何故、多くの６π電子系光化学的電子環状反応に於いて、開環量子収率は閉環量子収率よりも小さく、それらの和が１より小さいのか？

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What is the reason why the ring-opening quantum yield is smaller than the ring-closure one and their sum is smaller than unity in many 6π-electron photochemical electrocyclic reactions?

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In many 6π-electron photochemical electrocyclic reaction systems such as photochromic molecules of diarylethenes, there is an empirical rule that the ring-opening quantum yield is smaller than the ring-closure one and their sum is smaller than unity, the reason for which has not been clarified experimentally or theoretically for a long time. In this study, we have successfully revealed the reason why this empirical rule is fulfilled through nonadiabatic molecular dynamics (NAMD) simulations of both photochemical ring-opening and ring-closure reactions of CHD/cZc-HT, which is a 6π-electron electrocyclic reaction model system, on highly accurate potential energy surfaces at the highly accurate level of XMS-CASPT2.

Keywords :Photochemical electrocyclic reaction; Cyclohexadiene/Hexatriene; Quantum Yield; Conical Intersection; Nonadiabatic Molecular Dynamics;

フォトクロミック分子であるジアリールエテンなどの多くの６π電子系光化学的電子環状反応系では、開環量子収率が閉環量子収率より小さく、それらの和が１より小さいという経験則があり、その理由は長い間実験的にも理論的にも明らかにされてこなかった。本研究では６π電子系電子環状反応モデル系である CHD/cZc-HT の光化学的開環及び閉環反応を対象に超高精度ポテンシャルエネルギー（XMS-CASPT2 レベル）曲面上で非断熱分子動力学（NAMD）シミュレーションを実行することにより、この経験則が成立する理由を明らかにした。

$$QY(P|R) = \sum_{DP=\{P6,C4,O4,C2\}} B(P|DP,R) * D(DP|R)$$

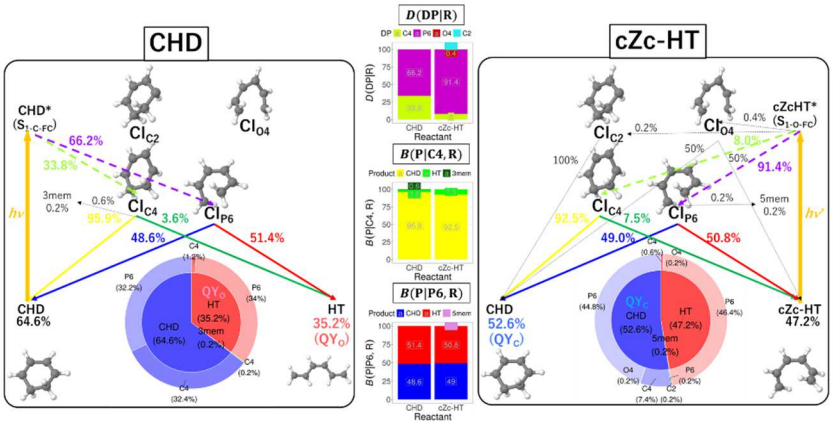

Figure 1: Schematic photochemical electrocyclic reaction pathways from S_1 Franck-Condon states of CHD(left) and cZc-HT(right) to products for each decay passway obtained by NAMD simulations.