ELECTROCYCLIZATION OF 7-AZAHEPTA-1,2,4,6-TETRAENE

I concluded the subchapter on pseudopericyclic reaction (Chapter 3.4) with a discussion of the controversy concerning the nature of the electrocyclization of 7-azahepta-1,2,4,6-tetraene **1**. Quickly summarizing form the book, based on which data one deems important, the reaction can be seen as either pericyclic or pseudopericyclic.

1 **2**

However, I offered David Birney's opinion as perhaps the proper way to interpret this reaction. David suggested that the TS has both pericyclic and pseudopericyclic character. I wrote that "what we have is a continuum from pericyclic to pseudopericyclic character, analogous to the S_N1 to S_N2 continuum for nucleophilic substitution".

Duncan has revisited this reaction,[1] employing both B3LYP and CASSCF(10,9) computations. He concludes that the reaction is “neither purely pericyclic nor pseudopericyclic” – just as Birney had indicated. Duncan does offer the possibility of a secondary orbital interaction involving the nitrogen lone pair. But it is nice to see confirmation of the interpretation that David originated for my book!

Source: http://comporgchem.com/blog/?p=71