

Is the Excited State Aromaticity a Driving Force for Planarization of Dibenzannelated 8 π -Electron heterocycles?

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Excited state aromaticity (ESA), as given by Baird's rule, can be a driving force for changes in excited state structures and other properties, such as observed for dibenzo[*b,f*]oxepin (Figure 1a).[1,2] Dibenzannelated heterocycles with central 8 π -electrons ring, found in a range of applications such as in antipsychotic drugs and photofunctional materials, often adopt a bent structure in the ground state (S_0) but can become planar in the first excited states (S_1 and T_1), fulfilling the requirements for excited state aromaticity.[3] Herein we report a quantum chemical investigation focused on how the position, type and number of heteroatoms in the central 8 π -electron ring can affect the S_1 and T_1 states of a range of dibenzannelated heterocycles (Figure 1b) and to extent aromaticity.[4] For molecules with one or two heteroatoms in the central ring, their optimal S_1 and T_1 structures are (nearly) planar and have $\pi\pi^*$ character, being influenced by ESA to a significant degree. Moreover, the effect is much stronger for molecules containing nitrogen while it is weaker for oxygen-based compounds, following the established aromaticity trend of the electronic ground state. On the other hand, compounds with N=N bonds are strongly puckered in the excited state as consequence of their nonaromatic $n\pi^*$ excited state.

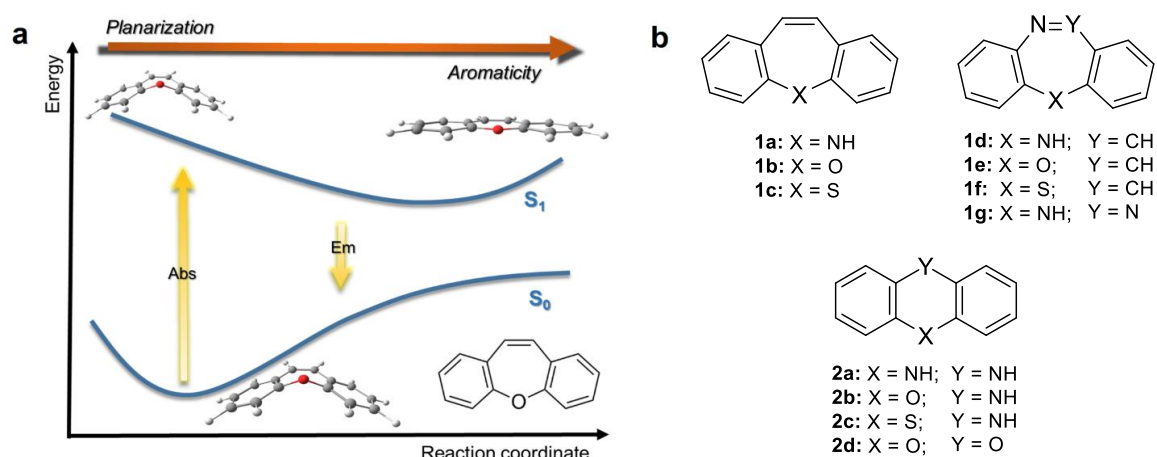


Figure 1: a) Schematic representation of the potential energy surfaces for planarization of dibenzo[*b,f*]oxepin in the S_1 state. b) Molecules investigated in this work.

References

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