

Intra- and intermolecular H-bonding of benzotriazole UV stabilizers evidenced using 1D nuclear Overhauser effect experiments

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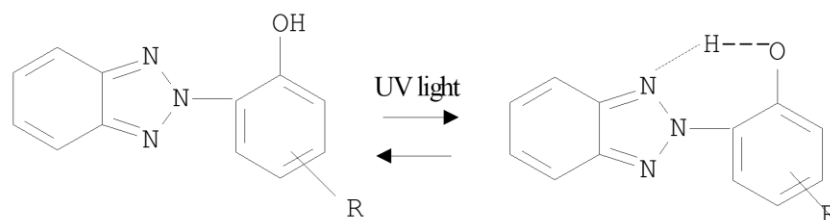
ABSTRACT

The UV absorber protection mechanism of 2-hydroxyphenylbenzotriazoles is based upon energy dissipation *via* an excited state proton transfer from the phenolic OH group to the triazole nitrogen(s). Using ¹H-NMR NOE experiments we have established that 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole (**UVA1**) exists in chloroform as an intramolecularly H-bonded form whereas in DMSO this bond is disrupted by the formation of intermolecular H-bonding to the solvent. Conversely, for compounds 2-(2'-hydroxy-3',5'-di(1,1-dimethyl propane))-benzotriazole (**UVA2**), and 3'-methylene-hydantoin-2-(2'-hydroxy-5'-methylphenyl)-benzotriazole (**UVA3**) having bulky substituents ortho to the phenolic OH group ¹H-NMR NOE experiments indicate that upon changing solvent from DMSO to chloroform the strength of the intramolecular H-bond is not appreciably affected. The implication of the H-bond strength upon the UV stabilizing effectiveness is discussed.

Keywords: benzotriazole, UV stabilizer, nuclear Overhauser effect NOE, spin diffusion

Introduction

The plastics industry represents a huge portion of the greater petrochemicals industry, making various products that are often structural, yet exposed to severe elements of nature, such as sunlight and heat. In the field of polymer chemistry photo-oxidation is the degradation of a polymer surface due to the action of light and oxygen (Zweifel, 1996). Photodegradation is the most important process in the weathering of plastics in the field (Feldman, 2002). Photo-oxidation causes polymer chain scission, resulting in the polymer becoming more brittle, and in discoloration and crack formation. This leads to mechanical failure and to the formation of microplastics, which is currently a key global concern. UV stabilizers prevent the degradation that plastics suffer under the effects of sunlight, UV rays, heat and reactions with oxygen. Therefore, UV stabilizers are essential in the prevention of photo-induced decomposition of plastics that are continuously subjected to sunlight or other sources of UV irradiation. One class of compounds that have been shown to be particularly effective light stabilizers are the substituted benzotriazoles (Bocian, 1983; Catalan, 1990, 1992, 1997; Durr, 2006; Flom, 1983; Huston, 1982; McGarry, 1997; Werner, 1979; Woessner, 1984, 1985,). These compounds are sold under the generic tradename Tinuvin[™]. Their mechanism of UV protection comes from the fact that when they absorb energetic UV photons which would normally destroy a polymer over a period of prolonged irradiation, they dissipate the excess of energy *via* a mechanism involving excited state intramolecular proton transfer (ESIPT) (Bocian, 1983; Durr, 2006; Flom, 1983; Huston, 1982; 3, McGarry, 1997)



Scheme 1. ESIPT reaction of benzotriazole

In the process of ESIPT photoexcited molecules relax their excess energy through tautomerization by proton transfer. Some molecules have different minimum-energy tautomers in their ground and excited electronic states. This means that in an excited electronic state for molecules like Tinuvin[™] the structure of the minimum-energy tautomer has a proton-transferred geometry between neighboring atoms and proton transfer in the excited state spontaneously occurs rapidly after

photoexcitation. The tautomerization is similar to the well-known keto-enol tautomerism (Benassi, 1996).

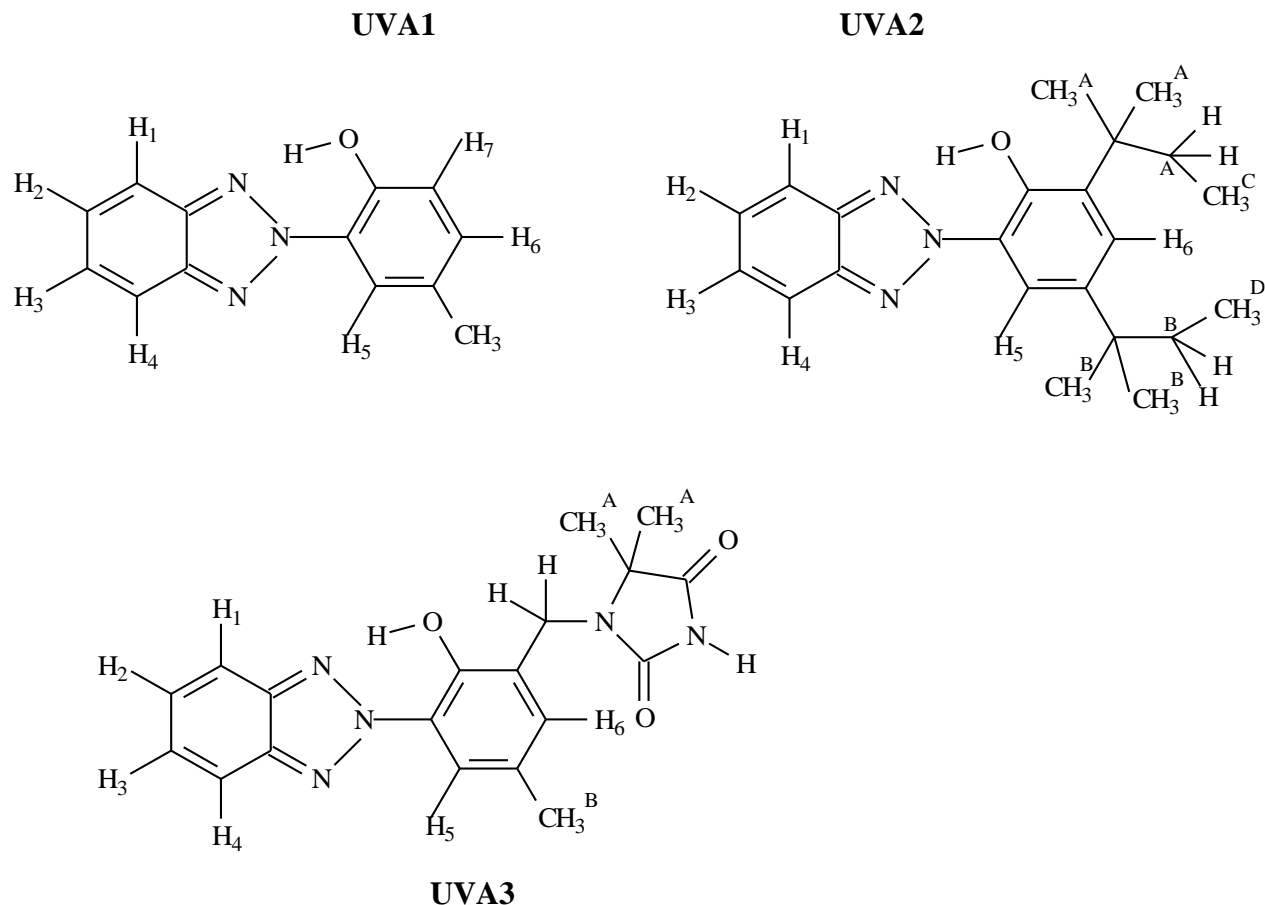
ESIPT is often implied to be occurring when anomalous red emission is observed with a very large Stokes shift from the maximum of the absorption spectrum. This is because the lower energy of the proton-transferred tautomer adds to the usual Stokes shift. Based on the characteristic that molecules usually have extraordinarily larger Stokes shift when ESIPT occurs, various applications have been developed using red-shifted fluorescence (Sheng, 2019). However, in the current work the application of interest is UV stabilization of plastics.

The effectiveness of this proton transfer mechanism depends upon the presence of a hydrogen bond between the phenyl hydrogen and the non-bridging nitrogen atoms on the benzotriazole ring (Catalan, 1992; McGarry, 1997). McGarry et al. (1997) have convincingly demonstrated that in DMSO competitive disruption of this bond allows photoinduced proton abstraction by the solvent leading to irreversible photochemistry and a reduction in the working lifetime of the benzotriazole. It has long been proposed that some equilibrium exists between UVA1 in an intermolecular hydrogen bonded form and in an intramolecular hydrogen bonded form (Durr, 2006). Here, we present ¹NMR and NOE data which support this hypothesis and further derive estimates of internuclear distance ratios between the phenyl proton and its closest neighbors in DMSO and chloroform. The effect of a bulky group ortho to the phenyl OH-group is also investigated.

Experimental

Materials

2-(2'-hydroxy-5'-methylphenyl)-benzotriazole (UVA1) 2-(2'-hydroxy-3',5'-di(1,1-dimethylpropane))-benzotriazole (UVA2) and 3'-methylene-hydantoin-2-(2'-hydroxy-5'-methylphenyl)-benzotriazole (UVA3) (Scheme 2) were supplied by Great Lakes Chemical Italia and used as received. Approximately 10 mg of each was respectively dissolved in non-polar, poorly H-bonding chloroform-d 99.96% atom % D, stored over silver, Merck,) and polar, H-bonding DMSO-d (99.96% atom % D, Aldrich) using sonication.



Scheme 2. Benzotriazoles used in the investigation.

Instrumentation

^1H NMR and two dimensional ^1H - ^1H -NOESY

^1H NMR and two dimensional ^1H - ^1H -NOESY spectroscopic studies were done on a Varian VXR 400 spectrometer in phase sensitive mode using the hypercomplex method to achieve quadrature in F1. The data were collected with a slit width of 4081.6 Hz in both dimensions with 2K data points in the F2 domain and 100 increments in the F1 domain. An optimized 2s mixing time was used. ^1H -TOE (truncated or driven NOE (Saunders, 1988)), ^1H -NOE, ^1H -NMR and T1 inversion recovery ^1H -NMR experiments were done on a Bruker AF 200NR 200 MHz spectrometer in the deuterated solvents described in the materials section.

Truncated NOE

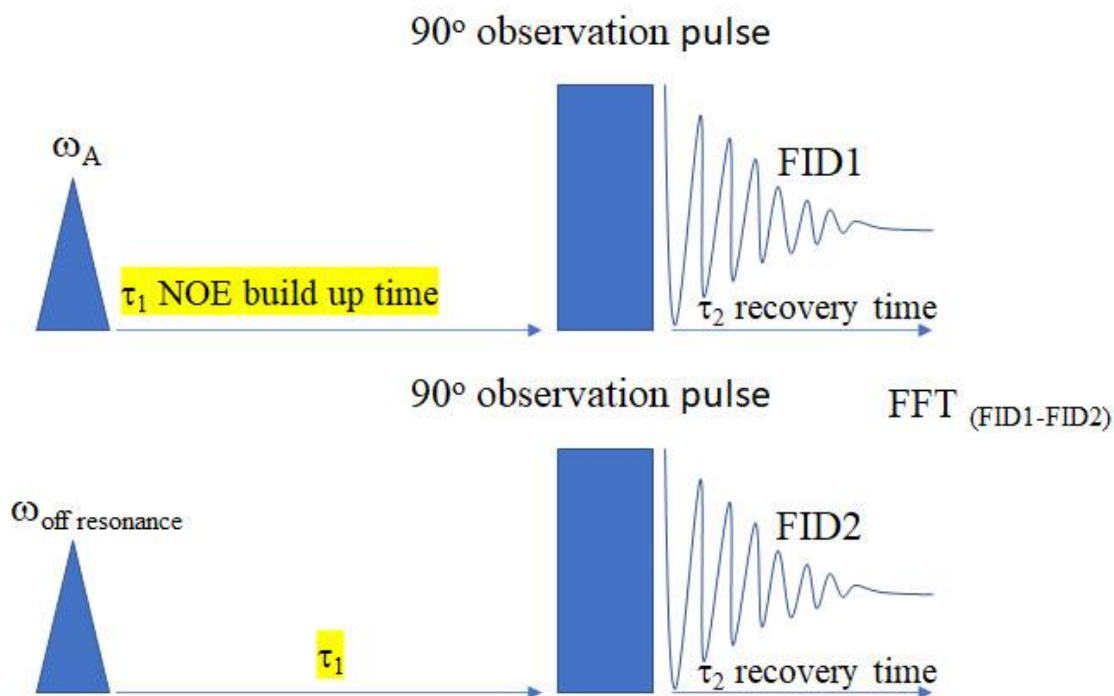


Figure 1 The pulse sequence for the truncated NOE experiment

The pulse sequence for the truncated NOE experiment is shown in Figure 1 and summarized below.

(ω_A) - delay τ_1 - 90° observation pulse - recovery time τ_2

$\tau_1(\omega_{\text{off-resonance}})$ - delay τ_1 - 90° observation pulse - recovery time τ_2)_n

The experiment starts with a selective low power pulse applied to resonance of interest, Spin A. This low power pulse is set to a power and duration that is insufficient to fully saturate Spin A. An observation pulse then follows, after a waiting time, τ_1 during which the NOEs are built up. A reference spectrum with an off resonance applied frequency without NOE is recorded after a waiting period τ_2 during which the spin system is allowed to recover. This is done to counter any shifts induced by the applied field ω . The on-and off resonance free inductive decays are then subtracted, one from the other to determine the NOE at each of the variable mixing times τ_1 . The process is repeated n-times for acquiring sufficient signal to noise ratio, for a range of τ_1 values.

T₁ (spin-lattice) inversion relaxation.

Inversion relaxation or recovery experiments (Figure 2) monitor the longitudinal relaxation (parallel to the external B₀ field) of magnetized nuclei following inversion along the z-axis using a 180° RF pulse. The degree of longitudinal relaxation is monitored as a function of time using a second 90° pulse to rotate any z-axis magnetization into the xy-plane where its intensity can be monitored by the NMRs detector coils. The z-axis magnetization decays from a maximum negative (fully inverted) value through zero (null) magnetization and back to a maximum positive (fully recovered) value. The time when zero magnetization is observed is referred to as the null time (Neuhaus, 1996). Long null times correspond to systems with long T₁s caused by less efficient longitudinal relaxation. The time dependence of the inversion recovery is obtained using a variable delay between the 180° pulse and the 90° pulse.

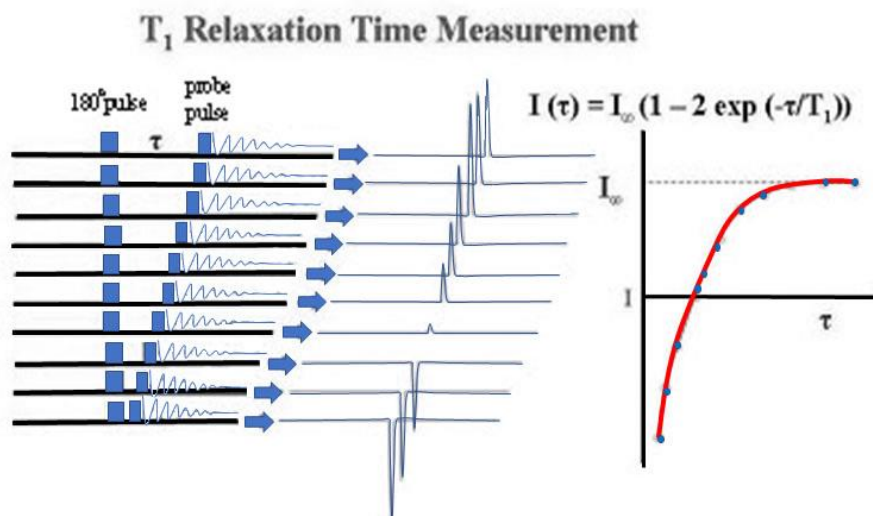


Figure 2. The T₁ recovery experiment

Results and Discussion

¹H-NMR assignments were assisted with one dimensional ¹H-NOE experiments and two dimensional ¹H-¹H-NOESY experiments.

UVA1: DMSO-*d*₆ (δ, ppm): OH 10.35, H1 and H4 8.0, H5 7.66, H2 and H3 7.5, H6 7.22, H7 7.06, CH₃ 2.3

CDCl₃ (δ, ppm): OH 11.11, H1 and H4 7.9, H5 8.16, H2 and H3 7.45, H6 7.13, H7 7.06, CH₃ 2.39

UVA2: DMSO-*d*₆ (δ, ppm) : OH 11.24, H1 and H4 8.10, H5 8.0, H2 and H3 7.58, H6 7.28, CH₂^A 1.94, CH₂^B 1.65, CH₃^A 1.42, CH₃^B 1.3 CH₃^{C/D} 0.65.

CDCl₃ (δ, ppm): OH 11.74, H5 8.22, H1 and H4 7.93, H2 and H3 7.46, H6 7.23, CH₂^A 1.99, CH₂^B 1.69, CH₃^A 1.45, CH₃^B 1.35 CH₃^{C/D} 0.70.

UVA3: DMSO-*d*₆ (δ, ppm) : NH 11.0, OH 10.84, H1 and H4 8.07, H5 7.87, H2 and H3 7.58, H6 7.26, CH₂ 4.53, CH₃^B 2.34, CH₃^A 1.28.

CDCl₃ (δ, ppm): OH 11.61, NH 8.59, H5 8.16, H1 and H4 7.93, H2 and H3 7.48, H6 7.30, CH₂ 4.72, CH₃^B 2.38, CH₃^A 1.38.

Table 1. Null times in the inversion recovery of **UVA1**

Solvent	OH	H5	H1, H4	H2, H3	H6	H7	CH ₃
DMSO- <i>d</i> ₆	1	1.5	1.5	1	1	1	0.5
CDCl ₃	3.25	2.5	2	1.5	2	2	1.25

Table 2. Null times in the inversion recovery of **UVA3**

Solvent	OH	NH	H5	H1, H4	H2, H3	H6	CH ₂	CH ₃ ^A	CH ₃ ^B
DMSO- <i>d</i> ₆	1.25	0.5	1	1	0.63	0.5	0.15	0.18	0.3
CDCl ₃	1.75	0.6	1.5	1.25	0.9	1	0.25	0.25	0.5

Table 3. Null times in the inversion recovery of **UVA2**

Solvent	OH	H5	H1, H4	H2, H3	H6	CH ₃ ^A	CH ₃ ^B	CH ₃ ^{C/D}	CH ₂ ^A	CH ₂ ^B
DMSO- <i>d</i> ₆	1.5	0.6	1	0.7	0.2	0.14	0.18	0.4	0.13	0.15
CDCl ₃	2	1.25	1.5	1.3	0.5	0.35	0.4	0.7	0.4	0.4

The null times for **UVA1**, **UVA2** and **UVA3** from inversion recovery experiments are given in Tables 1-3. Longitudinal, or spin-lattice relaxation occurs due to loss of magnetism (against the B₀ field) *via* transfer of thermal energy to the lattice *via* (magnetic) dipole-dipole interactions. These dipole-dipole interactions occur due to fluctuations in the local magnetic field of a proton caused by the motions of neighboring protons or electrons. The energy transfer is optimal when the relative rate of motion of the dipoles matches the Larmor frequency ν_0 (the precession rate of the

magnetism in the B_0 field). However, generally Figure 3 shows how T_1 will change with parameters such as viscosity and molecular size for small molecules at moderate viscosity as in the present case. The null times of all protons were always shorter in DMSO- d_6 than in deuterated chloroform for all three compounds. This is expected because T_1 is inversely proportional to correlation time (τ_c) for small molecules at relatively low field strength and moderate viscosity. τ_c is the time that it takes for a particle to rotate by 1 radian and thus τ_c is obviously slower with higher solvent viscosity (Neuhaus 1996). Even in DMSO- d_6 τ_c should be ps-timescale.

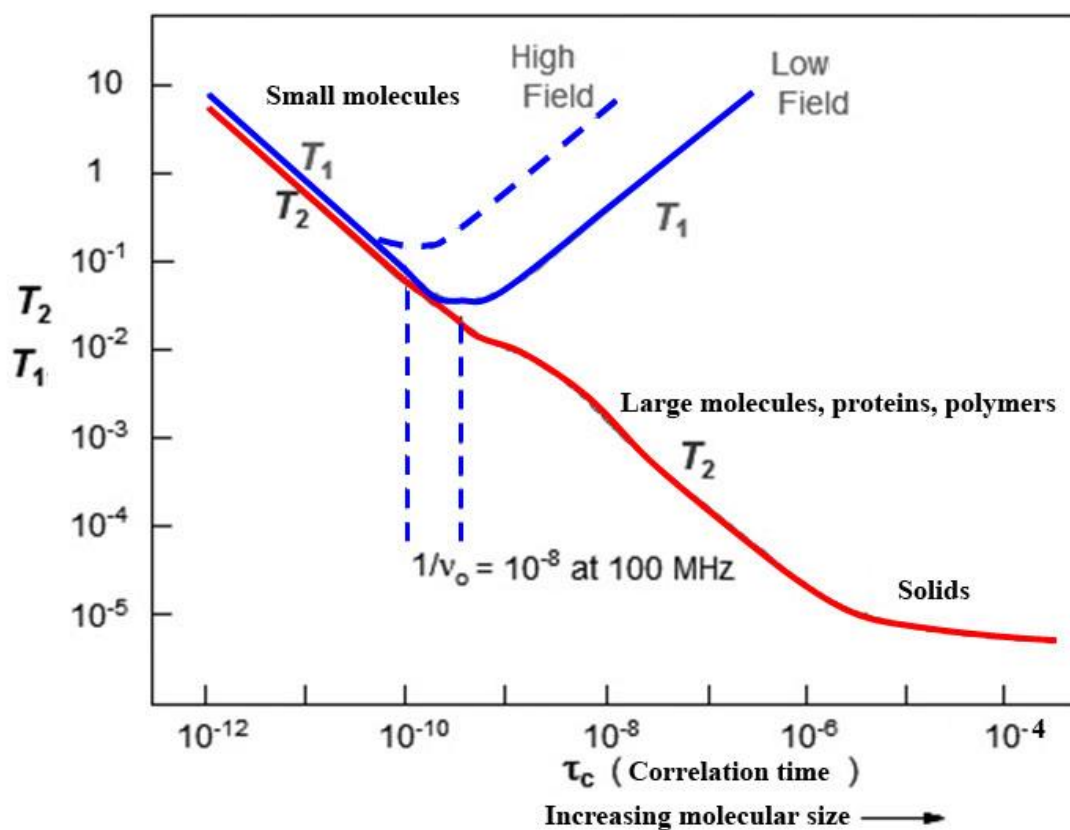


Figure 3. T_1 and T_2 with τ_c (molecular size and viscosity) (adapted from N. Bloembergen, E.M. Purcell, R.V. Pound "Relaxation Effects in Nuclear Magnetic Resonance Absorption" Physical Review 1948, 73, 679-746)

The protons bonded to sp^3 carbons (CH_n) on all three compounds relax as expected with groups having free motion nearby neighboring magnetic dipoles (protons) relaxing faster than those with less free motion and fewer dipolar neighbours. Protons bonded to sp^2 carbons relaxed more slowly (Neuhaus, 1996).

$$\tau_c = 4\pi\eta r^3/3kT \quad (1)$$

where η is the viscosity, r is the effective hydrodynamic radius, and kT are Boltzmann's constant and temperature.

It is interesting to note the null times of the phenyl protons of the three compounds studied in deuterated chloroform and DMSO- d_6 . From Tables 1-3 it is apparent that the solvent dependence of the T1 recovery of the phenyl proton of **UVA1** is relatively higher than the solvent dependence of this proton's recovery in the other two compounds. This suggests that in **UVA2** and **UVA3** the mobility of the phenyl protons is more restricted and/or the proton is always directed into H-bonding with the nitrogen atoms on the triazole ring irrespective of solvent. This is consistent with the concept that the bulky substituents on these compounds push the phenyl proton into an H-bonding configuration even in solvents like DMSO.

It is likely that, for **UVA1**, the phenyl proton is more isolated from its nearest neighbours in deuterated chloroform than it is in DMSO- d_6 due to the presence of an intramolecular H-bond in deuterated chloroform between the phenyl hydrogen and the non-bridging nitrogen atoms on the benzotriazole ring. In deuterated chloroform this bond holds the phenyl proton away from its nearest neighbours making intramolecular longitudinal relaxation less efficient. This bond is disrupted in DMSO- d_6 and the phenyl proton can get closer to H7 and longitudinally relax more quickly.

¹H-TOE

The TOE experiment monitors the build-up of the NOE as a function of time. From such experiments the initial build-up rate of the NOE can be estimated, and this value of initial rate can be used to estimate relative internuclear distances. For the initial NOE build up rate the following relationship is used (Neuhaus, 1996):

$$\sigma_{IS,t} = f_I(S) \text{ at time } t. \quad (2)$$

Where σ_{IS} is the initial cross relaxation rate of spins I and S, $f_I(S)$ is the fractional enhancement of S upon saturating I and t is the NOE build-up time.

$$\sigma_{IS} = \zeta r_{IS}^{-6} \quad (3)$$

Where ζ is a variable dependent upon the correlation time and r_{IS} is the internuclear distance between spins I and S. When comparing distances, by using a reference distance, the ratios of cross relaxation rates can be used to estimate relative distances. In many cases differences in τ_c can be ignored with little error. Values of σ_{IS} are obtained from the initial slope of the NOE build-up curve.

The NOE build-up curves shown in Figure 4 have been obtained for the H1, H4 protons and the H7 proton for **UVA1** and H1, H4 and the CH₂ (methylene bridge) protons for **UVA3** in DMSO-*d*₆ and in deuterated chloroform upon irradiation of the phenyl proton.

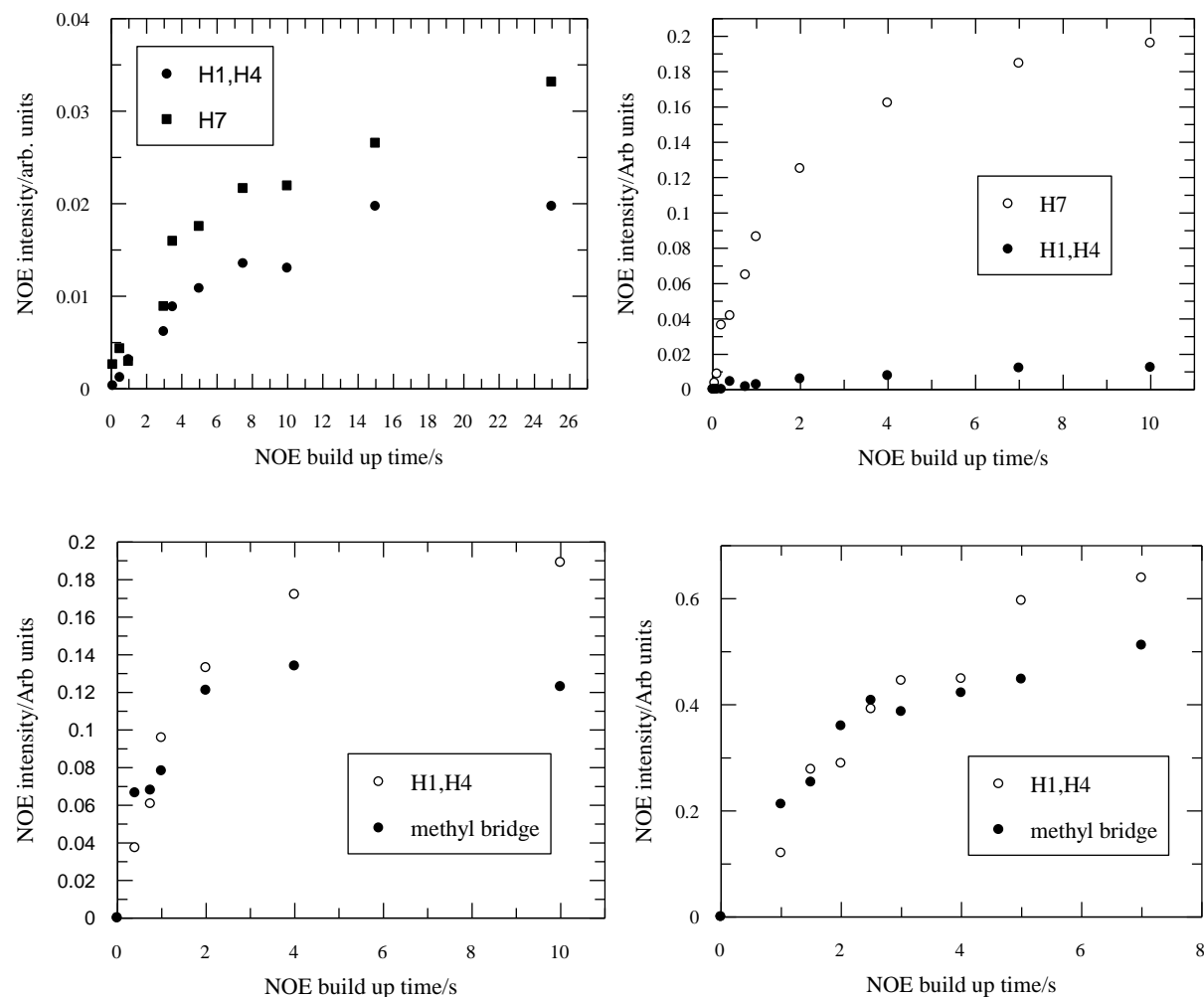


Figure 4. **Top left**, NOE build-up curves for H7, H1 and H4 on **UVA1** in deuterated chloroform. **Top right**, NOE build-up curve for H7, H1 and H4 on **UVA1** in DMSO-*d*₆. **Bottom left**, NOE build-up curve for H1, H4 and the methylene bridge protons of **UVA3** in deuterated chloroform, **Bottom right**, NOE build-up curve for H1, H4 and the methylene bridge protons of **UVA3** in DMSO-*d*₆.

In these curves the absolute NOE intensity is plotted and not the fractional enhancement. From these NOE build-up curves it is immediately apparent that, for **UVA1** the phenolic OH group proton must be closer to H7 than it is to H1 and H4 in both DMSO-*d*₆ and deuterated chloroform. However, in DMSO-*d*₆ the phenolic OH group proton must be positioned relatively much closer to H7 than it is in deuterated chloroform. This fully supports the view that any intramolecular H-bonding that occurs in deuterated chloroform is disrupted in DMSO-*d*₆ and the phenyl OH-group proton can swing out of plane and towards H7.

Quantification of this statement using the initial rate of NOE build-up suggests that in deuterated chloroform the ratio $r_{(H7-OH)}:r_{(OH-H1,H4)}$ is 0.89, whereas in DMSO-*d*₆ this ratio is reduced to 0.56. Note that H1 and H4 are in fact equivalent upon the 200 MHz NMR time scale due to rotation about the bridging C-N bond; however, only one of these protons at a time will be spatially close to the phenyl proton and receive an NOE. Also note that, since a simple comparison is being made between build-up times for different spins on the same molecular sample, under exactly the same experimental conditions, this method is internally referenced.

Similar build-up curves obtained for **UVA3** demonstrate that the relative NOE build up rates for this compound in DMSO-*d*₆ and deuterated chloroform are very similar and, therefore, the internuclear distance are, also more similar in these two solvents. This result indicates that the 3'-methylene-hydantoinyl group forces the phenyl proton into a position suitable for intramolecular H-bond formation even in strongly H-bonding media.

¹H-¹H-NOESY

Using ¹H-NOESY on **UVA2** it was observed that the cross peak intensity for the OH proton and H1, H4 and the ortho iso-butyl protons is relatively unchanged upon changing solvent from deuterated chloroform to DMSO-*d*₆. This again supports the view that substitution with a bulky group ortho to the phenolic OH group encourages intramolecular H-bonding even in competition

with strongly H-bonding solvents. However, to be clear, the more appropriate methodology for accurately evaluating relative internuclear distances is the 1-dimensional truncated NOE experiment, rather than, often more popular, ¹H-NOESY. This is because the entire sequence of the ¹H-NOESY experiment takes so long that usually only a single mixing time τ_1 is used, which for small molecules is usually between 1-3 s. However, in the 1D version it is possible to vary τ_1 over a wide range of 1s to 10s of seconds in the same total accumulation time as for a single ¹H-NOESY experiment with a single mixing time τ_1 . For structural determinations, the 2D ¹H-NOESY is unrivalled, but for determination of relative internuclear distances the 1D NOE experiment has many advantages.

Conclusion

The present work provides firm evidence that for **UVA1** in non-H-bonding solvents there is an intramolecular H-bond between the phenolic OH-group and the non-bridging nitrogen atoms on the benzotriazole ring. This bond is disrupted by hydrogen bonding solvents due to competitive intermolecular H-bonding. In compounds such as the **UVA3** the presence of the bulky group ortho to the phenolic OH-group promotes the intramolecular H-bond even in strongly H-bonding solvents such as DMSO. Since the geometry of the Frank-Condon excited state is the same as the ground state, this enhanced intramolecular H-bonding should increase the efficiency of excited state intramolecular proton transfer relative to intermolecular proton transfer to groups in hydrogen bonding dispersive media which can lead to irreversible photochemistry. This in turn should give compounds such as **UVA3** a greater stability and longer working lifetime compared to **UVA1**.

Conflict of Interests.

There are no conflicts of interest related to this publication.

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