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# Reply to “Comment on the ‘Nature of Bonding in the Thermal Cyclization of (Z)-1,2,4,6-Heptatetraene and Its Heterosubstituted Analogues’”

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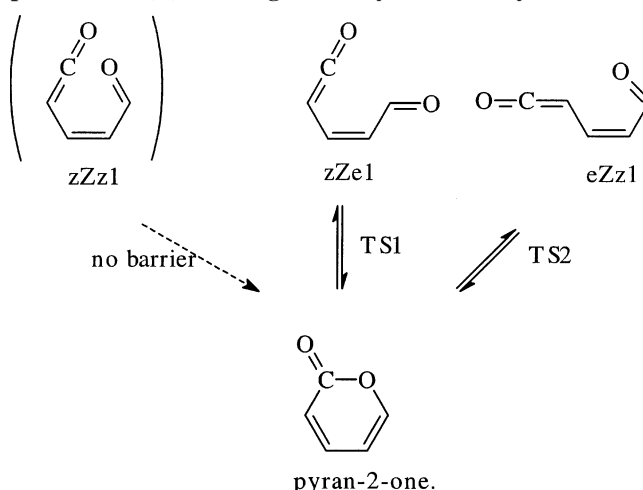
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The criticism raised by Matito, Solà, Duran, and Poater concerning our work on “Nature of bonding in the thermal cyclization of (Z)-1,2,4,6-heptatetraene and its heterosubstituted analogues”<sup>1</sup> continues the controversy about the nature of bonding in the cyclization reaction mechanisms.

(i) The authors based their arguments on the examination of the covariance analysis for a transition structure for the pseudopericyclic cyclization of 5-oxo-2,4-pentadienal (**D**) to pyran-2-one. They have reported that the corresponding TS has been obtained at the HF/6-31G(d,p) level because both the B3LYP/6-31G(dlp) and B3LYP/6-31+G(d) methods give a reaction path without an energy barrier. In effect, it has been already reported by Birney<sup>2</sup> that such a TS was not obtained at higher levels of theory. Although the HF geometry seems suitable to deal with bonding, the inclusion of correlation effects will be indispensable for a correct and complete discussion based on the covariance (i.e., fluctuation) analysis of populations among ELF basins, and therefore, the data presented in the Comment are at least incomplete. We recall in this point that Birney has reported two transition states, TS1 and TS2 (see Scheme 1).

It has also been already explicitly noted that both TS1 and TS2 correspond to simple *rotational transition structures* for the rotation around single bonds in the zZel and eZzl conformers of **D** which interconverts to form the pyran-2-one system, on a “chute” potential energy surface: “one of the eight possible conformations of **D** (zZzl) does not exist but closes without a barrier via a pseudopericyclic pathway to pyran-2-one. IR spectra of **D** in Ar matrixes are consistent with three conformations (zZel, eZzl, and eZel). Calculated rotational barriers from zZel and eZzl to pyran-2-one are consistent with the observed kinetics for the decay of **D**.”<sup>2</sup> From the geometrical structure of both TS1 and TS2, it can be noted that the C1–O5 distances are quite long (3.364 and 3.140 Å, respectively), “suggesting little bonding at the transition states”.<sup>2</sup> It is clear for us that such a type of rotational TS or the HF/6-31G(d) structure is not suitable enough to probe the usefulness of covariance analysis in order to assert the pericyclic or pseudopericyclic nature of the bonding for this reaction. Moreover, it should be noted that, in the context of covariance analysis, main contributions,  $B_{ij}$ , from any basin  $j$ ,  $\Omega_j$ , to the variance of population in

SCHEME 1. Three of the Conformations for 5-Oxo-2,4-pentadienal (**D**) Yielding to the Pyran-2-one System<sup>a</sup>



<sup>a</sup> zZzl does not exist, and TS1 and TS2 correspond to simple rotational transition structures for rotation around single bonds in zZel and eZzl, respectively (see text and ref 2 for details).

basin  $i$ ,  $\sigma^2(\tilde{N}_i, \Omega_i)$ , will decrease with the distance of neighboring domains in agreement with the expected behavior of delocalization of the hole correlation function  $h(\mathbf{r}_1, \mathbf{r}_2)$  in such a pair regions  $i$  and  $j$ .<sup>23</sup>

$$\begin{aligned} \sigma^2(\tilde{N}_i, \Omega_i) &= \int_{\Omega_i} \int_{\Omega_j} \pi(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 - \tilde{N}_i(\tilde{N}_i - 1) \\ &= \sum_{j \neq i} B_{ij} = \sum_{j \neq i} (\tilde{N}_i \tilde{N}_j - \langle \tilde{N}_{ij} \rangle) \\ &= - \sum_{j \neq i} \int_{\Omega_i} \int_{\Omega_j} \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) h(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned} \quad (1)$$

Thus, on the basis of the fact that a ground state zZzl conformation for **D** and a related transition structure for a direct ring closure via a nucleophilic attack of the pair at O5 to the C1 carbene center do not exist (at a good enough level of theory) and given the nature and physical sense for the above-mentioned covariance analysis (i.e., fluctuation) of populations in the ELF basins for **A**, **B**, and **C**, we have assigned a pericyclic bond interaction to the controversial cases of **A** and **B**. It will be certainly necessary to establish further comparisons using a better suitable model for a pseudopericyclic transition structure. These studies are currently being performed in our group, and they will be submitted for publication elsewhere.

(ii) We clarify here the reading of covariance data in Tables 1–3, where the percent information in the form “**i**(%)”, which stands simply for the quantity  $[B_{ij}/\sigma^2(\tilde{N}_i, \Omega_i)] \times 100$ , should be read out as the contribution of the bold marked basin population **i** to the variance of the corresponding named row basin population. For instance, from Table 1 in our work, the main contributions of basins V(C1,C2), V(C2,C3), V(C5,C6), V(C6,H6), V(C6,N), and V(H8,N) to the variance of the V(N) basin population are 5.1, 7.0, 4.4, 4.6, 33.6, and 25.9%, respectively. From this point of view, we must note that the suggested way to compare covariance contributions to a given basin coming from adjacent bonding and lone pair basins for the clockwise and counterclockwise directions should be fully reviewed in Figure 1 in the Comment.

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(iii) Also, we must finally recall that, from examination of eq 1, any partition of the variance of basin populations in terms of contributions from other regions is in essence arbitrary. As it has already been emphasized in the literature, such a way to *interpret* delocalization from the analysis of covariance in the ELF domains has proved to be very useful in the examination of bonding fluctuation patterns in several stationary and reacting systems.<sup>4</sup> Reported evidence in some simple systems<sup>1,4b,c</sup> suggests that pericyclic and pseudopericyclic topologies can also be directly characterized using this scheme of analysis.

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## References and Notes

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