

Excited State Intramolecular Proton Transfer (ESIPT) in Anthrol Carbaldehydes

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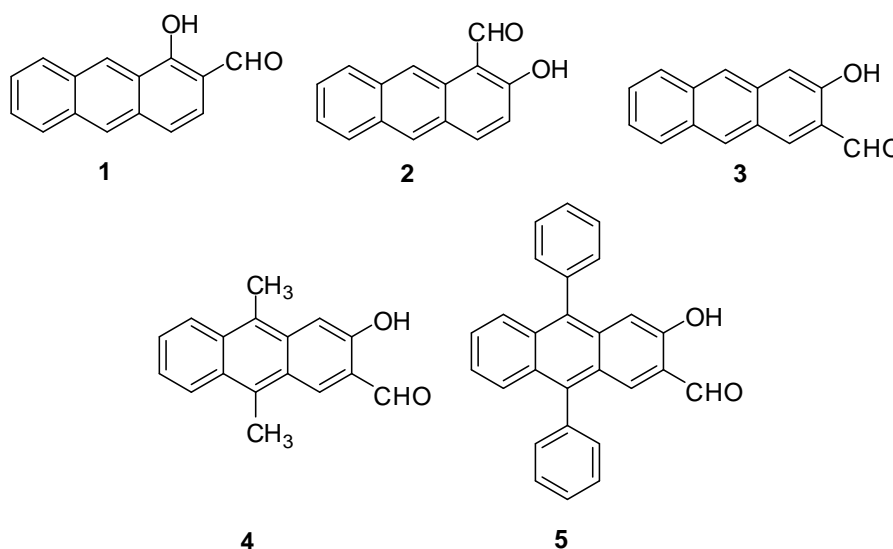
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ESIPT has been intensively investigated over five decades because of its fundamental aspect in chemistry and biology,^[1] as well as numerous applications in material science,^[2] sensing and bioimaging.^[3] The most common acidic group in ESIPT reactions is phenolic OH,^[4] whereas the basic site is usually a carbonyl group.^[5] Thus, among the first molecules that were experimentally found to undergo ESIPT were simple salicaldehyde derivatives. The reaction scope has later been extended to naphthol carbaldehyde derivatives.^[6] However, to date, ESIPT in anthrol carbaldehydes has not been documented.



Photophysical properties and reactivity in ESIPT for anthrol carbaldehydes **1-5** have been investigated computationally and experimentally by steady-state and time-resolved fluorescence and laser flash photolysis (LFP). Contrary to analogous naphthol derivatives, 1,2-disubstituted anthrol carbaldehydes **1** and **2** are not ESIPT reactive. The main deactivation channels from S_1 for **1** and **2** are fluorescence ($\Phi_F = 0.1-0.2$) and ISC to an almost isoenergetic T_2 state. The triplet states from **1** and **2** were detected by LFP. On the contrary, 2,3-disubstituted anthrols **3-5** undergo efficient barrierless ultrafast ESIPT. However, the typical dual emission from locally excited states and ESIPT tautomers were not observed

since ESIPT proceeds via a conical intersection with S_0 delivering keto-tautomer in the hot ground state. Therefore, anthrols **3-5** are about ten times less fluorescent, and their emission originates from less-populated conformers that cannot undergo ESIPT. Keto-tautomers for **3-5** were detected in CH_3CN by LFP ($\lambda_{\text{max}} = 370 \text{ nm}$, $\tau = 30\text{-}40 \text{ ns}$). The difference in ESIPT reactivity for **1-3** was fully disclosed by calculations at ADC(2)/aug-cc-pVDZ level of theory, and particularly, by calculating the charge redistribution upon excitation to S_1 . Only 2,3-disubstituted anthrols exhibit polarization in S_1 that increases electron density on carbonyl and decreases on phenolic OH, setting the stage for ultrafast ESIPT.

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