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

Carlos M. Estévez, $^{\dagger,\$}$ Robert D. Bach, *,† K. C. Hass, ‡ and W. F. Schneider ‡

Department of Chemistry and Biochemistry University of Delaware, Newark, Delaware 19716 Ford Research Laboratory, SRL MD-3028 Dearborn, Michigan 48121-2053

Received November 25, 1996

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.¹ 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.² 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 S1-enol tautomer to the S1'-keto form. Subsequent rapid nonradiative decay to the S₀ state and back transfer of the proton recovers the original S₀-enol structure.^{3,4} This closed cycle occurs on an ultrafast time scale, with time constants in a nonpolar solvent of ~ 100 fs for the proton transfer, ~ 150 fs for the internal conversion to the ground state, and ~ 600 fs for back transfer of the proton.⁵ While facile excited state intramolecular proton transfer (ESIPT) also occurs in closely related systems like 2-(2'-hydroxyphenyl)benzothiazole (HBT) and 2-(2'-hydroxyphenyl)benzoimidazole (HPBI), such systems are not nearly as effective photostabilizers as TIN-P, presumably because the internal conversion process is less efficient.³

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.^{3,4} 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.⁶

A potential source of molecular distortion in the S_1 state that has not been previously addressed is rehybridization of the substituted nitrogen (N₂). A recent computational study of charge transfer (CT) in aminobenzonitriles suggests that rehy-

Elsässer, T. Chem. Phys. Lett. **1995**, 240, 35–41. (b) Chudoba, C.; Riedle, E.; Pfeiffer, M.; Elsässer, T. Chem. Phys. Lett. **1996**, 263, 622.

(6) Potter, C. A. S.; Brown, R. G.; Vollmer, F.; Rettig, W. J. Chem. Soc., Faraday Trans. **1994** 90, 59-67.

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

In the present computational study we have explored the nitrogen (N₂) rehybridization motif using 2-(2'-hydroxyphenyl)benzotriazole (TIN-H, R = H, (1)) as a model for TIN-P (R =CH₃). The CIS/3-21G level⁸ geometry optimizations on the first excited state of 1 afforded in addition to the anticipated S_1 planar keto stationary point, an S1" 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°, N2 is significantly pyramidalized (the angle θ , the deviation from planarity of N2 and N3 calculated as the difference between 360° and the sum of the three bond angles, is 30.7°), and approximately 0.5 e⁻ are transferred to the benzotriazole ring. CNDO/S calculations do predict significant charge transfer from the phenolic ring to the benzotriazole in the S₁ state of TIN-P.^{2a} 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'') .⁹ 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**.¹⁰



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 S₁'-keto and S₁''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⁻ in S₁'', which is accompanied by rehydridization at N₂ ($\theta = 26.2^{\circ}$). In order to obtain more robust estimates of the relative energetics accompanying excitation and

^{*} Author to whom correspondence should be addressed.

[†] University of Delaware.

[‡] Ford Research Laboratory.

[§] Present address: Departamento de Química Física, Facultade de Química, Universidade de Santiago de Compostela, Santiago de Compostela, Galicia, Spain.

Heller, H. J.; Blattmann, H. R. Pure Appl. Chem. 1972, 30, 145.
 (2) (a) Catalán, J.; Fabero, F.; Guijarro, M. S.; Claramunt, R. M.; Santa María, M. D.; Foces-Foces, M. C.; Hernández Cano, F.; Elguero, J.; Satre, R. J. Am. Chem. Soc. 1990, 112, 747–759. (b) Catalán, J.; del Valle, J. C. Am. Chem. Soc. 1993, 112, 5423 (c) Riekar, L: quipped schemistic schemis

R. J. Am. Chem. Soc. 1990, 112, 147–759. (b) Catatali, J.; def Valle, J. C.
 J. Am. Chem. Soc. 1993, 115, 4321–4325. (c) Rieker, J.; Lammert-Schmitt, E.; Goeller, G.; Roesller, M.; Stueber, G. J.; Schetter, H.; Kramer, H. E.
 A.; Stezowski, J. J.; Hoier, H.; Henkel, S.; Scmidt, A.; Port, H.; Wiechmann, M.; Rody, J.; Rytz, G.; Slongo, M.; Birbaum, J.-L. J. Phys. Chem. 1992, 96, 10225.

⁽³⁾ Orsom, S. M.; Brown, R. G. Prog. React. Kinet. 1994. 19, 45–91.
(4) (a) Flom, S. R.; Barbara, P. F. Chem. Phys. Lett. 1983, 94, 488–493. (b) Woessner, G.; Goeller, G.; Rieker, J.; Stezowski, J. J.; Daltrozzo,

E.; Neureiter, M.; Dramer, H. E. A. J. Phys. Chem. **1985**, 89, 3629–3636. (5) (a) Chudoba, C.; Lutgen, S.; Jentzsch, T.; Riedle, E.; Woerner, M.; Elsässer, T. Chem. Phys. Lett. **1995**, 240, 35–41. (b) Chudoba, C.; Riedle,

⁽⁷⁾ Sobolewski, A. L.; Domcke, W. Chem. Phys. Lett. 1996, 250, 428. (8) (a) RHF, MP2, and CIS optimizations, QCISD(T) energies, and the conical intersection search were done with Gaussian 94.^{8b} The CASSCF calculations were performed with both Gaussian 94.^{8b} and MOLCAS 3^{8c} programs, and for CASPT2 calculations MOLCAS 3^{8c} 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.; Fülscher, M. P.; Kellö, V.; Lindh, R.; Malmqvist, P.-Å.; 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).

^{(10) (}a) Bearpark, M. J.; Bernardi, F.; Clifford, S.; Olivucci, M.; Robb. M. A.; Smith, B. R.; Vreven, T. J. Am. Chem. Soc. **1996**, *118*, 169. (b) Manthe, U.; Koppel, H. J. Chem. Phys. **1990**, *93*, 1669.



Figure 1. Energy diagram of the ground and first singlet excited state for compounds 2 and 3. Relative energies computed at CASPT2/CAS(12,-10)/6-31G(d) (in parentheses) on the geometries shown at the bottom for compound 3 and at CASPT2/CASSCF(14,12)/ANO [in square brackets] on the geometries shown at the top for compound 2. Energies given in eV refer to the S_1 - S_0 energy gap at the three geometries. Energy differences between the enol, keto, and folded keto forms in the same state are in kcal/mol. Selected distances are in Å and angles in deg.

relaxation, state-averaged CASPT2/CASSCF(14,12)/ANO^{8,11} single point calculations were performed at the S₀-enol, S₁'keto, and S₁"-folded keto geometries (Figure 1). The CASPT2 vertical excitation energy of 2 (4.32 eV) is surprisingly close to the experimental absorption band $(3.65 \text{ eV})^3$ in TIN-P, despite the omission of the benzene ring in the former. The calculated $S_0'-S_1'$ gap (2.28 eV) is also quite close to the observed TIN-P red fluorescence (2.0 eV).³ The decrease in the calculated energy gap from the S_0 -enol structure to the S_1 '-keto forms reflects a simultaneous stabilization of S₁ and destabilization of S₀ upon formation of the keto tautomer. Rehybridization at N₂ and molecular folding cause the two surfaces to approach even closer, such that the $S_0''-S_1''$ gap decreases to only 0.48 eV. The narrowness of this energy gap provides further evidence for enhanced internal conversion in the folded geometry and possibly the existence of a conical intersection.

Unfortunately, even 2 is too large to search directly for a conical intersection at a reliable level of theory. We therefore examined highly abbreviated model 3 that retains only the fundamental chromophore in TIN-P (shaded atoms in 2). The ground state structure of 3, obtained at the CASSCF(8,6)/6-31G(d) level is reasonably similar to 2 (Figure 1) and in agreement with previous calculations¹² and the larger models above; the S_1 '-keto form is more stable than the S_1 -enol. Using the algorithm of Bearpark et al.13 with a state-averaged CASSCF(8,6)/6-31G(d), the lowest energy point of the intersection seam of the S₀ and S₁ states was located. This crossing point is lower in energy than the S₁'-keto form, and the geometry at this point clearly resembles the S₁"-folded structures of 1 and **2**, including the marked pyramidalization at N_2 . In analogy with 1 and 2, in S_1'' approximately 0.8 e⁻ are transferred from the OCC (phenol) portion of 3 to the NNC (triazole) portion. Single point CASPT2 calculations at the CASSCF crossing point confirm the close approach of the two surfaces (energy gap = 0.11 eV, Figure 1).

From the present results, we can elaborate on the standard model of the photophysics of TIN-P and related molecules. TIN-P is vertically excited to the S1 state, which causes a transfer of charge to the triazole ring and results in a rapid transfer of a proton to form S_1' . The molecule either fluoresces from S_1' or, if in an environment which provides sufficient conformational freedom, further relaxes by rehybridization and folding about N₂. The unique molecular architecture of the triazole functionality with its three contiguous nitrogen lone-pairs undergoes an electronically induced geometric distortion in S_1 that decreases the S_0 - S_1 energy gap, likely leading to an intersection of the two surfaces. The decreasing energy gap facilitates internal conversion to the S₀ surface, and back transfer of the proton in the ground state regenerates the original enol form. These results are consistent with the very recent observation of irreversible proton transfer on the S₁ surface.^{5b} Our frequencies calculations on models 1-3 for keto- S_1' and folded- S_1'' show the two lowest modes (an internal rotation between rings and a out-of-plane wagging of the central N₂ atom) that can modulate molecular folding. The third vibrational frequency corresponds to a bending mode that modulates the O····N separation with similar frequency numbers in the planar and the folded keto form in agreement with the vibrational coherence observed after proton transfer.5b

In summary, we present a model for the efficient conversion of exciting photon energy to vibrational energy within TIN-P and related molecules, involving large amplitude motions during internal conversion that facilitate dissipation of this energy in the surrounding medium. This mechanistic picture is consistent with the experimental observation of rapid and strongly temperature and viscosity dependent internal conversion,^{3,4} followed by slower redistribution of vibrational energy.⁵

Acknowledgment. This work was supported in part by the National Science Foundation (CHE-9531242). We are also thankful to the National Center for Supercomputing Applications (Urbana, Illinois) for computer time.

Supporting Information Available: Cartesian coordinates for compounds 1-3 optimized at different levels of theory and an energy table for relaxation of 1-3 are given (7 pages). See any current masthead page for ordering and Internet access instruction.

⁽¹¹⁾ The [10s4p3d]/[7s3p] ANO basis set was contracted to [4s3p]/[2s] K. Pierloot, B.; Dumez, P.-O.; Widmark, B. O. *Theor. Chim. Acta* **1995**, *90*, 87–114.

^{(12) (}a) Duan, X.; Scheiner, S. Chem. Phys. Lett. **1993**, 204, 36. (b) Hass, K. C.; Schneider, W. F.; Estévez, C. M.; Bach R. D. Chem. Phys. Lett. **1996**, 263, 414.

⁽¹³⁾ Bearpark, M. J.; Robb, M. A.; Schlegel, H. B. Chem. Phys. Lett. 1994, 223, 269.