Unexpected Electronic Effects on Benzotriazole UV Absorber Photostability: Mechanistic Implications Beyond Excited State Intramolecular Proton Transfer

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Electron withdrawing groups at the 5-position of benzotriazole ultraviolet absorbers (UVA) surprisingly improve photopermanence despite weakening the intramolecular hydrogen bond believed to be responsible for photostability. These results, encountered in coatings, thermplastics, and solvents, contradict the assumption from the widely accepted view of UVA photostability that a stronger H-bond would generate a more stable UVA. Calculations suggest the involvement of a conical intersection in benzotriazole excited state deactivation and support a significant role for charge transfer. Modifications to the traditional model of UVA photostability are discussed which more fully consider electronic factors and molecular motions other than H-transfer.

INTRODUCTION

Derivatives of 2-(2-hydroxyphenyl)benzotriazole (BZT) are widely used as UV absorbers (UVA) to protect polymers from degradation caused by exposure to sunlight. Such compounds strongly absorb UV radiation without undergoing significant degradation themselves. Despite their high stability, some loss of absorber is observed that over time can limit the effectiveness of BZTs in more demanding applications. While exudation or other physical loss of UVA can occur,[1] it is clear that photodegradation reactions play a significant role in the loss of UVA performance. Furthermore, as the quantum yield for photoloss, φ_{loss}, is typically on the order of 10^{-6} or 10^{-7}, small absolute differences in loss rates between UVAs can have a measurable impact on polymer service life.[2]

The structural feature most associated with benzotriazole stability is the intramolecular hydrogen bond between the benzotriazole ring nitrogen atoms and the phenolic hydroxyl group. The hydrogen bond is involved in an extremely efficient excited state intramolecular proton transfer (ESIPT), followed by rapid internal conversion to the ground state and regeneration of the starting material. The time frame for this process is on the order of 1 picosecond, resulting in extremely short excited state lifetimes.[3] While other compounds also undergo a similar proton transfer, many (such as hydroxyphenylbenzothiazoles and benzoxazoles) are far less stable than BZT derivatives. This difference presumably is due to the much faster rate of internal conversion for BZT. Examination of the internal conversion process has led some authors to suggest a large amplitude torsional component to the radiationless deactivation of BZT,[4,5] Kramer et al.[6] proposed the existence of additional quenching processes based on the temperature dependence of BZT fluorescence quantum yield and decay lifetimes. Estévez et al.[7] described a folding of the molecule via rehybridization of the central nitrogen atom leading to an intersection of the excited state and ground state energy surfaces, i.e., a conical intersection.

Many investigations have described the factors involved in BZT degradation. To a greater or lesser extent, all workers have implicated a form of the UVA in which the intramolecular H-bond has been disrupted, the nonplanar conformer in *Figure* 1. In this form, ESIPT is not believed to occur, the excited state lifetimes are much longer (170 ps in DMSO),[8] and a greater probability exists for destructive

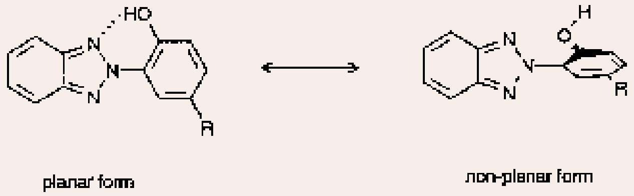

Figure 1—Rotomeric equilibrium between planar and nonplanar BZT UVAs.

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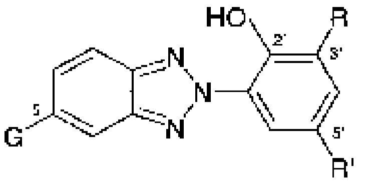
Table 1—Absorption Loss of BZT in Melamine Coatings



$R' = -CH_2CH_2CO_2Y$

Cmpd	R	Y	G	A_0[a]	Abs Loss - 1200 hr
1	H	CH_3	H	2.35	1.40
2	t-Bu	CH_3	H	2.57	0.53
3	cumyl	CH_3	H	2.88	0.34
4	t-Bu	C_8H_{17}	SPh	4.56	1.47
5	t-Bu	C_8H_{17}	H	2.84	0.44
6	t-Bu	C_8H_{17}	SO_2Ph	2.94	0.27

(a) A_0 = initial absorption at long wavelength λ max.

chemistry or intersystem crossing to the triplet. Highly polar, aggressive solvents such as DMSO significantly disrupt the intramolecular hydrogen bond, generating more nonplanar BZT as measured by FTIR, UV absorbance, fluorescence, and ^{1}H NMR.[9] Heller[10] suggested that a large group ortho to the hydroxyl could shield the hydrogen bond from such a disruption, shifting the equilibrium toward the planar form. Consistent with this, Catalán et al.[11] observed the dramatic effect of an ortho t-butyl group on the UV spectra and photopermanence of benzotriazole derivatives in DMSO solution. DeBellis et al.[8] verified this effect in melamine coatings where BZTs substituted by the bulky cumyl group at 3′ (ortho to the hydroxyl) proved more permanent than those substituted by hydrogen and even t-butyl.

A stronger H-bond is also less likely to be disrupted by the environment. Given the importance of preserving the intramolecular hydrogen bond, and the effectiveness of sterically protecting it in intrusive environments, one may conclude that a stronger H-bond would correlate with a more stable BZT.[12] This is shown to be false. Electron donating groups on the benzotriazole ring do increase the basicity at nitrogen and generate a stronger hydrogen bond.[13] However, this does not create a more photostable BZT. Instead, we found that substituting the benzotriazole ring with electron withdrawing groups (EWG) dramatically improves the photostability of BZT UVAs in all environments tested even though this reduces basicity and weakens the H-bond. These results warrant a reevaluation of some generally accepted ideas regarding UVA photostability.

Table 2—Benzotriazole O-H Stretch (IR, cm^{-1})

R	R'	G	Solvent S[a]	 CCl_4
t-Bu	CH_3	OCH_3	2920	
t-Bu	CH_3	CH_3	2930	
t-Bu	CH_3	H	2940	
t-Bu	t-Bu	H	3070	3131
t-Bu	t-Bu	CN		3162
t-Bu	t-Bu	SO_2Ph		3154

(a) Methylcyclohexane / 2-methylbutane, reference 13.

EXPERIMENTAL

BZTs were prepared according to the general procedures of U.S. Patent 5,977,219.

Melamine Coatings

Acrylic melamine clearcoats were prepared from a 6 to 4 mixture of an experimental acrylic polyol and hexamethoxymethyl melamine (Resimene® 747, Solutia), to which was added 0.25% of a flow modifier (Modaflow®, Solutia) and 0.7% dodecylbenzene sulfonic acid (Nacure® 5225, King Industries). UVAs were incorporated typically at 1-3% along with 1% of a hindered amine light stabilizer (Tinuvin® 123, Ciba), concentrations based on wt% of coatings solids. The viscosity was reduced with xylene for spin coating onto quartz discs to give a coating thickness near 50 microns, and cured by heating at 127°C for 30 min. The coated discs were exposed in an Atlas Ci65 Xenon Arc Weatherometer, 0.55 W/m^2 irradiance at 340 nm, using both inner and outer borosilicate Type S filters (Automotive Exterior Cycle SAE J 1960). Loss of UVA was determined by monitoring loss of absorbance at λ max of the longer wavelength band (> 340 nm).

Thermoplastic Films

Polycarbonate (PC) films, 25 microns thick, were cast from room temperature methylene chloride solutions of polycarbonate flake (Lexan® 145, GE Plastics) and between 1 and 3% benzotriazole derivative (wt% based on polycarbonate) using a calibrated drawdown bar. Poly(vinyl chloride) (PVC) films (Geon 27), with similar BZT concentrations, were solvent cast as for PC from solutions in warm tetrahydrafuran (THF). The free standing films were mounted in cardboard holders, secured in metal frames, and exposed in an Atlas Ci65 Xenon arc weatherometer under dry conditions (ASTM G26). Loss of UVA was determined by monitoring loss of absorbance over a smooth 10 nm portion of the UV curve near λ max of the longer wavelength band (> 340 nm).

UV-Vis and Fluorescence Spectra

UV-Vis spectra were determined on a Perkin-Elmer Lambda-2 spectrometer. Fluorescence spectra were measured with a Spex FluoroMax-2 spectrometer, BZT concentrations were adjusted to an optical density of approximately 0.3 at the excitation wavelength of 330 nm.

RESULTS

We have studied BZT photochemistry in a variety of environments in an attempt to better define the subtle effects that influence BZT photostability/degradation. Toward this end, BZTs with various substitutions were incorporated into model acrylic melamine, PVC, and polycarbonate films and exposed to standard Xenon weathering conditions. Similar exposures of the same BZTs in various solvents in Rayonette reactors were also examined. The loss of UVA was measured by the decrease in absorbance at λ max of the longer wavelength band (> 340 nm). For thermoplastic films the data was taken from examination of a smooth 10 nm section of the curve on the red side of the longer wavelength absorbance to reduce complications resulting from the UV absorbance of polymer degradatioin products. The results were analyzed using the method of Iyengar and Schellenberg,[14] which is analogous to Pickett's "infinite absorption" zero order kinetic scheme.[15] Typically, each absorption scan was monitored from 250-450 nm to guard against complications arising from absorption or scatter due to polymer degradation. Gathering the data required running several different exposure series. Because some variations between series can be expected despite standardized conditions, we limit our direct comparisons to compounds within the same series.

Acrylic Melamine Coatings

The first three entries in *Table* 1 represent previously reported results from these laboratories showing the value of sterically shielding the phenolic hydroxyl in acrylic melamine coatings.[8] An ortho-t-butyl substituent reduces absorption loss by a factor of about 2.5, cumyl by a factor of 4. The exact absorption measurements will vary as other substituents are changed, but the general trend remains the same.

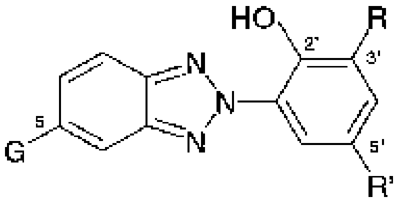
Entries (4), (5), and (6) demonstrate a significant effect of the 5-substituent among otherwise identical compounds. While the rapid loss of sulfide (4) may also reflect additional chemistry of the thioether, the improved photoperm-anence of sulfone (6) is unmistakable.

The stability of compound (6) could be due to some specific quality of the sulfone, or to a general electronic effect. The strength of the H-bond to nitrogen can be deduced from IR spectra by measuring the corresponding decrease in the frequency of the hydroxyl O–H stretch. As shown in *Table* 2, strong EWGs such as 5-sulfonyl or cyano weaken the H-bond, presumably by reducing the basicity of nitrogen. Conversely, the electron donating 5-methoxy derivative has been shown to have a stronger H-bond than similar 5-H BZTs.[13]

It has been suggested that strengthening the H-bond in this way should generate a more photostable BZT.[12b] The data in *Table* 3 clearly show the opposite to be true. The methoxy compound (7) exhibits a surprisingly high loss rate while the electron withdrawing cyano group of compound (11) improves the BZT durability despite, or perhaps because of, the differences in H-bond strength.

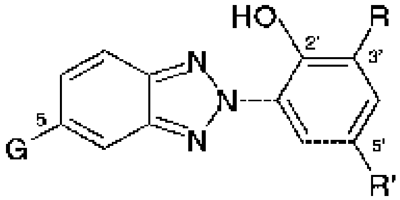
Table 4 compares the effect of different EWGs at the 5-position on the stability of BZTs in melamine coatings. The stronger EWGs, sulfone and CF_3, exert a larger effect than the mildly electron withdrawing

Table 3—BZT Photoloss in Melamine Coatings



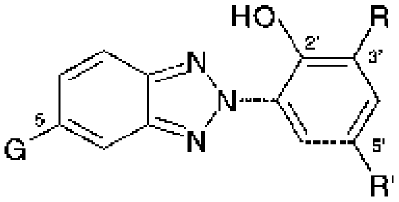
Cmpd	R	R'	G	A_0	Abs Loss	
					1200 hr	2420 hr
7	t-BU	Me	OMe	2.69	1.19	2.00
8	H	cumyl	H	2.92	0.45	1.09
9	t-Oct	t-Oct	H	2.46	0.38	0.74
10	t-Bu	$-(CH_2)_3OH$	H	2.70	0.37	0.72
11	t-Bu	t-Bu	CN	2.75	0.31	0.53

Table 4—Effect of 5-EWG on BZT Photoloss in Melamine Coatings



Cmpd	R	R'	G	A_0	Abs Loss	
					1520 hr	3000 hr
12	cumyl	t-Oct	H	2.09	0.27	0.46
13	t-Bu	t-Bu	SO_2Ph	2.25	0.24	0.46
14	cumyl	t-Oct	Cl	2.39	0.20	0.40
15	cumyl	t-Oct	F	2.00	0.17	0.32
16	cumyl	t-Oct	SO_2Ph	1.99	0.12	0.26
17	cumyl	t-Oct	CF_3	2.32	0.11	0.22

Table 5—BZT Photoloss in Thermoplastic Film

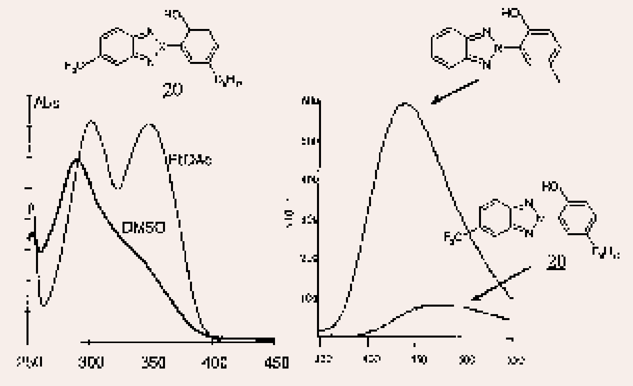


BZT Photoloss in PVC

Cmpd	R	R'	G	A_0	Abs Loss - 1100 hr
18	H	t-Oct	H	1.66	0.14
21	cumyl	cumyl	H	1.14	0.12
21	cumyl	cumyl	H	2.21	0.13
19	cumyl	t-Oct	$SO_2\ C_9H_{19}$	1.15	0.055

BZT Photoloss in PC

Cmpd	R	R'	G	A_0	Abs Loss	
					1200 hr	2000 hr
18	H	t-Oct	H	2.45	0.12	0.20
20	H	t-Oct	CF_3	2.65	0.015	0.02



Absorption spectra of cmpd 20 in EtOAc and DMSO

Emission spectra of cmpd 20 and 5-H BZT in DMSO

Figure 2—Spectra of compound (20) showing the decrease of the longer wavelength absorbance in DMSO vs. ethyl acetate due to the destruction of the intramolecular H–bond and the reduced refluorescence of (20) relative to a similar 5–H substituted BZT.

halogens. Comparing the photoloss of (12) and (13) with (16) and (17) shows that combining a strong EWG, such as sulfone or CF_3 at the 5-position, with the sterically encumbering 3′ cumyl further improves BZT photostability in melamine coatings. The stability of the better performing compounds of this series compare quite favorably with bis-xylyl triazine UV absorbers, for example, in a similar melamine coatings study, (17) exhibited only 85% of the photoloss of a bis-xylyl hydroxyphenyl triazine (0.24 vs 0.29 absorption loss at 3000 hr).

Thermoplastics

Similar compounds were evaluated in solvent cast thermoplastic films. The loss rates in relatively nonpolar PVC are shown in *Table* 5. The first three entries show almost identical photoloss regardless of ortho substitution or starting absorption (within the linear loss rate region, $A_o >$ 1) as reported by Pickett and Moore for poly(methyl methacrylate) (PMMA) films.[15b] While in PVC there is no longer a benefit of sterically shielding the hydroxyl group, the positive effect of the electron withdrawing sulfone substituent is clear.

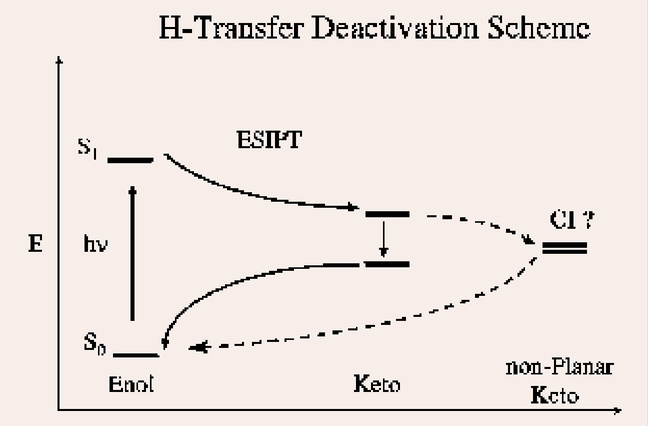


Figure 3—Schematic representation of the ESIPT BZT excited deactivation cycle. Solid arrows represent traditional Förster scheme. Dashed arrows represent the modifications suggested by Estevez, further excited state relaxation through additional geometric distortions and the possibility of internal conversion through a conical intersection (CI).[7]

Results in polycarbonate were even more dramatic (*Table* 5). As in PVC, there was no positive effect from alkyl or cumyl substitution ortho to the hydroxyl, however the 5-trifluoromethyl substituent provided an order of magnitude improvement over an otherwise identically substituted BZT.[16]

DISCUSSION

These results demonstrate the value of a 5-EWG in improving the photostability of BZTs. Contrary to expectations, compounds with weaker H-bonds exhibit improved photostability. The effect is general for polar and nonpoplar environments yet appears to be electronic in nature. Halogen substitutents confer a moderate increase in stability while derivatives with more strongly electron withdrawing substituents, such as sulfone, cyano, and trifluoromethyl, are substantially more stable. Any reduction in photoloss through exudation due to physical factors such as molecular weight, compatibility, or even steric effects is considered negligible given the range of substituents tested. For example, cyano and CF_3 have approximately the same effect as the larger and generally less soluble phenylsulfone, while methoxy and phenyl-mercapto, certainly as sterically encumbering as cyano or chloro, provide less durable derivatives. Extending conjugation of the pi system as with sulfone or cyano fails to explain the results in light of the effect of fluoro and especially CF_3.

The effect of a 5-EWG on the emission spectra of a BZT is as intriguing as the reduction in photoloss. As stated previously, BZTs are believed to exist in open and closed conformers, the position of the equilibrium being determined by environmental factors. Little chemistry is expected from the closed form as it relaxes to starting material in about 1 ps. The open form, however, fluoresces strongly at approximately 400 nm, phosphoresces under appropriate conditions, and has been implicated in the photogeneration of BZT phenolate anion.[9] Substitution ortho to the hydroxyl has been shown to decrease or eliminate these phenomena, especially in intrusive media such as DMSO and melamine coatings.

A weaker intramolecular H-bond should lead to a greater amount of the open form, yet the BZTs substituted with strong 5-EWGs display less emission than their 5-H analogues. It seems, therefore, that the substituents have an impact on the excited state dynamics. Most significantly, compound (20), which is unsubstituted at 3′, exhibits almost no fluorescence or phosphorescence even in DMSO solution despite clear evidence that the intramolecular H-bond is significantly disrupted (*Figure* 2).[17] Photolysis of the DMSO solutions (Rayonette reactor, 12 350 nm bulbs, 4 300 nm bulbs) demonstrated that the reduction in fluorescence is not due to competing photochemical reactions as (20) is again the more stable compound.

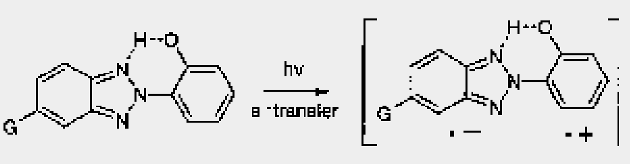
The presence of a 5-EWG then is shown to improve the photostability of BZTs either in situations where the intramolecular H–bond is largely intact, as with cumyl substituted (19) in PVC, or where it is largely disrupted, as with (20) in DMSO. The question now arises whether these BZTs are more stable because the normal deactivation processes are more efficient, or if other deactivation pathways are operating that are not normally considered. For example, the enhanced photostability of (19) in PVC would be consistent with greater efficiency in the generally accepted ESIPT process; however, the UV absorbance and fluorescence data from (20) in DMSO suggest an increase in the rate of internal conversion of the open conformer. Also, is the fluorescence of (20) in DMSO reduced by an improvement in the efficiency of a poorly functioning internal conversion mechanism already available to the unsubstituted derivative, or does an otherwise unattainable pathway become available upon substitution?

Internal Conversion

Accommodating these results may require refinements to the traditional model of UVA photostability referenced herein. One possible rationalization would be that upon returning to the ground state, back transfer of hydrogen would be more favored for the less basic derivatives (weaker N–H bond). However, the decrease in emissions of the 5-EWG substituted compounds argues against strictly a ground state phenomena. Also back transfer is already rapid for unsubstituted BZTs, on the order of 500 femtoseconds, and any increase in this rate would have a negligible effect on permanence.

Despite the deceptive simplicity of the intramolecular Förster model, calculations and spectral measurements suggest that excited state deactivation is more complex than H-transfer/back transfer alone. The solid arrows in *Figure* 3 schematically represent the Förster ESIPT cycle; excitation to excited state enol, proton transfer to excited keto, relaxation to ground state keto, and return to starting enol. A weak, temperature dependent BZT emission near 650 nm has been assigned to fluorescence of the keto form and offered as proof of the process. The energy gap represented by this fluorescence is still large, on the order of 2 eV (45 - 50 kcal/mol), and not wholly consistent with the rapid rate of deactivation observed. A closer look at the internal conversion process is warranted.

The possible involvement of conical intersections in the dynamics of BZT internal conversion may help explain some of the results. As the gap between the excited state and ground state energy surface approaches zero, a crossing of the two surfaces can occur. A molecule that readily attains the appropriate geometry for such a crossing will experience extremely rapid internal conversion with a probability for returning to the ground state approaching unity. The overall product distribution, i.e., return to starting material or progression to products, is determined by the energy profile and geometry at this crossing.[18-20]



Scheme 1

Calculations by Estevez et al.[7] revealed that the planar keto conformer of a BZT is not the lowest energy configuration on the excited state energy surface. The BZT can relax further by rehybridizing the substituted, central, ring nitrogen producing a bend or fold in the triazole ring. This relaxation not only lowers the energy of the excited state, but also raises the energy of the ground state thus reducing the S_1/S_0 energy gap. The reduction permits a more efficient, therefore more rapid, internal conversion, (depicted in *Figure* 3 by the dashed arrows). Further minor distortions could reduce the energy gap to zero, producing a conical intersection. The red fluorescence, usually only observed at very low temperature and assigned to the BZT keto, could arise from molecules trapped in a shallow well in the vicinity of the conical intersection.

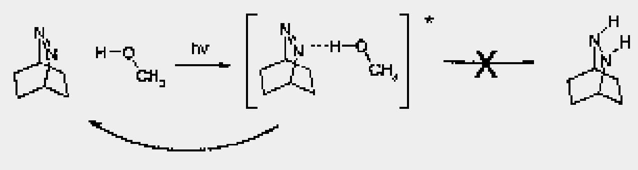
Thus, by allowing for the involvement of another molecular motion in the deactivation process, a geometry approaching a conical intersection can be attained. The calculations suggest a two step process, H-transfer followed by ring folding. However it is possible that altering a compound with select substituents could change the shape of the energy surfaces, and thereby the locus of the conical intersection, to favor a single step process.

Charge transfer also emerged from the calculations as an important factor favoring nitrogen rehybridization. Catalan et al.[21] had earlier ascribed the difference between BZT and benzoxazole photostability to the role of charge transfer in BZT internal conversion. The possibility then arises that the EWG at the 5-position operates partly by facilitating charge transfer from the phenol to the benzotriazole portion of the molecule. By facilitating charge transfer (*Scheme* 1), these substituents by inference would facilitate other molecular processes involved in attaining the conical intersection geometry.

Table 6—Calculated S_1/S_0 Energy Gaps of 5-Substituted o-Hydroxyphenyl Benzotriazoles (kcal/mol)

		C_s Symmetric Keto Form		Keto Rotamer	
5-Substitution	FC Geometry	S_1/S_0 Energy Gap	Stabilization of S_1	S_1/S_0 Energy Gap	Stabilization of S_1
–H	80.6	51.7	7.1	7.9	32.0
$-OCH_3$	76.8	51.6	3.6	8.4	27.6
$-CF_3$	79.7	52.6	4.6	3.9	32.8

State energies were calculated using the INDO/S method with a singles excitation CI consisting of 20 occupied into 20 unoccupied orbitals. PM3 geometries were used for all structures. The C_s symmetric keto geometry was obtained from a PM3 optimization within C_s symmetry. The keto rotamer geometry was obtained by a 90° rotation of the single bond between the aromatic systems, starting from the C_s symmetric keto geometry.



Scheme 2

Our own calculations (see *Table* 6) have shown the impact of electronically diverse substitutents, i.e., hydrogen, electron rich methoxy, and electron poor CF_3, on BZT potential energies. Little effect of substitution is observed on the S_1/S_0 energy gaps of the planar keto form; 51.7, 51.6, and 52.6 kcal/mol, respectively. However, as the molecule is allowed to rotate about the central BZT nitrogen–phenol bond, the energy gap narrows dramatically for all three cases, but the resulting gap of 3.9 kcal/mol for the CF_3 derivative is only half that of the other two cases. These values are consistent with the improved photostability the 5-EWG BZT, as a smaller difference in potential energies should provide for more rapid internal conversion.

Also, from these calculations one sees only a small effect from H-transfer on the energy levels of the BZT excited state. As shown in *Table* 6, the narrowing of the gap between S_0 and S_1 for the keto form is due largely to raising the ground state energy as the excited state potential energy is reduced by only 3.6-7.1 kcal/mol. Consistent with compounds known to form twisted intramolecular charge transfer states (TICTs),[22] a larger decrease in S_1 energy, ~ 30 kcal/mol, is obtained through decoupling of the aromatic subunits by rotation about the N–phenol bond, accompanied by electron transfer from phenol to triazole. This raises questions about the exact role of H-transfer in the BZT internal conversion. While its impact on raising ground state energy is vital in reducing the S_1/S_0 energy gap, its role on the excited state surface appears both subtle and complex. Is the small decrease in potential energy of S_1 enough to drive deactivation or is H-transfer a prelude to the more important charge transfer process?

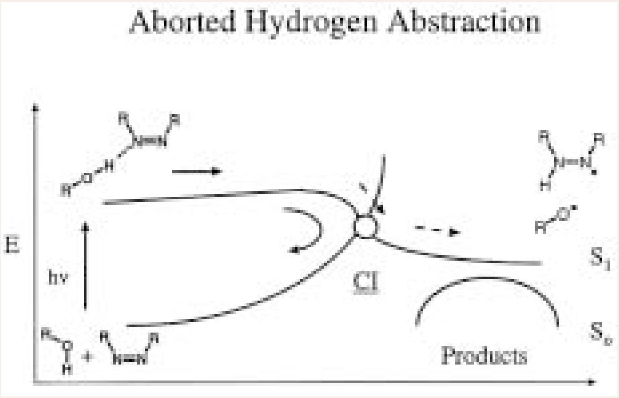


Figure 4—Schematic representation of the potential energy surface of azo excited state deactivation by alcohols.[23] Solid arrows depict deactivation and return to starting materials through a conical intersection prior to formation of radical intermediates.

Either by ring folding via nitrogen atom rehybridization, rotation about the N–phenol bond or some other process, calculations predict a certain amount of nonplanarity along the path of BZT excited state deactivation. The electronic nature of the 5-EWG substituents may improve BZT photopermanence by providing for both greater charge transfer efficiency and more facile geometric distortions.

However, we are still presented with a dilemma. The above discussion refers to the process associated with relaxation of the initially closed, H-bond intact conformer. However, the data from DMSO solution show that even when the H-bond is disrupted, internal conversion is still facilitated by the presence of the 5-EWG.

Aborted Hydrogen Abstraction

To more fully understand the dynamics of BZT internal conversion we may need to consider a model other than the conventional Förster intramolecular H-transfer. Recently, the concept of an "aborted hydrogen abstraction" has been described in the excited state quenching of azo compounds by alcohols.[23] For example, photochemical reduction of 2,3-diazabicyclo[2.2.2]oct-2-ene does not occur in the presence of methanol although interaction with the alcohol quenches the fluorescence of the diazo excited state (*Scheme* 2).

In this intermolecular process, reaction is short circuited through a conical intersection after only partial hydrogen transfer to the azo (see *Figure* 4); that is, the excited state energy surface of the bimolecular complex intersects the ground state surface along the pathway of H-transfer, but at a coordinate prior to full transfer. The bimolecular complex returns to the ground state and regenerates starting materials.

A similar intramolecular version of this process would be an attractive explanation of BZT internal conversion. Full H-transfer may not be required in the deactivation cycle. Such speculation is consistent with the extremely rapid rate of the ESIPT process. The weak red fluorescence assigned to the proton transferred species could then represent a small portion of molecules that either bypass this conical intersection, diverge from this pathway at some point, or even progress along an alternate path on the S1 energy surface. The exact location of this crossing and whether it is attained via a multiple step or single step process could be greatly affected by the substitution described here.

Furthermore, while intramolecular H-transfer would be most efficient and less likely to generate products, this model allows one to speculate that under appropriate circumstances the open form of the BZT could undergo efficient, nondestructive internal conversion through a partial, bimolecular H-transfer. The lack of fluorescence from compound (20) in DMSO could be due to an additional bimolecular deactivation process made more efficient through the presence of the 5-EWG, i.e., a second conical intersection. Conversely, perturbations to the energy surface due to BZT substituents may allow the open, intermolecularly H-bond conformer the geometric freedom to access to the same intersection as the closed form.

In revising *Figure* 3, the added dotted line and circle of *Figure* 5 introduce two additional possibilities for internal conversion into the deactivation scheme of BZTs. One

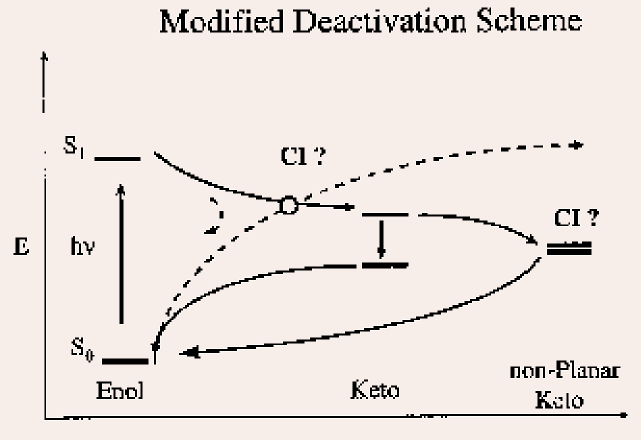


Figure 5—BZT deactivation scheme modified to include the presence of one or more conical intersections. CI represented by the circle and dashed line suggests the possibility that internal conversion can occur without full portion transfer through either a modified ESIPT process, an intermolecular H–transfer process, or a process independent of any H–transfer.

possibility is that a second conical intersection becomes available to suitably substituted BZTs. Another is that the actual internal conversion process occurs through a conical intersection whose locus can be affected by electronic substitution patterns and can occur at coordinates requiring less geometric distortion than full hydrogen transfer.

The preceding discussion seeks to expand the possibilities of the existing model and serves mainly to identify areas requiring further study in light of the surprising electronic effects encountered. Implicating the possibility one or even more than one conical intersection between excited and ground state energy surfaces allows one to consider relaxation pathways in addition to the traditional, two-dimensional ESIPT process. A weaker H-bond brought about by the 5-EWG may facilitate the molecular motions required for attaining the conical intersection geometry. Greater charge transfer efficiency may further favor geometric distortions responsible for radiationless decay. Deactivation of the open form is also enhanced by the 5-EWG which may require consideration of a bimolecular process. Despite years of study the exact nature of BZT internal conversion remains unclear and significant work remains before the process can be fully understood.

CONCLUSION

Substitution of benzotriazole UVAs by electron withdrawing groups at the 5-position dramatically improves the photopermanence of the resulting derivatives despite weakening the intramolecular hydrogen bond deemed responsible for photostability. This electronic effect is general and improves the stability of BZTs in a variety of environments. These results are in apparent contradiction to aspects of the current understanding of UVA photostability and require a more detailed examination of their excited state deactivation. Although still important to the photostability of BZTs, questions arise about the exact role of H-transfer in this process. The possible role of conical intersections in the internal conversion of BZTs and the electronic effect of substitution on charge transfer and geometric distortions may offer some insight into the dynamics of UVA photostability.

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