THE ROLE OF $\pi\sigma^*$ STATE IN INTRAMOLECULAR CHARGE TRANSFER OF 4-(DIMETHYLAMINO)-BENZONITRILE AND RELATED MOLECULES

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The solvent-polarity dependence and temporal characteristics of the transient absorption of 4-(dimethylamino)benzonitrile, DMABN, and 4-(dimethylamino)benzethyne, DMABE, demonstrate the presence of the $\pi\sigma^*$-state absorption at about 700 nm and the $\pi\pi^*$ (LE)-state absorption at about 520 nm and 450 nm. The rise and decay times of the $\pi\sigma^*$-state transient differ from those of the $\pi\pi^*$-state transients in both compounds. Moreover, the peak position of the $\pi\sigma^*$-state absorption is blue-shifted and more intense in acetonitrile as compared to *n*-hexane, whereas the band positions of the $\pi\pi^*$-state absorptions are essentially the same in the two solvents. For DMABN in acetonitrile, the rise time ($\sim$ 4.3 ps) of the twisted intramolecular charge transfer (TICT)-state transient at 330 nm is identical to the decay time of the $\pi\sigma^*$-state transient. The 4.8 ns decay time of the TICT-state absorption of DMABN is longer than the 2.9 ns decay time of the intramolecular charge-transfer (ICT) fluorescence, indicating that the fluorescent ICT state differs from the TICT state observed in transient absorption. These results are consistent with the presence of a low-lying $\pi\sigma^*$ state in DMABN (and DMABE), and the role the $\pi\sigma^*$ state plays in the formation of the TICT state of DMABN.