used to discern between a pericyclic and pseudopericyclic mechanism, a recent one is also based on an ELF analysis,^[20] but as yet none of them have been proved definitive except for the recent work by López et al.,^[21] which provides a way to characterize a restricted group of electrocyclic processes (those involving ring closures) by means of ellipticity calculations along the reaction path. On the other hand, the here-reported electron distribution of TS studied by means of the ELF provides a clear picture of the electron rearrangement, which reveals the mechanism of the reaction for several electrocyclic processes with the only need of the TS structure. We believe that the qualitative conclusions reached herein should not be altered in a significant way by the use of larger basis sets and higher-level theoretical methods. In particular, the TS geometry and the energy barrier of reactions A–C have been calculated using larger basis sets and more accurate

methods yielding the same qualitative results.^[9] Furthermore, some authors have demonstrated the adequacy of these calculations to study pericyclic processes by showing that the B3LYP/6-31G* results are similar to those derived from experimental data or more accurate theoretical calculations.^[22–25] In addition, it is worth noticing that the ELF function has been proven quite insensible to basis-set changes and only slight changes have been observed with exact calculations on small atoms.^[26]

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