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Comprehensive Investigation of the Photophysics, Photochemistry, and Kinetics of a Wide Variety of Photochromic Hydrazones in Various Solvents

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Abstract: The photophysics, photochemistry, and kinetics of two major families of photochromic hydrazones have been studied by means of microsecond and nanosecond laser flash techniques. In addition, picosecond fluorescence spectroscopy was used in some cases in order to aid in the elucidation of the photochromic mechanisms. Several derivatives of benzaldehyde (hydrazones) have been studied. All of them showed anti to syn isomerization. The derivatives of 2-hydroxybenzaldehyde hydrazones were found to undergo intramolecular proton transfer originating from the hydroxyl group. In the latter type of compounds, anti to syn isomerization and proton transfer were found to be competitive processes originating in the lowest excited singlet state. This result plus other data on the risetime for proton transfer dictates that the isomerizations occur in <5 ps. The photophysics and photochemistry of the excited-state intramolecular proton transfers were found to be strongly dependent upon the substituents and the hydrogen-bonding character of the solvent. For all of the 2-hydroxybenzaldehyde derivatives the excited-state intramolecular proton transfer results in the nonadiabatic formation of a cis-keto form. The ground-state thermally reverse proton transfer occurs on the microsecond time scale. In hydrogen-bonding solvents, it was found that the excited-state intramolecular proton transfer results also in the nonadiabatic formation of a trans-keto form. Several 1-naphthoquinone 2-phenylhydrazones have been shown to undergo syn to anti isomerization except for 1-naphthoquinone 2-diphenylhydrazone which showed an anti to syn isomerization. In addition, competitive photochemical processes including intramolecular proton transfer (from hydrogen on nitrogen) are also found to occur in some cases depending upon the nature of the solvents. The same is true for the 1-phenylhydrazone of 1,2-naphthoquinone. The hydrazone form of the 4-phenylhydrazone of 1,4-naphthoquinone shows direct syn ↔ anti isomerization in contrast to that found by earlier researchers. In all of the foregoing, the processes occur in the lowest excited singlet state.

Introduction

Very few flash spectroscopy experiments have been carried out on benzaldehyde hydrazones and none on 2-hydroxybenzaldehyde substituted ones. Condorelli et al.[1] have reported that both the syn and anti isomers of para-substituted benzaldehyde (4-nitrophenyl)hydrazones have great thermal and photochemical stability at room temperature and therefore are easily separable using chromatography. Irradiation of the anti isomers using steady-state techniques leads to the expected blue shifts attributed for syn isomers, which show significant smaller extinction coefficients than the anti isomers. It has also been reported that the ratio of the quantum yields of anti to syn isomerization for direct excitation was low compared to that from triplet sensitized excitation. This has been interpreted to mean that the mechanism for direct excitation largely involves isomerization via the lowest excited singlet state versus the lowest excited triplet state.

(Phenylazo)naphthol derivatives have been the subject of much research since they are used as commercial dyes. It has been known for a long time that these compounds exist in solution in a tautomeric equilibrium between the azo and the naphthoquinone hydrazone forms. Several studies have been carried out on the azo derivatives,[2-5] but very few studies have been performed on the hydrazone form.

We examined four *o*-naphthoquinone phenylhydrazones which may show an intramolecular proton-transfer mechanism (from nitrogen) as well as C–N double bond isomerization. Two of them, the 2-naphthoquinone 1-phenylhydrazone (SUD) and 2-naphthoquinone-1-(4′-nitrophenyl)hydrazone (RED) are respectively known as the pigments Sudan and Para Red. Steady-state experiments carried out on SUD at low temperature in different solvents have been reported.[2] The photochromism of SUD has been tentatively ascribed[2] to both C–N double bond isomerization and hydrazone to azo conversion. More recently, picosecond absorption spectroscopy has been used to study the anti to syn isomerization of SUD.[6] It has been proposed that the C–N double bond isomerization of SUD occurs via an intermediate form which might have a pyramidal form.[6]

Results from steady-state irradiation of 1-naphthoquinone 2-diphenylhydrazone (N2DPH) at low temperature in different solvents indicated[7] the existence of this compound in two isomeric forms which have been ascribed to C–N double bond isomers.

Finally, we looked at 1-naphthoquinone 4-phenylhydrazone (N4PH). This compound is known to exist in solution in tautomeric equilibrium with 4-(phenylazo)-1-naphthol.[3] On cooling, this equilibrium shifts toward the hydrazone form in methylcyclohexane or toward the azo form in ethanol. Several steady-state studies have been carried out on the azo form[3,8] which has been found to undergo a N–N double bond isomerization. Few studies have been performed on the hydrazone tautomer since it has been reported[3] that no direct photoconversion involving the hydrazone seemed to take place; however, see later discussion.

In the course of our work, we also studied several different phenyl-, (nitrophenyl)-, and naphthylhydrazones of benzaldehyde, salicylaldehyde (2-hydroxybenzaldehyde), methoxybenzaldehyde, and hydroxyacetophenone. The purpose of our investigation was (1) to identify the nature of the species thermally and photochemically produced, (2) to obtain related kinetic data, and finally (3) to propose the nature of the excited states and mechanisms involved in the different types of photochemistry (photochromism).

Experimental Section

The synthesis of phenylhydrazones starting from an aldehyde and a hydrazine is generally straightforward. However, several critical points need to be emphasized.

The most commonly used synthetic procedure involves the condensation of the carbonyl compound with a solution of the corresponding phenylhydrazine in ethanol and sulfuric acid followed by recrystallization of the precipitate. In a parallel manner, phenylhydrazine hydrochloride and the carbonyl compounds in warm ethanol were mixed, and then

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water was added dropwise to precipitate the phenylhydrazone. Filtration and recrystallization followed. Thin-layer chromatography (TLC) tests were used to check the purity of the products. Melting point tests were used to identify the products for which data had been reported.

However, particularly on the basis of TLC and melting point tests, several other compounds or impurities were detected for the naphthoquinone phenylhydrazones. These impurities have been attributed to two major sources. First of all, side reactions could have occurred during the condensation of the naphthoquinones such as the condensation of the second carbonyl function. Also, the method described above usually leaves traces of acids which remain even in the recrystallized samples and catalyze the syn–anti isomerization reactions before or during the melting process and thus change the melting behaviors of the hydrazones.[2]

It has been reported[9,10] that the classical synthesis of acetaldehyde (2,4-dinitrophenyl)hydrazone gave a ratio of 2 to 1 for the syn and anti isomers, respectively. Prolonged standing or addition of acid affected the syn–anti equilibrium in solutions. A first attempt to solve the latter problem involved washing the precipitate collected during the suction filtration with a 5% aqueous sodium bicarbonate solution followed by recrystallization of the product.[9] It seemed that, for most of the hydrazones of questionable purity that were synthesized, the problem of purity still remained the same. Finally, we thought that beside the potential isomerization processes, other undesirable side effects could occur that were related to the presence of the water. Therefore, we decided not to add water to enhance the precipitation process, but instead, we removed most of the ethanol by evaporation using a stream of dry nitrogen gas. Either the remainder of the solvent was removed under vacuum (10^{-4} Torr, 30 °C) or the compound was left in the solvent for a direct and first crystallization. A further recrystallization from 95% ethanol was the final procedure, and the samples were stored under dry nitrogen at -5 °C. The results were much better than the usual procedures, but in some cases, the products still needed further purification. Therefore, instead of looking for a pure product, we prepared the compounds, whatever their purities, and then separated them via silica gel column chromatography usually employing 20/80 ethyl acetate/hexane as the eluting solvent mixture.

All the solvents were used spectrograde and were dried, kept over 3-Å molecular sieves, and used without further purification. Absorption spectra were recorded on either a Cary 15 or Hewlett-Packard 8450 A UV/visible spectrophotometer. Both quartz and Pyrex 2–10-mm-path-length cells were used for absorption measurements.

Fluorescence spectra were recorded on a Perkin-Elmer LS-5 spectrofluorometer. To detect and measure the time profiles of some extremely short fluorescence signals obtained after excitation of a sample by a 30-ps laser pulse, a Hamamatsu temporal disperser and analyzer (commonly called a "streak camera") was used. These coupled devices have an intrinsic resolution time of 30 ps.

Laser flash spectroscopy was employed to study optical density changes (ΔOD) due to the existence of potential transients when irradiating the studied compounds. This was commonly done over the 300-ns to 400-μs time domain and in some cases to 1 ms.

The microsecond laser flash experiments were carried out using a Q-switched neodymium/yttrium aluminum garnet (Nd:YAG) laser with an 11-ns pulse width. The excitation pulses at 532 and 355 nm were generated using KDP (potassium deuterium phosphate) crystals from the 1064-nm fundamental emitted by the laser. The laser excitation beam was focused on solutions contained in rectangular quartz cells with 5- or 10-mm path lengths along the monitoring light. The intensity of the laser radiation was controlled by the use of wire mesh screens. The common chosen energy range was 5–12 mJ/pulse at 532 nm and 1–6 mJ/pulse at 355 nm since, in some cases, transient signals and/or depletions were weak or no excited-state transients existed up to the maximum energy. A kinetic absorption spectrometer was used to monitor optical density changes (ΔOD) after excitation. It consisted of a continuously operating 150-W xenon arc lamp (monitoring source), two electromechanical shutters, quartz lenses, target cell holder, a Bausch and Lomb high-intensity monochromator, and a photomultiplier tube (Hamamatsu R 9278). Detector output analogue signals were processed by a Biomation 8100 digitizer and computer combination (PDP 11/70). Monitoring light levels were kept to a minimum, using an adjustable light attenuator and appropriate filters, to prevent photochemical processes from occurring in the time period between the opening of the electromechanical shutter of the kinetic spectrometer and the excitation pulse. Bubbling nitrogen gas through each solution was used to degass the samples. In addition, oxygen was bubbled in separate experiments to examine the oxygen quenching of potential triplet transient species.

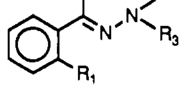
Table I. Spectral Absorption Data of Benzaldehyde Hydrazone Derivatives

	λ_{max}^{abs} (nm) anti isomer			λ_{max}^{abs} (nm) transients (t, μs)		λ_{max}^{abs} (nm) syn isomer	
	benz[a]	acn[b]	EtOH[c]	benz[a]	EtOH[c]	benz[a]	EtOH[c]
BH	388	400	399	370[d]		370	
	298	327		(>400)			
		298					
MBH	398			370		370	
	300			(>400)			
HBH	387	396	399	440[e]	510	360	
	330	330		(250)	(2, 40)		
	300	298					
HAH	384		396	480[f]	510	360	
	328			(~320)	(45)		
	312						
nitro-HBH	379		407		520[e]	350	360
	300				(1, 5)		
2HBNH	345		345	460[g]	460[g]	320	320
	355		361	(90)	(3, 20)		
4BNH	344		345	320	320	320	320
				(~400)	(~400)		440

[a] Benzene. [b] Acetonitrile. [c] Ethanol. [d] Same result in acetonitrile. [e] Also a maximum existed at 360 nm (>400 μs). [f] Also a weak maximum existed at 360 nm. [g] Also a maximum existed at 320 nm (>400 μs).

Results

We studied the photophysics and photochemistry of benzaldehyde (4′-nitrophenyl)hydrazone *and* six of its derivatives in different solvents using laser flash spectroscopy techniques. The compounds are based on the general formula for a hydrazone



where R_1 will be -H, -OH, or $-OCH_3$, R_2 will be -H or $-CH_3$, and R_3 is phenyl, nitrophenyl, or naphthyl (R_3 contains the primed numbers for location of any substitution). The absorption spectral data of these compounds and their photoproducts are summarized in Table I.

Benzaldehyde (4′-nitrophenyl)hydrazone (BH) in benzene at room temperature had a strong absorption band maximum at 388 nm (onset at 440 nm for $OD_{388\,nm} \approx 1$) and a weaker absorption band maximum at 298 nm.

In ethanol at room temperature, the stronger maximum was red shifted to 399 nm (onset at 490 nm for $OD_{399\,nm} \approx 1$). Also, the band was much broader and showed a much more extended tail at longer wavelengths than in benzene. This band shape suggests the existence of different species which can be related to intermolecular hydrogen bonds between ethanol molecules and the imine nitrogen atom and/or the amine nitrogen proton of the hydrazone molecule.

Laser flash irradiation at 355 nm in nitrogen-saturated benzene and acetonitrile at room temperature gave a product with an absorption maximum at 370 ± 10 nm showing no decay in the 0.5–400-μs time range. An accompanying maximum negative optical density change (ΔOD) at 400 ± 10 nm resulting from the ground-state depletion did not show any recovery over the same time domain. These results were not affected by the presence of oxygen (vs nitrogen), nor did triplet energy transfer occur to β-carotene.

Steady-state emission spectroscopy in benzene at room temperature showed one fluorescence band with a maximum at 455 nm. However, time-resolved emission spectroscopy could not be used because of the low intensity.

The 2-methoxybenzaldehyde (4′-nitrophenyl)hydrazone (MBH) in benzene at room temperature had a strong absorption maximum at 398 nm (onset at 450 nm for $OD_{398\,nm} \approx 1$) and a weaker maximum at 300 nm. Steady-state emission spectroscopy in benzene at room temperature showed one fluorescence band with a maximum at 467 nm. Time-resolved emission spectroscopy at

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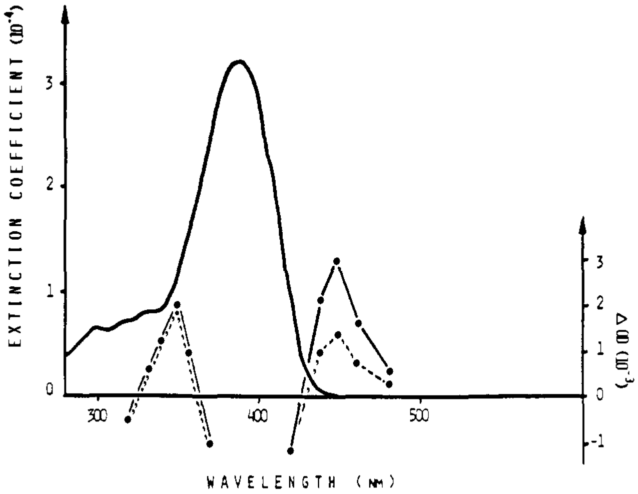


Figure 1. Ground-state (—) and transient spectra 1.5 μs (•—•) and 250 μs (•---•) after the flash of HBH in benzene.

room temperature gave a fluorescence lifetime of 60 ps.

Laser flash irradiation at 355 nm in nitrogen-saturated benzene at room temperature gave a product with an absorption maximum at 370 ± 10 nm showing no decay in the 0.5–400-μs time range. An accompanying maximum negative ΔOD at 400 ± 10 nm resulting from the ground-state depletion did not have any recovery over the same time domain. The presence of oxygen (vs nitrogen) did not affect these results.

The 2-hydroxybenzaldehyde (4′-nitrophenyl)hydrazone (HBH) in benzene at room temperature showed a strong absorption maximum at 388 nm (onset at 435 nm for $OD_{388\,nm} \approx 1$) and weaker maxima at 330 and 300 nm, Figure 1. Moreover, again as for BH in ethanol, the band was much broader in this latter solvent than in the other ones and also had a much broader tail at longer wavelengths in ethanol than in benzene. Again, the presence of intermolecular hydrogen bonding is suspected to be the source of the latter phenomena.

Laser flash irradiation of HBH at 355 nm in nitrogen-saturated *benzene* at room temperature gave, as before for BH and MBH, a product with an absorption maximum at 365 ± 10 nm having no decay over the 0.5–400-μs time range as well as a short-lived transient with an absorption maximum at 450 ± 10 nm, Figure 1, showing a single first-order decay to the original baseline with a lifetime of 250 μs. An accompanying maximum negative ΔOD at 400 ± 10 nm resulting from the ground-state depletion showed very little recovery over the 0.5–400-μs time domain. It was expected that a partial recovery with a lifetime of ~250 μs would have been seen. However, given the weakness of the intensity of the positive ΔOD signal at 440 nm (~5 × 10^{-3} ΔOD), the estimated lifetime of the decay (~250 μs), and the time scale (400 μs) available to measure the recovery, a signal of only ~2 × 10^{-3} ΔOD could have been obtained. This signal was within the noise and lamp drift and could not be observed. All of the foregoing results were unaffected by the presence of oxygen (vs nitrogen), and no triplet energy transfer occurred to β-carotene.

Steady-state emission spectroscopy carried out at room temperature showed the presence of one fluorescence band with a maximum at 450 nm in benzene and at 512 nm in ethanol. Note that, in ethanol, this fluorescence band was much broader than in benzene.

Laser flash irradiation of HBH at 355 nm in nitrogen-saturated *ethanol* at room temperature gave quite different results than in benzene with a short-lived transient with an absorption maximum at 515 ± 10 nm, Figure 2, decaying to a slightly residual positive ΔOD via two first-order processes with lifetimes of ~2 and ~40 μs. An accompanying maximum negative ΔOD at 400 ± 10 nm representing the ground-state depletion recovered to a residual negative ΔOD via two first-order processes as above (lifetimes of ~2 and ~40 μs). No positive ΔOD appeared in the 330–370-nm range in contrast to the case in benzene. Again, these phenomena were unaffected by the presence of oxygen (vs nitrogen).

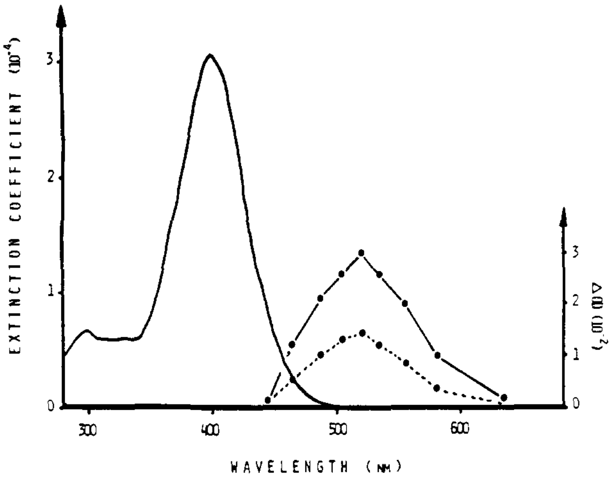


Figure 2. Ground-state (—) and transient spectra 1.5 μs (•—•) and 40 μs (•---•) after the flash of HBH in ethanol.

Parallel experiments made in acetonitrile at room temperature gave results similar to those obtained in benzene.

We performed time-resolved emission spectroscopy experiments on HBH at room temperature in both benzene and ethanol. No decay trace distinguishable from the lamp decay trace was observed, leading us to believe that the fluorescence lifetime was less than 30 ps.

The 2-hydroxyacetophenone (4′-nitrophenyl)hydrazone (HAH) had results quite similar to the preceding HBH (2-hydroxybenzaldehyde (4-nitrophenyl)hydrazone) regarding absorption and flash data except that there was only a single first-order decay of ~45 μs.

The 5-nitro-2-hydroxybenzaldehyde phenylhydrazone (nitro-HBH) in benzene at room temperature had a major absorption band with a maximum at 379 nm (onset at ~430 nm for $OD_{379\,nm} \approx 1$) with a slight shoulder in the 385–400-nm region and a weaker band with a maximum at 300 nm. In ethanol at room temperature, the strong maximum was red shifted to 407 nm (onset at ~575 nm for $OD_{407\,nm} \approx 1$). Moreover, again the band was much broader in ethanol than in benzene. Also, it showed a weak inflection/shoulder at 450 nm and a much broader tail in the 430–575-nm region.

Laser flash excitation of nitro-HBH at 355 nm in nitrogen-saturated *benzene* at room temperature gave a product with an absorption maximum at 350 ± 10 nm. We were not able to determine the decay lifetime of this product due to the low intensity of the related positive ΔOD signal. A weak absorption maximum at 480 ± 20 nm was also observed. We assumed this decay to be a first-order process decaying to the baseline in order to obtain an idea of its lifetime. We estimated a lifetime of ~320 μs. The accompanying negative ΔOD at 330 and 380 nm resulting from the ground-state depletion did not show any recovery in the 0.5–400-μs time range. Oxygen (vs nitrogen) did not affect the foregoing results.

Upon flashing nitro-HBH at 355 nm in nitrogen-saturated *ethanol* at room temperature, the transient spectrum showed the presence of a product with an absorption maximum at 360 ± 10 nm with no decay in the 0.5–400-μs time domain. Also, an absorption maximum at 520 ± 15 nm was observed having a decay to the original baseline via two first-order processes with lifetimes of 1 and 5 μs. An accompanying negative ΔOD at 410 nm related again to the ground-state depletion recovered to a residual negative baseline via two first-order processes of 1 and 7 μs. An isobestic point was noticed at 480 nm in ethanol; in addition, oxygen (vs nitrogen) did not change any of the foregoing results.

The 2-hydroxybenzaldehyde 2′-naphthylhydrazone (2HBNH) in benzene at room temperature had a strong absorption band with a maximum at 345 nm and another of near equal intensity at 355 nm (onset at 430 nm for $OD_{345\,nm} \approx 1$). In ethanol at room temperature, the absorption spectrum was very similar to the spectrum observed in benzene. Neither in benzene nor in ethanol was the absorption spectrum affected by addition of trichloroacetic acid (TCA).

Laser flash irradiation of 2HBNH at 355 nm in nitrogen-saturated *benzene* at room temperature gave a product with an absorption maximum at 320 ± 10 nm with no decay in the 0.5–400-μs time domain. Also, an absorption maximum at 460 ± 10 nm existed which decayed to the original baseline via a first-order process with a lifetime of ~85 μs. A depletion at 370 ± 10 nm recovered to a residual negative baseline via a first-order process with a lifetime of ~70 μs. It would be expected that a recovery with a lifetime of ~85 μs would have been observed. However again, given the weakness of the intensities of the positive ΔOD signal at 460 nm (~5 × 10^{-3} ΔOD) and of the partial recovered signal at 370 nm (~3 × 10^{-3} ΔOD), and given the noise and lamp drifts, substantial errors occur in the estimations of lifetimes. Therefore, we believe that the lifetime of the partially recovered first-order process at 370 nm matches that of the first-order decay at 460 nm. The presence of oxygen (vs nitrogen) did not affect the results, nor did triplet energy transfer occur to β-carotene.

Upon flashing 2HBNH at 355 nm in nitrogen-saturated *ethanol* at room temperature, a product appeared with an absorption maximum at 320 ± 10 nm with no decay in the 0.5–400-μs time domain. Also, an absorption maximum at 460 ± 10 nm existed, decaying to the original baseline via two first-order processes with lifetimes of >1 ms and ~20 μs, respectively. Again, the ground-state maximum depletion at 350 ± 10 nm recovered to a substantial residual negative baseline. We were not able to determine the lifetime of the recovery processes due to the low intensity of the negative ΔOD signal.

The 4-hydroxybenzaldehyde 2′-naphthylhydrazone (4HBNH) in benzene at room temperature showed a strong absorption band with a maximum at 344 nm and a shoulder at 355 nm (onset at 430 nm for $OD_{344\,nm} \approx 1$). In ethanol at room temperature, the absorption spectrum was very similar to the spectrum observed in benzene. None of the foregoing spectra were modified by the addition of trichloroacetic acid (TCA).

Laser flash irradiation of 4HBNH at 355 nm in nitrogen-saturated *benzene* at room temperature gave a product with a maximum of absorption at 320 ± 10 nm with no decay in the 0.5–400-μs time range. The ground-state depletion at ~360 nm did not show any recovery in the same time domain. Laser flash irradiation at 4HBNH at 355 nm in nitrogen-saturated *ethanol* at room temperature gave a weak absorption maximum at 320 ± 20 nm with no decay in the 0.5–400-μs time range. The ground-state depletion at 380 nm did not show any recovery in the same time domain. All the foregoing results observed in benzene and ethanol were unaffected by the presence of oxygen (vs nitrogen).

We also studied the photophysics and photochemistry of five phenylhydrazones of 1,2-naphthoquinone and 1-naphthoquinone 4-phenylhydrazone using laser flash spectroscopy techniques. All of these compounds were found to undergo photochemistry. For the nomenclature chosen here, the first part of the name gives the location of the unreacted keto position as, for example, 1-naphthoquinone.

The 1-naphthoquinone 2-phenylhydrazone (N2PH) in *benzene* at room temperature had a main absorption band maximum at 498 nm, while in methylcyclohexane, the maximum was blue shifted to 489 nm, for ethanol at room temperature, the maximum appeared at 493 nm, and in acetonitrile, the absorption spectrum of N2PH was very similar to the spectrum observed in ethanol.

Laser flash irradiation at 532 nm in nitrogen-saturated *ethanol* at room temperature gave a product with an absorption maximum at 460 ± 10 nm showing no decay over the 0.5–400-μs time range. Accompanying negative ΔOD's at 380 ± 10 nm and 530 ± 10 nm resulting from the ground-state depletion did not show any recovery in the same time domain. The foregoing results were unaffected by the presence of oxygen (vs nitrogen), and no triplet energy transfer to β-carotene was observed. Laser flash irradiation at 355 nm in nitrogen-saturated solutions of *benzene* and *acetonitrile* at room temperature gave results parallel to those above in ethanol.

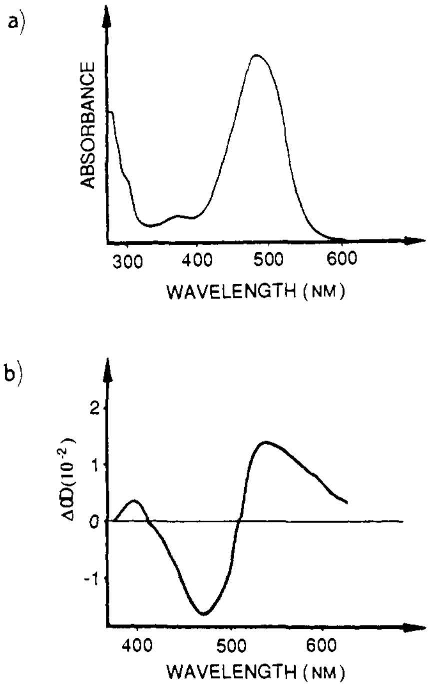


Figure 3. Ground-state (a) and transient spectrum 0.3–400 μs after the flash (b) of N2DPH in ethanol.

The 1-naphthoquinone 2-(4′-nitrophenyl)hydrazone (N2-nitroPH) in methylcyclohexane at room temperature showed a strong absorption band with a maximum at 498 nm. In benzene at room temperature, the maximum was at 502 nm. In ethanol at room temperature, the maximum appeared at 493 nm. Laser flash irradiation in *benzene* resulted principally in strong depletion along with a +ΔOD transient maximum near 450 nm. Recovery of the depletion over 400 μs was only slight or nonexistent as was the decay of the transient. The depletion maxima at 370 and ~500 nm corresponded to the absorption maxima of N2nitroPH.

The 1-naphthoquinone 2-diphenylhydrazone (N2DPH) in ethanol at room temperature had an absorption maximum at 476 nm, Figure 3. Laser flash irradiation at 532 nm in nitrogen-saturated *ethanol* gave a strong intensity maximum at 530 nm showing little decay in the 0.5–400-μs time scale, Figure 3. The accompanying negative maximum ΔOD at 470 ± 10 nm, Figure 3, resulting from the ground-state depletion did not show any recovery kinetics over the same time domain. The presence of oxygen (vs nitrogen) did not affect the results, nor was triplet energy transfer to β-carotene observed.

The 2-naphthoquinone 1-phenylhydrazone (SUD for Sudan), the inverse of N2PH, in *benzene* and in *acetonitrile* at room temperature had a strong broad absorption band with a maximum at 475 nm and two shoulders at ~420 and ~510 nm, the former shoulder being three-fourths the intensity of the main peak. In *ethanol* at room temperature, the maximum appeared at 480 nm and the shoulders showed up again at ~420 and ~510 nm, the former shoulder being this time two-thirds the intensity of the strong peak.

Upon laser flash irradiation of SUD at 532 nm in nitrogen-saturated *benzene* at room temperature, we observed immediately after the pulse *only* a bleaching of the entire 350–590-nm spectral region (no +ΔOD transient was seen). No recovery kinetics were detected over the 0.5–400-μs time scale. The presence of oxygen (vs nitrogen) did not affect the results, nor was triplet energy transfer to β-carotene observed.

Laser flash irradiation of SUD at 532 nm in nitrogen-saturated *ethanol* at room temperature also gave again a bleaching of the entire 350–540-nm spectral region. However, in addition, we saw a transient with a +ΔOD maximum at 550 ± 10 nm which decayed to the original baseline via a first-order process with a

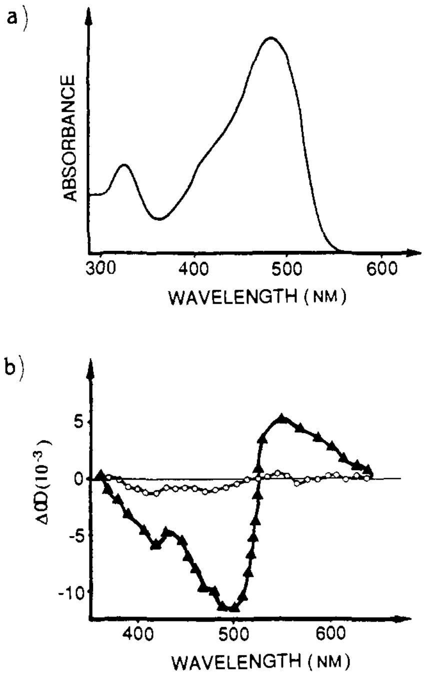


Figure 4. Ground-state (a) and transient spectrum 1.5 μs (▲) and 100 μs (○) after the flash (b) of RED in methanol.

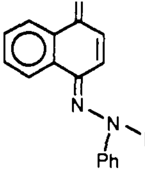
lifetime of ~2 μs. The ground-state depletion, maximum at 500 ± 10 nm, only recovered about 25% to a residual permanent negative ΔOD baseline, lifetime >400 μs. The recovery was monitored at 480 and 400 nm and was found to fit a first-order process with a lifetime of ~2 μs at both monitoring wavelengths (same lifetime as decay). The presence of oxygen (vs nitrogen) did not affect the foregoing results nor did 355- vs 532-nm excitation.

The 2-naphthoquinone 1-(4′-nitrophenyl)hydrazone (RED for Para Red), the inverse of N2nitroPH, in *methanol* and *acetonitrile* at room temperature showed a strong absorption band with a maximum at 483 nm, Figure 4. In *benzene* at room temperature, the stronger maximum appeared at 485 nm; moreover, a shoulder also showed up at ~500 nm.

Upon laser flash irradiation of RED at 532 nm in nitrogen-saturated *benzene* and *acetonitrile* solutions at room temperature, we observed immediately after the pulse, only a bleaching of the entire 350–530-nm spectral region (no transient +ΔOD absorption was observed). No recovery was detected over the 0.5-μs to 1-ms time scale. The presence of oxygen (vs nitrogen) did not affect the results, nor was triplet energy transfer to β-carotene observed.

Laser flash irradiation of RED at 532 nm in nitrogen-saturated *methanol* also gave a bleaching of the entire 380–530-nm spectral region. However, in addition we saw a transient spectrum with a maximum near 550 nm (±10 nm), Figure 4, similar to that of SUD. The kinetics were more complex than for SUD (which only differs by the absence of a $-NO_2$ group on the phenylhydrazone moiety). In the spectral region from 500 nm and shorter, there occurred solely a first-order recovery to the baseline (not for SUD) with a lifetime of ~32 μs. On the other hand in the +ΔOD 550-nm region, a growth appeared followed by a decay. Both the growth lifetime of ~4 μs and decay lifetime of ~32 μs were first order. The decay was to the baseline. The presence of oxygen (vs nitrogen) did not affect the foregoing results.

The 1-naphthoquinone 4-phenylhydrazone (N4PH) is known[3] to exist in solution as an equilibrium mixture with its tautomer 4-(phenylazo)-1-naphthol. On cooling, this equilibrium shifts toward the latter (azo) in ethanol or toward the former (hydrazone) in methylcyclohexane.[3]



In *ethanol* at room temperature, the absorption spectrum of N4PH had a strong absorption band with a maximum at 405 nm with a significant shoulder at ~470 nm, the shoulder being half the intensity of the maximum. In ethanol at −75 °C, the maximum and the shoulder showed up at 413 and ~485 nm, respectively. At this temperature, the shoulder was one-fifth the intensity of the maximum. In *methylcyclohexane* at room temperature, the maximum and the shoulder showed up at 397 and ~460 nm, respectively. Again, at this temperature, the shoulder was half the intensity of the maximum. In methylcyclohexane at −75 °C, a strong maximum appeared at 483 nm and an inflection was noticed at ~420 nm. In benzene at room temperature, two maxima appeared at 406 and 448 nm. The peak at 406 nm was slightly higher than the peak at 448 nm. In *acetonitrile*, the two maxima showed up at 407 and 451 nm, respectively. However, in this solvent, the latter peak was slightly higher than the former.

Laser flash irradiation at 355 nm of N4PH in *ethanol* at −75 °C gave two bands of +ΔOD with maxima at 340 ± 10 nm and 480 ± 10 nm with no decay in the 0.5–400-μs time domain. The ground-state depletion at 400 ± 10 nm did not show any recovery over the same time domain. In *methylcyclohexane*, laser flash irradiation at 532 nm of N4PH at −75 °C gave a product with a maximum of absorption at 400 ± 10 nm which did not show any decay in the 0.5–400-μs time domain.

Discussion

A. Phenylhydrazones. Condorelli et al.[1] have reported that *anti*-benzaldehyde (4′-nitrophenyl)hydrazone (BH), in benzene solution has a $\pi \rightarrow \pi^*$ transition at 388 nm ($\epsilon = 34360$), whereas the syn isomer has a $\pi \rightarrow \pi^*$ transition at 370 nm ($\epsilon = 27040$). We have carried out a study of this same compound using laser flash spectroscopy techniques. This was done to compare the quality of agreement between our spectral results using laser flash techniques with those of Condorelli who employed steady-state techniques. We also wanted to determine if transients existed in the photochemistry of this compound.

We observed a shift in the absorption maximum originally at 388 nm to 370 nm upon flashing BH in benzene at 355 nm. This shift is the same as that seen before[11] when the anti isomer was converted to the syn isomer by steady-state irradiation. Also, recall that we saw no transient with a decay lifetime less than 400 μs and the presence of oxygen (vs nitrogen) did not affect the results. We believe anti to syn isomerization around the C–N double bond occurred, as assigned previously,[1] via the lowest singlet excited state.

Upon flashing HBH, the 2-hydroxy derivative of BH, at 355 nm in benzene and acetonitrile, we observed again a blue shift in the absorption maximum originally at 388 nm to 365 nm with no decay in the 0.5–400-μs time range. This result is parallel to the findings obtained with BH. Therefore, we attribute this blue shift to the anti to syn isomerization around the C–N double bond. However, additionally there was a short-lived transient with an absorption maximum at 450 ± 10 nm with a decay lifetime of ~250 μs. This, therefore, is in marked contrast to the case of BH (the structure of which does not contain a hydroxy group in the ortho position). The assignment of this transient will be made by case analogy to the salicylideneaniline (SA) and 2-(2′-hydroxyphenyl)benzothiazole (HBT) derivative cases.

Several derivatives of the foregoing compounds SA and HBT have been studied and were found to undergo intramolecular proton transfer in the first excited singlet state.[11-21] In most of

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the usual solvents at room temperature, the transient obtained via excited singlet state intramolecular proton transfer showed a maximum absorption in the 470–480-nm region for SA and in the 430–470-nm region for HBT.[15-17] Their decay lifetimes were in the 2–400-μs time domain. Therefore, on the basis of the similarity of the structures of HBH, SA, and HBT regarding the location of the hydroxy group which is ortho-substituted relative to the imine group, as well as the similarities of the transient spectrum and lifetimes observed, we assign the transient spectrum of HBH to a ground-state species resulting from an excited singlet state intramolecular proton transfer.

For comparison, we studied the case of MBH. Under experimental conditions as above for HBH, upon flashing MBH at 355 nm in benzene at room temperature, we saw a blue shift of ~20 nm in the absorption (maximum) originally at 398 nm to 380 ± 10 nm, with no decay in the 0.5–400-μs time domain. This phenomenon is again assigned as the result of an anti to syn isomerization around the C–N double bond. Moreover, in contrast to HBH, we did not see any other transient over the 350–750-nm spectral region within the same time domain (0.5–400 μs). For HBH, this further corroborates our assignment of the transient at 450 ± 10 nm to be the result of a ground-state species resulting from excited singlet state intramolecular proton transfer (from the hydroxyl to the imine nitrogen).

We have so far discussed the excited-state intramolecular proton transfer for the 2-hydroxybenzaldehyde (4′-nitrophenyl)hydrazone. However, we have reported similar results for HAH (hydroxyacetophenone (nitrophenyl)hydrazone), nitro-HBH and 2HBNH (2-hydroxybenzaldehyde naphthylhydrazone). Given the common presence of a hydroxy group in the ortho position for all of these compounds and the parallel flash spectroscopic results, intramolecular proton transfer is the photochemical mode operating as for HBH. In the case of 4HBNH, on the other hand, we have reported results similar to those obtained with BH and MBH. Indeed the hydroxy group is in the para position for 4HBNH. Thus, no intramolecular proton transfer was observed, and geometric isomerization was the only operative photochemical mode (as for BH and MBH).

Our investigations have shown that, in the case of the 2-hydroxybenzaldehyde hydrazone derivative in *benzene*, the maximum of the transient absorption decays to the original baseline via a simple first-order process and the maximum depletion recovers to a residual negative ΔOD baseline via a first-order process of the same lifetime. Thus, we believe that, in benzene, a ground-state cis-keto form exists (colored form), and this relaxes thermally to an original enol form via a reverse ground-state intramolecular proton transfer. In *ethanol*, the decay and the ground-state *partial* recovery were found to fit a simple first-order process for HAH and two first-order processes as for HBH, nitro-HBH, and 2HBNH. These latter facts lead us to believe that, in this solvent, an isomer of the cis-keto form is also obtained for HBH, nitro-HBPH, and 2HBNH. By case analogy to SA, we believe that the other isomer has a trans (or twisted) character although no proof of such a structure has been established. Moreover, one should note that non-hydrogen-bonding solvents enhance the strength of the intramolecular hydrogen bond while hydrogen-bonding solvents weaken this intramolecular hydrogen bond and may favor framework changes like a C–N double bond isomerization. The remaining permanent negative ΔOD observed in the 0.5–400-μs time domain makes us believe that the relaxation process of the colored species does not lead to the exact original enol form or that a competitive side mechanism occurred. A new species could be formed by direct excitation of the hydrazone intermolecularly hydrogen-bonded to ethanol. Recall the ground-state spectrum data of HBH in ethanol where the presence of intermolecular hydrogen bonding was suspected to be the source of the large tail broadness of the absorption band at longer wavelengths. It is also important to note that, in any solvent used, the rate of thermal reverse proton transfer of the photochemically produced keto species was observed to be several orders of magnitude slower than the excited-state intramolecular proton transfer. This infers a much higher activation energy in the ground state than in the excited state for enol re-formation. This probably largely originates from conformational changes required to afford the appropriate geometry for proton back-transfer.

In the case of HBH, we did *not* observe a large Stokes shift of the fluorescence. Also in the case of MBH and HBH, where we carried out emission spectroscopy experiments, the intensities of fluorescence were high. In benzene as well as in ethanol, the long-wavelength absorption band and the emission band have overlapping onsets, indicating that the emission originates from the lowest singlet excited state of the original enol molecule in all cases. Furthermore, no other luminescence band was detected at longer wavelengths. *This is in marked contrast to the case of SA (salicylideneaniline) and HBT ((hydroxyphenyl)benzathiazole) where it has been found that emission occurred from the proton-transferred photoproducts.*[11-19] Thus, we tend to believe that keto species are *not produced adiabatically* since no fluorescence originating from the colored forms of HBH in ethanol or benzene was detected (and no large Stokes shift of fluorescence was observed); see discussion below.

Nanosecond[18] and picosecond[19] emission spectroscopy led to the proposal that, upon irradiation at 355 nm, SA underwent an excited-state intramolecular proton transfer, producing an excited-state cis-keto form which contained a substantial amount of excess vibrational energy. This vibrationally nonrelaxed excited-state form was reactive toward the formation of the trans-keto form in the ground state and also was rapidly converted to the relaxed ground-state cis-keto form by vibrational relaxation.

In the case of our HBH, we believe the cis-keto form was not produced in its excited state as previously discussed above. We propose that, upon irradiation, HBH undergoes an excited-state intramolecular proton transfer leading to a cis-keto ground state that is not vibrationally relaxed which in turn thermally forms the ground-state trans-keto form. Also, the vibrationally "hot" cis-keto ground state can relax to the vibrationally relaxed cis-keto form. Following these processes, the trans-keto form thermally decays to the original enol form via the cis-keto form. Our results also infer that the reverse proton transfer is enhanced in hydrogen-bonding solvents as shown by the decrease of the lifetime in ethanol compared to non-hydrogen-bonding solvents. We believe that, in hydrogen-bonding solvents, the reverse proton transfer may be mediated, in part, by exchanges with molecules of the solvent.

Finally, we discuss the time concordance between the observed anti to syn isomerization of the enol form and the excited-state intramolecular proton transfer. From a topochemical point of view, the intramolecular proton transfer occurs within a six-membered ring framework and is known to be fast. In the case of SA and HBT, the excited-state intramolecular proton transfer has been reported[16,21] to show a risetime of <5 ps at 4 K. Also recall the fluorescence lifetime of HBH is <30 ps. We believe that the anti to syn isomerization and the proton transfer are competitive processes, both originating in the lowest excited singlet state. Our results also show that this competition is sensitive to the hydrogen-bonding character of the solvent. In benzene the anti to syn isomerization is much more favored than in ethanol. Note that it might have been expected that in non-hydrogen-bonding solvent, the anti to syn isomerization may be less favored because of the relatively strong intramolecular hydrogen bond. *These results carry the important implication that the double bond isomerization is occurring in less than 5 ps.*

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B. Naphthoquinone Phenylhydrazone Derivatives. The phenomenon of azo–hydrazone tautomerism of hydroxyazo compounds has been the subject of much research and is well documented in the literature.[22,23] The state of tautomeric equilibrium for ortho and para hydroxy compounds is primarily determined by structural factors within the molecule. Millefiori et al.[24] have mentioned that certain derivatives of SUD were essentially azo compounds, but several researchers[22,25] have reported that the presence of a strong intramolecular hydrogen bond in SUD and N2PH (ortho cases) has the effect of favoring the existence of the hydrazone tautomer and of stabilizing the equilibrium against external influences such as changes of solvent. No such stabilization is possible in the case of N4PH derivatives (para cases), and this tends to render the azo–hydrazone tautomeric equilibrium of these compounds much more susceptible to the influence of environmental factors.[22,26] In a general manner, it has been believed that an increase in the solvent polarity displaces the tautomeric equilibrium toward the more dipolar hydrazone form. In addition, the NH and the OH groups of both tautomers are capable of forming hydrogen bonds with suitable solvents. Due to the stronger hydrogen-bonding ability of the OH group compared with that of the NH group, mainly the azo form is stabilized.

Furthermore, the position and nature of substituents on the phenyl ring have a bearing on the state of the tautomeric equilibrium. Both experimental results[27] and theoretical considerations[28] have shown that, in the case of the derivatives of SUD, N2PH, and N4PH, there is a general tendency for electron-withdrawing groups to stabilize the hydrazone tautomers. An early explanation attributed[27] this to the fact that the PhC–NH bond of the hydrazone form was more polarizable than the PhC–NN bond of the azo tautomer. Thus, an electron deficiency at the carbon atom in the PhC–NH bond caused by an electron-withdrawing group substituted on the phenyl ring would favor the adoption of the hydrazone form. More recently, it has been pointed out[29] that the azo group –N=N– is an electron acceptor whereas the amino group –NH– is an electron donor.

We believe that the substituent influence on the azo–hydrazone tautomer equilibrium is more related to the conjugation character of the molecule. A para or ortho substituent with an electron-withdrawing mesomeric (–M) effect will generate an electron deficiency on the amino nitrogen atom. Thus, the hydrazone structure will provide a more conjugated molecule than the azo one. Therefore, the hydrazone form would be the more stable because of higher π delocalization energy and thus would be the more favored. On the other hand, a para substituent with an *electron-donating mesomer* (+M) effect will generate an electron excess on the phenylazo nitrogen atom. In this case, the azo structure will provide a much more conjugated molecule than the hydrazone form. Therefore, the azo form would be the more favored.

In the cases of N2nitroPH and RED, the strong *electron-withdrawing mesomeric* (–M) effect of the para-substituted nitro group should move the tautomer equilibrium toward the *hydrazone form* in any solvent. Indeed, the absorption spectra of N2nitroPH and RED were found to be insensitive to the change of solvents. In ethanol and methanol at room temperature, the strong absorption maxima of N2nitroPH and RED at 502 and 485 nm, respectively, have been assigned to the absorption of the hydrazone forms[2,25] while the inflection/shoulders in the 400–440-nm spectral region showed the slight existence of the related azo forms.[2,25] The N2PH molecule does not contain a para-substituted nitro group on the phenyl ring. However, its absorption spectrum was solvent independent[27] and very similar to the absorption spectrum of N2nitroPH. If again, like previous researchers,[2,25] we assign the strong absorption maximum at 498 nm of N2PH in benzene solution to the hydrazone band and the weak inflection/shoulder at 425 nm to the slight existence of the azo form, then the tautomeric equilibrium of N2PH is strongly biased toward the hydrazone form in any solvent.

The case of SUD is not so simple. Although we have mentioned earlier in this discussion that because of the strong intramolecular hydrogen bond, the hydrazone structure is favored and the tautomeric equilibrium would be stabilized against changes of solvent, we have reported a certain solvent dependence of the absorption spectrum of SUD: the height of the azo shoulder in the 370–440-nm spectral region decreased when going from a nonpolar non-hydrogen-bonding solvent to a polar non-hydrogen-bonding solvent. This even further decreased upon further change to a hydrogen-bonding solvent. But whatever the solvent used, the intensity of the absorption band originating from the azo shoulder was low compared to the intensity of the hydrazone peak. Thus, we believe that, in the case of SUD, the tautomer equilibrium is again biased toward the hydrazone form in any solvent.

When flashing N2PH at 355 nm in *benzene* at room temperature, we observed the existence of a product with a maximum of absorption at 450 ± 10 nm which did not show any decay in the 0.5-μs to ~1-ms time domain. Given this spectral datum and the associated time considerations, we can propose two possibilities for the mechanism generating such a product: (1) an intramolecular proton transfer leading to the azo form and (2) a C–N double bond isomerization. If H^+ transfer occurred, then the azo form should be produced and transient depletion or absorption with a maximum near 425 nm should occur. No such transient decay or recovery to ~1 ms was observed at any wavelength from 350 to 600 nm. For other phenylhydrazones where proton transfer occurs, as well as for salicylideneanilines and (hydroxyphenyl)-benzothiazoles, the transient commonly has a decay time in the $\leqslant$400-μs time domain. Moreover, several experimental studies[2,6] have shown that the lowest excited state of the hydrazone form of SUD and some derivatives is lower than the lowest excited state of the azo form. Therefore, since we excited close to the o–o band of absorption, the excited state presumably could not undergo an intramolecular proton transfer leading to the azo form and therefore the process of syn to anti isomerization would be the most reasonable possibility. The same is true for N2nitroPH in benzene.

Upon flashing SUD and RED in *benzene* and *acetonitrile* at 355 and 532 nm at room temperature, we saw in every case a bleaching of the entire 350–570-nm spectral region with no recovery in the 0.5-μs to 1-ms time domain and no transient spectrum with a +ΔOD was seen. Around 450 nm, the ground-state depletion was not as severe as it was expected to be. Therefore, we believe that, for both SUD and RED, a product with a maximum of absorption near ~450 ± 10 nm was indeed formed. One should note that in contrast to N2PH this product must have a much lower extinction coefficient than the original hydrazone form near 450 nm since, again, no positive ΔOD was detected around 450 nm (or the yield is very much smaller). Fischer et al.[2] have reported that after photoequilibration of SUD with excitation at 365 and 405 nm in a 1/1 ethanol/methanol mixture of −120 °C, the absorption spectrum at longer wavelengths than 300 nm was considerably reduced. The extrapolated spectrum showed a broad absorption peak around 450 nm. These latter data are in accordance with our findings. The flash data are consistent with the photochemical process being one of syn to anti isomerization; see later discussion.

From an earlier steady-state study, it has been proposed[7] that N2DPH, which cannot undergo an intramolecular proton transfer, existed in two isomeric forms, characterized by different absorption spectra, separated by a ground-state barrier of about 10 kcal/mol, and interconvertible by light. We have performed a study of this same compound using laser flash spectroscopy techniques. Again,

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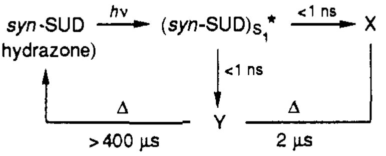
this was done to compare the quality of agreement between our results using laser flash techniques with those obtained from steady-state techniques. We also wanted to evaluate whether transients existed, and determine the kinetics of this photochromism.

Upon flashing N2DPH at 532 nm in ethanol, we observed the existence of a product with a strong absorption band at 550 nm plus depletion. Neither decay nor recovery was detected in the 0.5–400-μs time domain. These spectral results were in accordance with those seen before by steady-state irradiation.[7]

In the cases of N2PH and N2nitroPH, the syn isomer is expected to be the more stable because of the presence of the strong intramolecular hydrogen bond. However, with N2DPH, such a stabilization cannot occur. Moreover, the syn isomer shows a large steric hinderance between the oxygen atom and one phenyl ring. Therefore, we expect the anti isomer to be more stable. We attribute then the absorption band at ~460 nm in nonpolar solvents to the anti isomer and the absorption bands at ~370 and ~515 nm to the syn isomer. Thus, we believe that, upon laser flash irradiation (at 532 nm), N2DPH undergoes an anti to syn isomerization around the C–N double bond—the opposite of N2PH and N2nitroPH. In addition, there was no oxygen influence on the production or kinetics of transient spectra of any of the naphthoquinone phenylhydrazone derivatives in any solvent used (nor triplet energy transfer to β-carotene). We, therefore, believe that the C–N double bond isomerization of all of the foregoing compounds occurs via the lowest excited singlet state in any solvent.

Upon flashing SUD and RED in hydrogen-bonding solvents, we observed different phenomena. We first discuss the mechanisms of the photochromisms before speculating on the nature of the observed colored forms.

Recall that, upon flashing SUD at 532 and 355 nm in *benzene* at room temperature, we observed *only a bleaching* of the entire 350–510-nm spectral region, and again, the ground-state depletion around 450 nm was not as important as expected. Moreover, irradiation of SUD at both 532 and 355 nm in *ethanol* (or methanol) showed, in addition to the bleaching, the existence of a short-lived transient with an absorption maximum at 550 ± 10 nm with a first-order decay lifetime to the baseline of ~2 μs (in ethanol). Recall that the *ground-state depletion* only *partially recovered* (20–25%) to the baseline via a first-order process with a lifetime of ~2 μs, giving a residual permanent negative ΔOD (lifetime >400 μs). We may summarize our experimental results for the photophysics and photochemistry of SUD in *ethanol* by the following scheme:

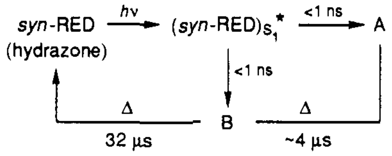


(1)

where discussion of the identity of X and Y will be considered after that for RED.

Upon flashing RED at 532 nm in *methanol*, we observed a bleaching of the entire 380–515-nm spectral region, and again, the ground-state depletion around 460 nm was not as important as expected. Recall that, in the spectral region from 380 to 515 nm, the ground-state depletion recovery was first order *to the baseline* (not for SUD), as was the decay of the transient +ΔOD maximum near 550 nm (both had the same lifetime of ~32 μs). Also, recall that in the 530–650+-nm region a first-order growth was present with a lifetime of ~4 μs (as well as the 32-μs decay being present). Finally it is worth repeating that, for RED in benzene and acetonitrile, *only* a bleaching occurred in the spectral region from 380 to 515 nm and no recovery was seen to 1 ms (no +ΔOD transient spectrum existed). It is thus clear that a H-bonding solvent causes a substantial change in the photochemistry of RED, moreover, that substantial alteration in the photochemistry is induced by the addition of a NO_2 group to SUD (RED vs SUD) in H-bonding solvents. However, the photochemistry in a non-H-bonding solvent appears to be similar for SUD and RED; that is, both are assigned as showing syn to anti isomerization.

The kinetic data and spectra in *methanol* can be fitted to the following scheme:

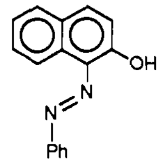


(2)

It is not known whether A and B are formed adiabatically or nonadiabatically. The nature of A and B will be discussed shortly.

In the case of *both* SUD and RED in *benzene* (and acetonitrile for RED), *only* depletion is seen which does not recover up to ~1 ms (not affected by O_2). The only two reasonable choices for the photochemistry (taking into account that any product is not from decomposition on the basis of the recovery of the depletion seen in methanol) are (1) syn ↔ anti isomerization and (2) proton or H atom transfer from the NH group to the C=O group. Recall the lifetime of the photoproduct was ≥1 ms. If the process were proton transfer, the lifetime should clearly be notably shorter on the basis of all the information available on proton transfer type photoproducts of salicylideneanilines and (hydroxyphenyl)-benzothiazoles. If the process were intramolecular H atom extraction, then a triplet transient would very likely exist which was not observed, and the H atom back-transfer should have a lifetime considerably shorter than 1 ms. Therefore, we believe that the photoprocess is syn → anti isomerization of the hydrazone form. Note that there is no distinguishable spectrum for the anti isomer which means the syn and anti spectrum are reasonably similar (the depletion spectrum really is a combination of syn and anti).

In the case of *SUD* in *ethanol*, a significant long-lived depletion ($\tau \geq 1$ ms) with a small fraction (20–25%) of a short-lived first-order recovery ($\tau \approx 2$ μs) occurred. There also was a relatively weak +ΔOD transient spectrum (maximum 550 nm) which had a first-order decay lifetime of 2 μs. Neither of these were affected by O_2 (vs N_2). In view of the latter, the +ΔOD does not result from a triplet transient. In order to account for the results in RED along with those in SUD in a H-bonding solvent, we believe that X is a proton-transferred form to give



This then decays in 2 μs to the anti hydrazone (Y) whose spectrum resembles that of syn (thus giving the appearance of a recovery of syn). The anti hydrazone Y appears stable on the time scale available to us (>400 μs).

The addition of a p-NO_2 group on the phenyl ring of the hydrazone moiety of SUD to make RED causes a noticeable change in at least the kinetics of the reactions compared to SUD. Firstly, it would seem that if the ~550-nm maximum is associated with a proton-transferred product in SUD, it would also have to be associated with a proton-transferred product in RED. In the case of RED in a H-bonding solvent, the principal differences compared to SUD are that for RED the depletion occurs with a first-order recovery lifetime of ~32 μs (vs 400 μs for SUD for most all of the recovery, ~2 μs for 20–25%) and there is a distinguishable first-order build-up process, with a lifetime of ~4 μs, on top of the absorption present immediately after the flash. The absorption with a maximum at ~550 nm completely decays by a first-order process with a lifetime of ~32 μs (same as the recovery). It is clear that the NO_2 group has had a marked effect.

We believe that, for RED, A (eq 2) is a conformer of the proton-transferred form as given above for SUD. This then forms the anti hydrazone B (the buildup), which then decays to the syn hydrazone (RED); remember the anti form is already present because it is produced competitively in <1 ns; see eq 2. All photochemical processes occur from the excited singlet state.

Fischer et al.[3] have reported that, upon cooling N4PH, the tautomeric equilibrium shifts toward the hydrazone form of N4PH in methylcyclohexane or toward the azo form in methanol. The alcoholic solution of −140 °C contains practically only the trans azo form, which showed a strong absorption band with a maximum at $\sim$410 nm. Upon steady-state irradiation at 546, 365, 436, and 405 nm in ethanol, the trans azo form was found[3] to be photoequilibrated with its cis isomer which showed weak absorption maxima at $\sim$340 and $\sim$480 nm. In turn, the unstable cis isomer was thermally converted into the trans isomer via the phenylhydrazone. We have carried out a study of this same compound using laser flash spectroscopy techniques. First, we looked at the azo form in ethanol at −75 °C. This was done to compare the quality of agreement between our results using laser flash techniques with those of Fischer[3] who employed steady-state techniques. We also wanted to determine if transients could exist and be isolated at such temperature. We have reported that laser flash irradiation at 355 nm of N4PH in ethanol at −75 °C gave two bands of absorption with maxima at 340 ± 10 nm and 480 ± 10 nm. These results are the same as those seen before[3] when the trans azo was converted to the cis isomer by steady-state irradiation.

We have reported that flash irradiation at 355 nm of the hydrazone form of N4PH in methylcyclohexane at −75 °C (where the absorption maximum is at 483 nm) gave a product with a maximum positive ΔOD at 410 ± 10 nm which did not show any decay in the 0.5–400-μs time domain. Given the fact that no intramolecular proton transfer can occur and given the results we discussed earlier, we assign the spectral changes to be the result of the anti ↔ syn isomerization of N4PH in the hydrazone form. This isomerization is in marked contrast to what Fischer et al. have reported.[3] For them, no direct photoconversion involving the hydrazone form of N4PH seemed to take place.

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Norrish II Reactions of Neat Liquid-Crystalline Ketones. Comparison between Nematic and Solid Phase Order and Control of Photoproduct Distributions[1,2]

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Abstract: The Norrish II photoreactions of *trans*-1-(4-pentanoylphenyl)-4-pentylcyclohexane (**1a**) and *trans*-1-heptyl-4-(4-pentanoylphenyl)cyclohexane (**1b**) have been examined in their solid, nematic, and isotropic phases. The influence of phase on the product distributions is found to be negligible in the nematic but significant in the solid phases. Phase order, probed by deuterium NMR spectroscopy of the compounds deuteriated at the methylene α to the carbonyl group and by differential scanning calorimetry, has been correlated with the photochemical results. The lack of influence of the nematic phase on the Norrish II reactions of neat **1** is consistent with previously reported results obtained from irradiations of ketones doped in inert nematic matrices. The influence of solid phase order on the photoproduct selectivity of **1** is greater than that observed in some studies on analogous guest ketones in other solid phase hosts, but smaller than in others. A discussion of some of the factors leading to phase control over molecular motions along a reaction coordinate is presented.

Introduction

Norrish II photoreactions of ketones (Scheme I) have been employed for several years to probe the steric and electronic microenvironments afforded by a variety of ordered media.[3] Among these are liquid crystals,[4-11] where the control over the probe reactions by various phases has ranged from being very high to undetectable. In the solid phases of the same media, the control by solvent has been usually, but not always, greater. When analyzing results in these studies, it has been necessary to consider the influence of the ketones on their cybotactic region (i.e., the whole volume in which the molecular order of the solvent has been affected by the solute[12]) in addition to the intrinsic order of the medium.

As a means to avoid complications from a solute's disturbance of its local environment and to compare directly the control that liquid-crystalline and solid phases exert over a ketone's photoproduct selectivity, we have examined the Norrish II reactions of two mesogenic ketones, *trans*-1-(4-pentanoylphenyl)-4-pentylcyclohexane (**1a**) and *trans*-1-heptyl-4-(4-pentanoylphenyl)cyclohexane (**1b**), in their neat isotropic, nematic, and solid phases. Monotropic smectic phases form but are too unstable to obtain reliable data. The photolyses are complemented with results from differential scanning calorimetry (DSC), ^{2}H NMR spectroscopy on **1a** and **1b** deuteriated at the methylene group α to the carbonyl, and optical microscopy. We have also reinvestigated and reassigned the phases of **1a** and **1b** based upon our observations.

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(1) Part 43 in our series Liquid-Crystalline Solvents as Mechanistic Probes. For Part 42, see: Sheikh-Ali, B. M.; Weiss, R. G. *Liq. Cryst.* **1991**, *10*, 575.

(2) Dedicated to George S. Hammond on the occasion of his 70th birthday.

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