

Singlet Biradical Character: Radical Reactivity of Bis(Imidazolyl Radicals)

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Since the experimental evaluation of the biradical index is limited due to the instability of the biradicals, the biradical characters have generally been estimated by the theoretical calculations. Therefore, it is required to experimentally determine the biradical character. Recently, we have developed fast photochromic pentaarylbimidazole (PABI). The open-ring isomer of PABI is represented as a resonance hybrid of the open-shell biradical and the closed-shell quinoidal form. It was predicted that the biradical character of the open-ring isomer depends on the balance between the formal loss of a double bond character and the aromatic stabilization energy. As an experimental biradical index, we focused on the rate of the thermal recombination reaction. As a result, the large aromaticity of the bridging site connecting two imidazole rings increases the biradical character of the open-ring isomer, leading to the acceleration of the thermal back reaction rate. For bis(imidazole dimers) involving two photochromic units in a molecule, the tetraradical species are generated by two-photon absorption. The spin-spin interaction between the central bridging phenyl ring is the key feature to form the closed-shell quinoidal species. The increased biradical character promotes the strong antiferromagnetic interaction in the para position, generating para quinoidal species.

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