

## Novel Structural Modifications Associated with the Highly Efficient Internal Conversion of 2-(2'-Hydroxyphenyl)benzotriazole Ultraviolet Stabilizers

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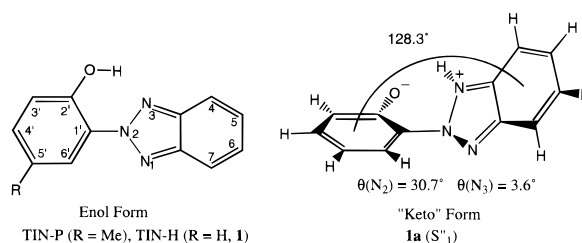
For more than four decades 2-(2'-hydroxyphenyl)benzotriazole and its derivatives (e.g., Tinuvin-P, TIN-P) have been the archetypical photostabilizer additives for polymeric materials.<sup>1</sup> A distinguishing, although not unique, feature of these substances is the presence of an intramolecular hydrogen bond, which is believed to be a key component in the mechanism for dissipation of light energy.<sup>2</sup> The high activity of these compounds has been associated with facile intramolecular proton transfer which occurs in the first excited state, converting the excited state  $S_1$ -enol tautomer to the  $S_1'$ -keto form. Subsequent rapid nonradiative decay to the  $S_0$  state and back transfer of the proton recovers the original  $S_0$ -enol structure.<sup>3,4</sup> This closed cycle occurs on an ultrafast time scale, with time constants in a nonpolar solvent of  $\sim 100$  fs for the proton transfer,  $\sim 150$  fs for the internal conversion to the ground state, and  $\sim 600$  fs for back transfer of the proton.<sup>5</sup> While facile excited state intramolecular proton transfer (ESIPT) also occurs in closely related systems like 2-(2'-hydroxyphenyl)benzothiazole (HBT) and 2-(2'-hydroxyphenyl)benzimidazole (HPBI), such systems are not nearly as effective photostabilizers as TIN-P, presumably because the internal conversion process is less efficient.<sup>3</sup>

Despite the longevity of TIN-P, the origin of its efficiency as a photostabilizer and in particular of the rapid internal interconversion from  $S_1'$  remains obscure. The nonradiative lifetime of the  $S_1'$  state is sensitive to temperature and physical environment, suggesting that some significant molecular distortions accompany internal conversion.<sup>3,4</sup> For example, it has been suggested that the existence of a twisted intramolecular charge transfer state is responsible for the viscosity dependence of internal conversion in related molecules such as HBT.<sup>6</sup>

A potential source of molecular distortion in the  $S_1$  state that has not been previously addressed is rehybridization of the substituted nitrogen ( $N_2$ ). A recent computational study of charge transfer (CT) in aminobenzonitriles suggests that rehy-

bridization of the cyano group from  $sp$  to  $sp^2$  can lead to stabilization of the CT state by several eV.<sup>7</sup>

In the present computational study we have explored the nitrogen ( $N_2$ ) rehybridization motif using 2-(2'-hydroxyphenyl)benzotriazole (TIN-H, R = H, **1**) as a model for TIN-P (R = CH<sub>3</sub>). The CIS/3-21G level<sup>8</sup> geometry optimizations on the first excited state of **1** afforded in addition to the anticipated  $S_1'$  planar keto stationary point, an  $S_1''$  folded keto structure **1a** that is 0.36 kcal/mol higher in energy. The intramolecular hydrogen bond remains intact in this latter structure, but the planes of the two ring systems are canted by 128°,  $N_2$  is significantly pyramidalized (the angle  $\theta$ , the deviation from planarity of  $N_2$  and  $N_3$  calculated as the difference between 360° and the sum of the three bond angles, is 30.7°), and approximately 0.5 e<sup>-</sup> are transferred to the benzotriazole ring. CNDO/S calculations do predict significant charge transfer from the phenolic ring to the benzotriazole in the  $S_1$  state of TIN-P.<sup>2a</sup> Most significantly, the  $S_0$ - $S_1$  energy gap is decreased from 3.25 eV at the planar-keto geometry ( $S_1'$ ) to 1.55 eV at the folded geometry ( $S_1''$ ).<sup>9</sup> While these CIS calculations are only suggestive, this energy gap narrowing is consistent with an enhanced rate of internal conversion of TIN-P and may reflect the existence of a conical intersection accompanying molecular folding as depicted below for **1a**.<sup>10</sup>



We decided to explore more computationally tractable, intermediate-size models. 2-(2'-Hydroxyphenyl)triazole **2**, obtained by deleting the fused ring from **1**, exhibits the same general structural modifications as the larger model. As with **1**, model **2** exists as the planar enol tautomer in the ground state, and on the CIS/6-31G(d) surface both  $S_1'$ -keto and  $S_1''$ -folded keto stationary points exist, the latter being more stable by 5.5 kcal/mol. Charge transfer to the triazole ring is approximately 0.6 e<sup>-</sup> in  $S_1''$ , which is accompanied by rehybridization at  $N_2$  ( $\theta = 26.2^\circ$ ). In order to obtain more robust estimates of the relative energetics accompanying excitation and

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(8) (a) RHF, MP2, and CIS optimizations. QCISD(T) energies, and the conical intersection search were done with Gaussian 94.<sup>8b</sup> The CASSCF calculations were performed with both Gaussian 94<sup>8b</sup> and MOLCAS 3<sup>8c</sup> programs, and for CASPT2 calculations MOLCAS 3<sup>8c</sup> was used. (b) Gaussian 94, Revision B.2; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995. (c) MOLCAS version 3; Andersson, K.; Blomberg, M. R. A.; Fülischer, M. P.; Kellö, V.; Lindh, R.; Malmqvist, P.-A.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Siegbahn, P. E. M.; Urban, M.; Widmark, P.-O. University of Lund, Sweden, 1994.

(9) Throughout the text,  $S_0$  and  $S_1$  refer to the ground and first excited state surfaces at the ground state enol geometry;  $S_0'$  and  $S_1'$  refer to these state surfaces at the  $S_1$  keto optimized geometry, and  $S_0''$  and  $S_1''$  refer to these surfaces at the folded geometry, obtained by CIS geometry optimizations (models **1** and **2**) or by explicit searching for a conical intersection (model **3**).

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