

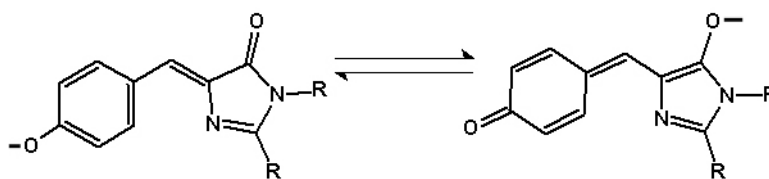
The Electronic Structure of the Methine Unit – Implications for Photoisomerization and Charge Separation in Organic Dyes.

Seth Olsen and Ross H. McKenzie

School of Mathematics and Physics and Centre for Organic Photonics and Electronics, The University of Queensland, Brisbane QLD 4072, Australia

Abstract

Methine is a limit of neutral sp^2 carbon where the Lewis octet rule is obeyed on average by participation in multiple resonant structures with different charge localization – for example, in the well-known chromophore of the green fluorescent protein (GFP)[1]:



Dyes which contain a methine unit are useful in many areas of science and technology[2], and include some of the first chemicals produced by modern organic syntheses. The resonance drawn above is a keystone of our understanding of their colour[3] and their nonlinear absorption.[4] Here, we will consider the consequences of the resonance for the non-radiative decay of these dyes. We will focus particularly on how the resonance above corresponds to a self-consistent solution to the quantum chemistry of the low-lying electronic states, which predicts photoisomerization via a manifold of charge-localized diabatic states. The nature of the charge-localized states, which meet in conical intersections where decay takes place, has interesting implications for common useful features of the dye family.

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