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# ESIPT or not ESIPT ? Revisiting recent results on 2,1,3-benzothiadiazole under the TD-DFT light Electronic Supporting Information

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## 1 Methods

We have used the latest revision of the Gaussian09 program[1] to perform all our computations, applying default thresholds and algorithms, except when noted below. Most calculations relied on the M06-2X hybrid exchange-correlation functional,[2,3] a choice justified by numerous previous benchmarks demonstrating the accuracy of this functional both vertical and adiabatic transition energies as well as for predicting band shapes.[4–7] M06-2X indeed stands as one of the best compromise approach for TD-DFT simulations as long as no long-range charge-transfer is taking place. We have also used CAM-B3LYP[8] and ωB97X[9] for test calculations on $G$ energies. Here, we have applied a recently proposed strategy[5] which is to determine the geometrical and vibrational parameters with the 6-31+G(d) atomic basis set, whereas the transition energies are corrected with a much more extended atomic basis set, namely 6-311++G(2fd,2p), so that all energies shown in the main text are very close to the basis set convergence limit.

For each molecule, both the ground and first excited states have been fully optimized using DFT/TD-DFT analytical gradients, considering both canonical and ESIPT forms. To achieve numerically stable and accurate values, we have tightened self consistent field ($10^{-10}$ *a.u.*) and geometry optimization ($10^{-5}$ *a.u.*) convergence thresholds, as well as used a (99,590) pruned DFT grid (so-called *ultrafine* grid). The nature of all structures, was confirmed by analytical (ground-state) or numerical (excited-state) Hessian calculations that returned no imaginary vibrational modes (minima). In addition, these calculations gave access to free energies.

Environmental effects (here dichloromethane and water) have been accounted for using the well-known Polarizable Continuum Model (PCM) model.[10] While geometry optimizations, Hessian calculations and Gibbs energies have been performed with the linear-response (LR) PCM approach for both ground and excited-states, all transition energies (absorption and fluorescence) have been corrected using the corrected LR scheme (cLR).[11,12] The cLR scheme corrects the cavity polarization by accounting for the change of electron density upon electronic transition. Therefore, it allows not only to compare structures having different changes of dipole moment amplitudes between the ground and excited states but also to estimate emission wavelengths (and hence Stokes shift) with more accuracy. Of course, while we applied the equilibrium PCM limit for optimization and vibrational TD-DFT calculations (slow phenomena), absorption and fluorescence wavelengths are corrected for non-equilibrium effects (fast phenomena). For the records, let us underline that attempts to locate **III** with gas-phase models failed and that only condensed phase calculations are therefore discussed in the body of the text. This is probably related to its zwitterionic character that remains challenging for single-reference approaches.[13]

The (photo)acidity has been evaluated by determining the logarithm of the acidic dissociation constant at the ground state GS ($pK_\mathrm{a}$) and the excited state ES ($pK_\mathrm{a}^*$). These quantities require the determination of the variation of the Gibbs energies in solution ($\Delta G_\mathrm{solv}$ and $\Delta G^*_\mathrm{solv}$) using the thermodynamic cycle (Born-Haber cycle BHC).[14,15] Following the BHC, $\Delta G_\mathrm{solv}$ is obtained for the ground-state by :

$$\Delta G_\mathrm{solv} = \Delta G_\mathrm{gas} - \Delta G^\mathrm{AH}_\mathrm{solv} + \Delta G^\mathrm{A^-}_\mathrm{solv} + \Delta G^\mathrm{H^+}_\mathrm{solv} + \Delta G_\mathrm{add} \qquad (1)$$

An additional energy contribution, $\Delta G_\mathrm{add}$ (-1.9 kcal/mol), should be included to account for the transfer of a solute molecule from a 1 atm gas phase into a 1M solvent standard states. The free energy of the proton in gas phase ($G^{H^+}_\mathrm{gas}$) and its solvation energy ($\Delta G^\mathrm{H^+}_\mathrm{solv}$) are derived from experiments and are taken to be -6.28 kcal/mol and -263.98 kcal/mol, respec-

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tively.[16,17] The same principle has been employed to obtain the $pK_a^*$ considering molecules in their ES. This thermodynamic approach implies the equilibrium between the solute (photoacid) and the solvent.

The charge-transfer assessment was made using Le Bahers dipolar approach that allows determining the distance between the barycenters of charge depletion and gain.[18,19] To determine these barycenters, one starts by computing the difference between the total densities of the excited and ground states:

$$\Delta\rho(\mathbf{r}) = \rho^{\mathrm{ES}}(\mathbf{r}) - \rho^{\mathrm{GS}}(\mathbf{r}). \tag{2}$$

One next splits $\Delta\rho(\mathbf{r})$ in two parts, that is one defines an increasing electronic density region:

$$\rho^{+}(\mathbf{r}) = \begin{cases} \Delta\rho(\mathbf{r}) & \text{if} \quad \Delta\rho(\mathbf{r}) > 0 \\ 0 & \text{if} \quad \Delta\rho(\mathbf{r}) < 0 \end{cases}, \tag{3}$$

and similarly for $\rho^{-}(\mathbf{r})$. Subsequently, the amount of charge transferred simply becomes,

$$q^{\mathrm{CT}} = \int \rho^{+}(\mathbf{r}) d\mathbf{r}, \tag{4}$$

a value that could, of course, be defined from $\rho^{-}(\mathbf{r})$. One next determines the barycenters corresponding to the $\rho^{+}(\mathbf{r})$ and $\rho^{-}(\mathbf{r})$ functions:

$$r^{+} = \left(x^{+}, y^{+}, z^{+}\right) = \frac{1}{q^{\mathrm{CT}}} \int \mathbf{r}\rho^{+}(\mathbf{r}) d\mathbf{r} \tag{5}$$

$$r^{-} = \left(x^{-}, y^{-}, z^{-}\right) = \frac{1}{q^{\mathrm{CT}}} \int \mathbf{r}\rho^{-}(\mathbf{r}) d\mathbf{r}. \tag{6}$$

The distance separating these two points being the charge-transfer distance:

$$d^{\mathrm{CT}} = \left|\left|r^{+} - r^{-}\right|\right|. \tag{7}$$

We used LR-PCM M06-2X/6-311++G(2df,2p) densities to determine the relevant charge transfer parameters. The density difference plot shown in Figure 2 in the main manuscript has been obtained with a contour threshold set to 0.0012 a.u.

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