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Fluorescence self-quenching of substituted *N*,α-diphenylnitrones in various solvents

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Abstract

Photophysical and photochemical properties for *N*,α-diphenylnitrone **1a**, α-*p*-methoxyphenyl-*N*-phenylnitrone **1b**, *N*-(*t*-butyl)-α-phenylnitrone **1c**, *cis*-α-cyano-*N*,α-diphenylnitrone **1d**, *trans*-α-cyano-*N*,α-diphenylnitrone **1e**, α-methoxycarbonyl-*N*,α-diphenylnitrone **1f** and α-ethoxycarbonyl-*N*,α-diphenylnitrone **1g** were investigated. Photolysis studies in polar and protic solvent such as ethanol revealed that the singlet-state formation was preferred in nitrones and this was confirmed by the fluorescence investigations. Absorption and fluorescence spectra indicated considerable shifts with variation in polarity of the solvent.

Keywords: Nitrone; Singlet state; Self-quenching; Fluorescence spectra; Photolysis

1. Introduction

Nitrones are a family of compounds that have been studied extensively [1–7] due to their stability i.e. easy to handle in air at ordinary temperature, but, under prolonged influence of light, rearrangement occurred. As well as, the synthetic utility of 1,3-dipolar cycloadditions between nitrones and alkenes has been thoroughly established [8]. The importance of these reactions stems from the utility of the obtained isoxazolidines as synthetic intermediates [9]. They are cleaved into their components, a carbonyl compound and an *N*-substituted hydroxylamine, by treatment with acid or base [10,11]. In the presence of another carbonyl compounds, nitrones can exchange their carbonyl components in acidic medium. Structurally, a nitrone is a tautomer of an oxime.

Two general routes exist for preparation of nitrones. The earlier method was nitrones formation by reaction of a hydroxylamine and a carbonyl compound [12–16]. The reaction conditions and their work-up were nearly easy, but their low yields were their major disadvantage. The other one was nitrones generation by reaction of oximes with a variety of alkylating agents, which offers one of the most convenient nitrones generation methods [17–23]. In 1988 Grigg and coworkers discovered a new reaction, now known as Grigg's nitrone generation, which involves the *N*-alkylation of oximes through conjugate addition to electron-deficient alkenes to produce nitrone 1,3-dipoles (nitrones formation step) [23]. The resulting nitrone intermediate, under the reaction conditions, further undergo 1,3-dipolarcycloaddition reactions to the same alkenes to give cycloadducts (cycloadditions step). Conjugate addition step is often slower for most of electron-deficient alkenes than the subsequent cycloadditions step under heating conditions. Therefore, cycloadducts instead of nitrones are usually produced in the Grigg reaction, indicating that this method cannot be a highly powerful synthetic route to nitrones.

In this paper, we would like to present the convenient synthetic access to *C*,*N*-diaryl nitrones from phenyl hydroxylamines and carbonyl compounds, as well as the photophysical and photochemical properties and reactivity of *N*, α-diphenylnitrone **1a**, α-*p*-methoxyphenyl-*N*-phenylnitrone

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1b, *N*-(*t*-butyl)-α-phenylnitrone **1c**, *cis*-α-cyano-*N*,α-diphenylnitrone **1d**, *trans*-α-cyano-*N*,α-diphenylnitrone **1e**, α-methoxycarbonyl-*N*,α-diphenylnitrone **1f** and α-ethoxycarbonyl-*N*,α-diphenylnitrone **1g** were investigated. Steady-state and time-resolved absorption and fluorescence spectroscopies were employed to investigate photochemical properties of these molecules in various solvents.

2. Experimental

2.1. Materials

Cyclohexane, ethanol, dichloromethane and acetonitrile (for fluorescence spectroscopy from Merck Chemical Co.) were used as solvents without further purification. All solvents were checked for purity by absorption and emission spectroscopy. *N*,α-Diphenylnitrone **1a**, α-*p*-methoxyphenyl-*N*-phenylnitrone **1b**, *N*-(*t*-butyl)-α-phenylnitrone **1c,** *cis*-α-cyano-*N*,α-diphenylnitrone **1d**, *trans*-α-cyano-*N*,α-diphenylnitrone **1e** were synthesized and purified according to the existing procedures [12–15].

2.1.1. α-Methoxycarbonyl-N,α-diphenylnitrone *1f*

Nitrosobenzene **3** was prepared by oxidation and then reduction of nitrobenzene according to the previously reported procedure with the yield of 77.6% [24]. Methyl α-bromophenylacetate pyridinium salt was synthesized by a three-step reaction. In the first step, α-bromophenylacetic acid was prepared via bromination with P/Br_2 and Br_2/CCl_4, respectively, according to the previously reported method [25] with 61% yield. In the second step, methyl α-bromophenylacetate was synthesized by conventional esterification of α-bromophenylacetic acid with methanol in the presence of concentrated sulfuric acid. After 3 h refluxing in oil bath, the ester solution was allowed to cool to room temperature. The obtained solution was neutralized with a saturated solution of sodium bicarbonate and then washed twice with distilled water. The organic layer was separated and dried over anhydrous magnesium sulfate. Removal of the solvent by distillation under normal pressure and then distillation of the obtained ester under reduced pressure produced methyl α-bromophenylacetate with 63% yield. In the last step, the pyridinium salt of methyl α-bromophenylacetate was prepared by stepwise addition of pyridine to a solution of methyl α-bromophenylacetate in ether. After 30 min stirring, the pale yellow precipitate appeared in a red solution. The precipitated pyridinium salt was collected by filtration, washed three times with petroleum ether and dried at room temperature for 24 h to leave a creamy salt with 88.6% yield. Into a 100 ml round-bottomed flask 2.54 g (8.33×10^{-3} mol) pyridinium salt, 0.85 g (7.9×10^{-3} mol) nitrozobenzene and 41.5 ml ethanol were added. The mixture was stirred until the heterogeneous mixture was converted to a clear solution. To this solution, 0.33 g NaOH in 8.4 ml distilled water (1N) was added drop-wise in 25 min and the solution temperature was kept at 20 °C. Ethanol was removed under reduced pressure to leave a viscous liquid. By cooling the residue an overnight in the refrigerator, a pale orange precipitate was formed. Recrystallization from hexane or cyclohexane gave 0.76 g (36.1%) white needle crystals. mp 96.9 °C (recrystallized from cyclohexane) and 93.6 °C (recrystallized from hexane). IR (cm^{-1}) (KBr): 3050 (w), 2945 (w), 1720 (s), 1590 (w), 1513 (m), 1475 (w), 1432 (m), 1263 (m), 1210 (m), 1125 (m), 760 (s), 685 (s); ^{1}H NMR (ppm) ($CDCl_3$, TMS): δ 3.49 (s, 3H), 3.52 (s, 3H), 7.425 (b, 16H), 7.95–8.38 (m, 4H). Elemental analysis: calculated for $C_{15}H_{13}NO_3$, C (70.57%), H (5.13%), N (5.48%); found C (70.6%), H (5.1%), N (5.2%). Mass spectrum: *m*/*e* 255, 239 ($M^{\bullet+} - O$), 196 ($M^{\bullet+} - CO_2Me$), 180 ($M^{\bullet+} - OCO_2Me$), 105 ($Ph–C{\equiv}O^{\bullet+}$), 91 ($NPh^{\bullet+}$).

2.1.2. α-Ethoxycarbonyl-N,α-diphenylnitrone *1g*

α-Ethoxycarbonyl-*N*,α-diphenylnitrone **1g** was prepared by condensation of nitrozobenzene with pyridinium salt of ethyl-α-bromophenylacetate in accordance to the above-mentioned procedures. The yield of this nitrone was 63.53% and its melting point was 74.2 °C (recrystallized from cyclohexane). IR (cm^{-1}) (KBr): 3060 (w), 2980 (w), 2930 (w), 1720 (s), 1595 (w), 1513 (m), 1485 (m), 1465 (w), 1455 (w), 1446 (m), 1375 (m), 1262 (s), 1215 (m), 1130 (m), 762 (s), 685 (s); ^{1}H NMR (ppm) ($CDCl_3$, TMS): δ 0.9 (t, $j = 2$ Hz, 2H), 1.42 (t, $j = 3$ Hz, 2H), 4.02 (q, $j = 6$ Hz, 3H), 4.45 (q, $j = 3$ Hz, 3H), 7.23 (m, b, 16H), 8.09–8.28 (m, 4H) ppm.

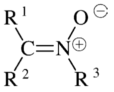
2.2. Apparatus and methods

Proton nuclear magnetic resonance (^{1}H NMR, 80 MHz) spectra were recorded on a Bruker AW-80 MHz instrument. Tetramethylsilane (TMS) was used as an internal reference. IR spectra were recorded on Philips PU-9716 IR spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wave number (cm^{-1}). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Mass spectra were recorded on a Varient-Sinngan GC–MS-DS 8430. The absorption spectra were recorded using a Perkin-Elmer UV-550SE and Shimadzu UV-160 spectrophotometer. Measurements of steady state fluorescence were made using a Shimadzu RF-5000 spectrofluorophotometer. Steady-state photolysis was carried out with a Hanovia high pressure mercury arc-lamp (150 W) with the wavelength region of light over than 280 nm.

3. Result and discussion

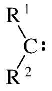
Nitrones are usually represented by formula such as **1**, which implies the presence of a positive charge on the nitrogen. However, it has been proven that this positive charge is delocalized between the nitrogen and the α-carbon. The extent of this delocalization will naturally be influenced by the substituents in the α-position as well as on the nitrogen.

Table 1
Chemical structures of nitrones **1a**–**1g**

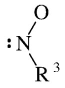
Nitrones 			
	R^1	R^2	R^3
1a	$-C_6H_5$	$-H$	$-C_6H_5$
1b	$-(C_6H_4)-OCH_3(p)$	$-H$	$-C_6H_5$
1c	$-C_6H_5$	$-H$	$-C(CH_3)_3$
1d	$-C_6H_5$	$-CN$	$-C_6H_5$
1e	$-CN$	$-C_6H_5$	$-C_6H_5$
1f	$-C_6H_5$, $-CO_2CH_3$	$-CO_2CH_3$, $-C_6H_5$	$-C_6H_5$, $-C_6H_5$
1g	$-C_6H_5$, $-CO_2C_2H_5$	$-CO_2C_2H_5$, $-C_6H_5$	$-C_6H_5$, $-C_6H_5$

The structures of some nitrone derivatives, with their fluorescence spectral changes in several solvents will be discussed, have been summarized in Table 1.

With respect to the nitrone structure there are two positions in the parent nitrone molecule: the α-position (or C-position) and the N-position

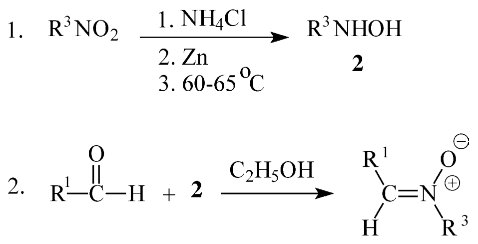


Component A

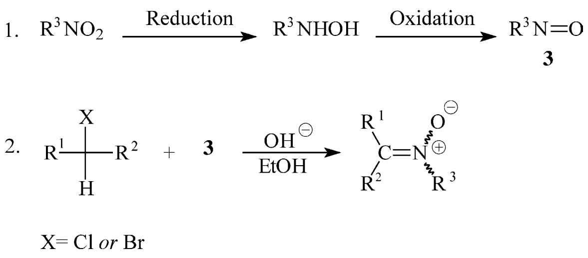


Component B

On the basis of nitrone substitution, two methods were predicted for nitrone synthesis. (a) Preparation of nitrones with hydrogen on α-position, so-called "Aldonitrones": this category of compounds obtained from the reaction of aldehyde of component A with the substituted hydroxylamine of component B (Scheme 1) and (b) synthesis of nitrones with three non-hydrogenic substituents on α- and N-positions, so-called "Ketonitrones": these nitrones are prepared from the reaction of α-halogenated derivative of component A with the nitroso compound of component B (Scheme 2).



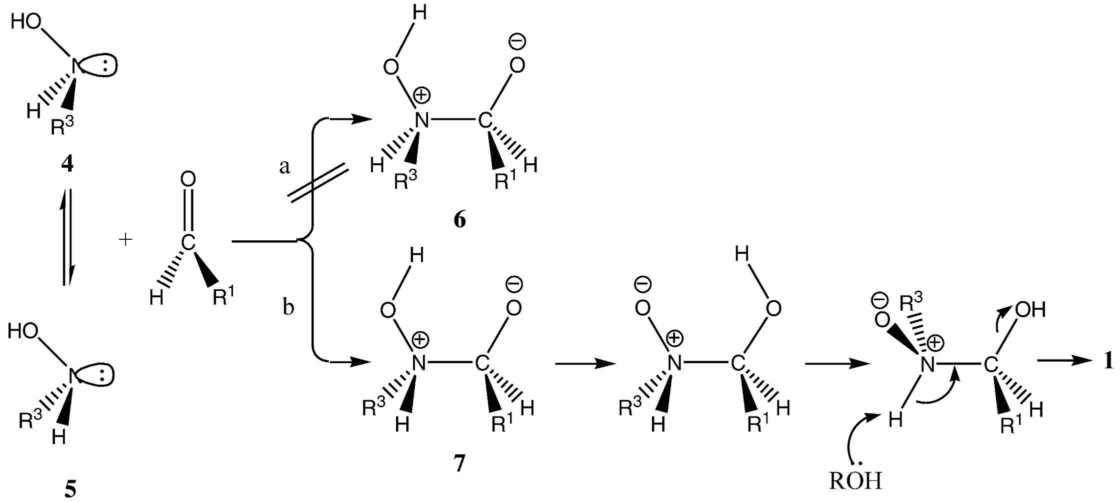
Scheme 1.



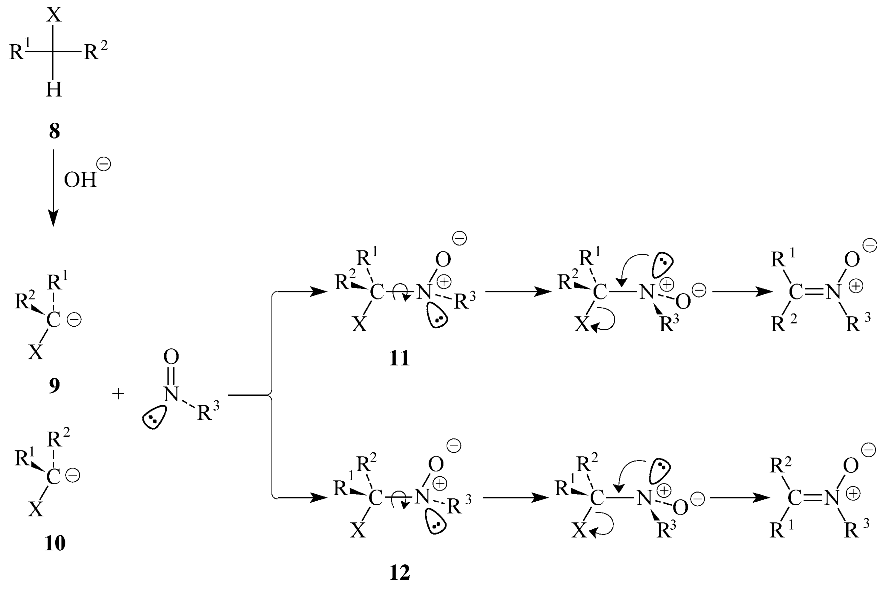
Scheme 2.

Aldonitrones usually exist entirely as *Z* isomers, whiles ketonitrones always show a mixture of *Z* and *E* isomers. This geometrical isomerism of nitrones is due to the low or high steric hindrance, which appeared in several steps of reactions. In aldonitrones, the substituted hydroxylamine such as all amines has a very low energy barrier for nitrogen inversion. Consequently, this inversion rate is so high that two enantiomers **4** and **5** could react with aldehyde identically. The repulsion between R^1 and R^3 groups increases the activation energy of the first route (a), resulting the easier formation of the *Z* isomer from second route (b) (Scheme 3).

In contrast to aldonitrones, in ketonitrones, the α-halogenated derivatives **8** produces carbanions **9** and **10** in basic media. By reaction of these two species with nitroso compounds, two intermediate compounds **11** and **12** will be obtained, respectively. In **11**, R^3 is anti with R^2 and gauche with R^1 but in **12**, R^3 is anti with R^1 and gauche with R^2. So, with regard to the type and bulkiness of the substituents, the steric hindrance could be observed in the two intermedi-



Scheme 3.



Scheme 4.

ates more or less and therefore, the formation of two isomers could be possible (Scheme 4).

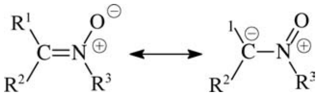
The obtained absorption data from UV spectra of nitrones **1a**–**1g** in acetonitrile, ethanol and methylene chloride have been summarized in Table 2.

All of these nitrones show similar behavior. In the UV region, three strong absorption bands are appeared at λ_{max} of 226–241, 240–298 and 302–330 nm corresponding to E1, E2 and K bands, respectively. In some case the E2 and E1 bands overlap with each other, which make the λ_{max} and ε_{max} determination difficult. In all cases a shift to lower wavelengths could be observed in ethanol as a protic solvent. This is due to the formation of hydrogen bonding between protons from the solvent and non-bonding electrons on the oxygen atoms, which causes the decrease of electronic density on the molecule. This will make the $\pi \rightarrow \pi^*$ transition more difficult. The presence of –OCH_3 group at *para* position in **1b** increases the conjugative system and a bathochromic shift could be seen. In **1c**, E1 and E2 are only observed and there is no trace of K-band. Entrance of a *t*-butyl group instead

Table 2
UV-spectroscopic data of nitrones **1a**–**1g** in various solvents

Nitrone	Solvent	E1, λ_{max} (ε_{max})	E2, λ_{max} (ε_{max})	K, λ_{max} (ε_{max})
1a	Acetonitrile	237 (9247)		316 (16337)
	Ethanol	231 (10647)	249 (6290)	314 (20024)
	Methylene chloride	237 (9992)		318 (16158)
1b	Acetonitrile	239 (10645)	260 (6566)	330 (23293)
	Ethanol	238 (10374)		324 (20972)
	Methylene chloride	241 (11246)		330 (23419)
1c	Acetonitrile	234 (5363)	298 (15108)	–
	Ethanol	226 (7038)	294 (17180)	–
	Methylene chloride	236 (6837)	298 (17067)	–
1d	Acetonitrile	230 (8636)	240 (6553)	316 (17907)
	Ethanol	224 (13490)	242 (5978)	317 (17740)
	Methylene chloride	232 (7289)	242 (5690)	320 (17805)
1e	Acetonitrile	238 (6608)		320 (7319)
	Ethanol	238 (7582)		322 (8153)
	Methylene chloride	240(10638)		328 (11162)
1f	Acetonitrile	234 (9486)	248 (6728)	306 (12340)
	Ethanol	226 (9326)	248 (7080)	306 (14046)
	Methylene chloride	238 (8362)	248 (7182)	306 (12554)
1g	Acetonitrile	234 (9647)	250 (7122)	305 (12870)
	Ethanol	226 (9581)	252 (6200)	302 (14465)
	Methylene chloride	236 (9027)		310 (13239)

of phenyl group decreases the conjugation length relative to **1a** and eventually a hypsochromic shift with decreasing in absorption intensity could be expectable. In all ketonitrones, R_2 is an electron-withdrawing group that induces a double bond and a single bond characteristic to N–O and C–N bond, respectively, as shown below:



Consequently, the resonance between two phenyl rings (R_1 and R_3 substituents) decreases. This will result in appearing of the K-band at lower wavelength relative to aldonitrones. Between ketonitrones **1d**–**1g**, **1d** and **1e** shift to higher wavelength relative to **1f** and **1g** because, the electronic density of $-CO_2R$ is not as much as –CN group. On the other hand, between **1d** and **1e**, the bathochromic shift for the *cis* compound (**1e**) comes from its geometry. In **1d** the oxygen and –CN group are in opposite direction with each other and cause the diminishing of the electronic density. A typical UV spectrum of nitrone **1e** is shown in Fig. 1.

To determine the transition state of nitrones, the spectral changes of the nitrone solution were investigated by UV spectrophotometer before and after irradiation of the nitrone **1a** in ethanol under argon and oxygen atmosphere using a high-pressure mercury vapor lamp. In an argon-saturated ethanol solution, the spectrum immediately after the UV excitation has a maximum at 210 nm. The intensity of this peak decreased within 26 min (13 × 2 min) and during this decrease, a new band at 230 nm was appeared, which was not related to the preliminary nitrone. The decay rate of transient bands in argon- and oxygen-saturated solutions was unchanged after 30 s irradiation, suggesting that the transient bands are due to the singlet transition of nitrones (Fig. 2). Together with this new band, an isosbestic point had been located at about 220 nm, indicating that two mixtures were responsible for these spectral changes. This can be understood in terms of electrocyclic rearrangement from oxaziridine forms **13** to amide forms **14** due to the migra-

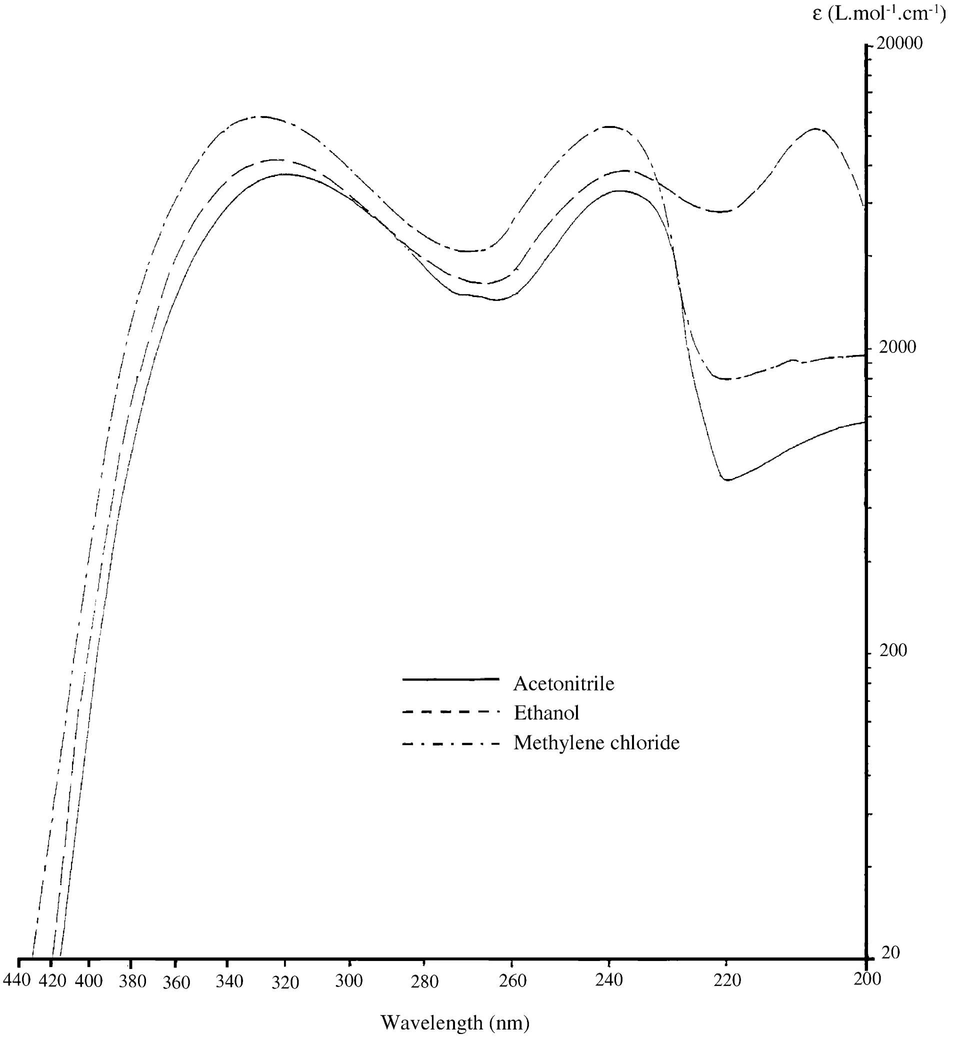


Fig. 1. Absorption spectra of *trans*-α-cyano-*N*,α-diphenylnitrone **1e** in various solvents with 1.0 cm optical path.

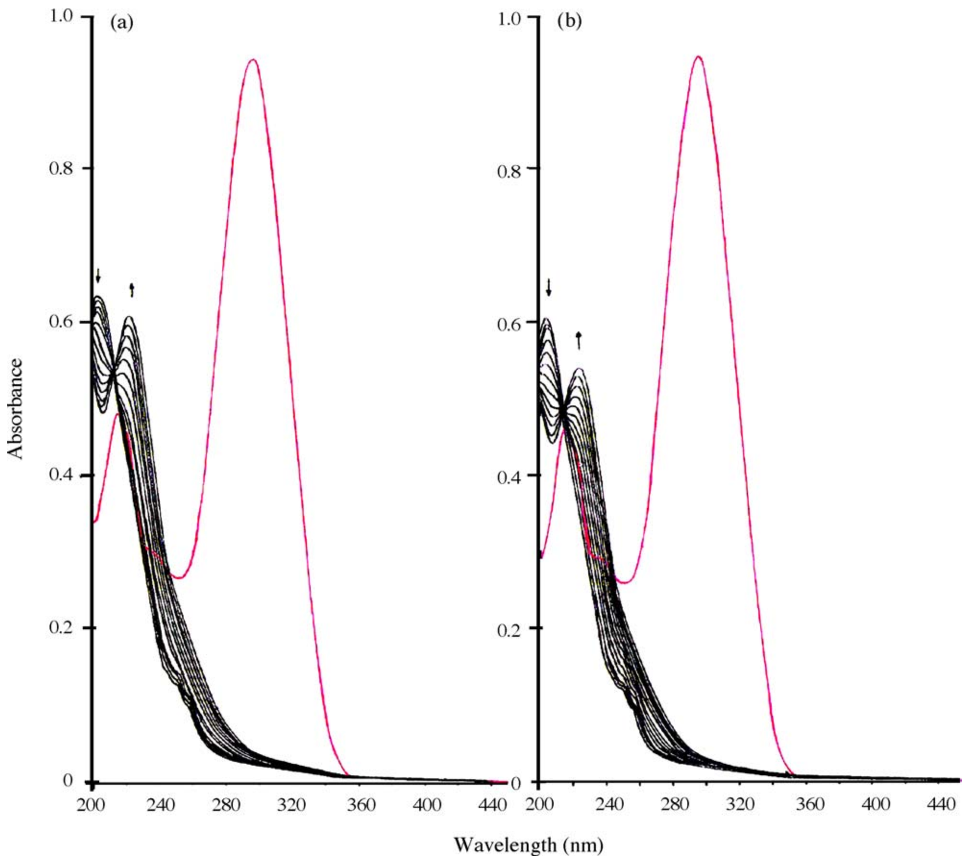
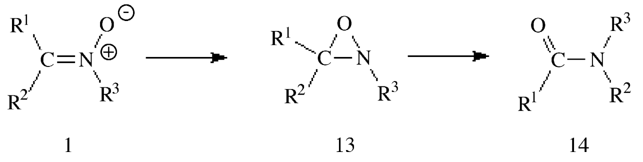


Fig. 2. Transient UV spectra of *N*,α-diphenylnitrone **1a** (1.17×10^{-4} M) in ethanol before (—) and after (——) photolysis: (a) Ar-saturated, (b) air-saturated.

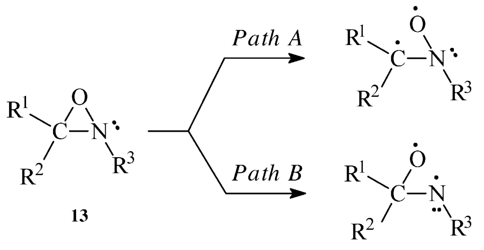
tion of oxygen atom on nitrogen to carbon atom according to Scheme 5.

Several studies have been performed on stability of oxaziridine containing alkyl [26], *N*- or α-aryl [27,28], α,α- or *N*,α-diaryl or triaryl [29–31] substituents. It has been revealed that the oxaziridines obtained from the photochemical reaction of diaryl nitrones are not separatable in most cases according to their instability and are converted directly to their corresponding amide via ring opening reaction. This ring opening reaction is related to electron-withdrawing or releasing of substituents. If the derivatives on carbon atoms are electron-withdrawing groups the N–O bond will be dissociated and amide compound will be formed. As the C–O bond cleavage occurs, the presence of electron-withdrawing group on the carbon atom will result in destabilization of the carbon radical and the consequent diradical. On the other hand, the presence of electron-releasing group on carbon atom causes the C–O bond cleavage and produces primary nitrones (Scheme 6). Electron-withdrawing groups on the nitrogen atom will cause the cleavage of N–O bond (path B). The resulting diradical are stabilized because of delocalization of the three electrons on the nitrogen atom. In contrast, electron-releasing groups on nitrogen will favor the reaction path through the cleavage of C–O bond (path A). N–O bond cleavage is the predominating route in diaryl nitrones and this proves the electron withdrawing characteristic of phenyl groups.

To investigate the fluorescence behavior of nitrones in several solvents, emission spectra of all nitrones were recorded in acetonitrile, ethanol and methylene chloride by fixing the excitation wavelength at 310 nm. Consequently, a new



Scheme 5.



Scheme 6.

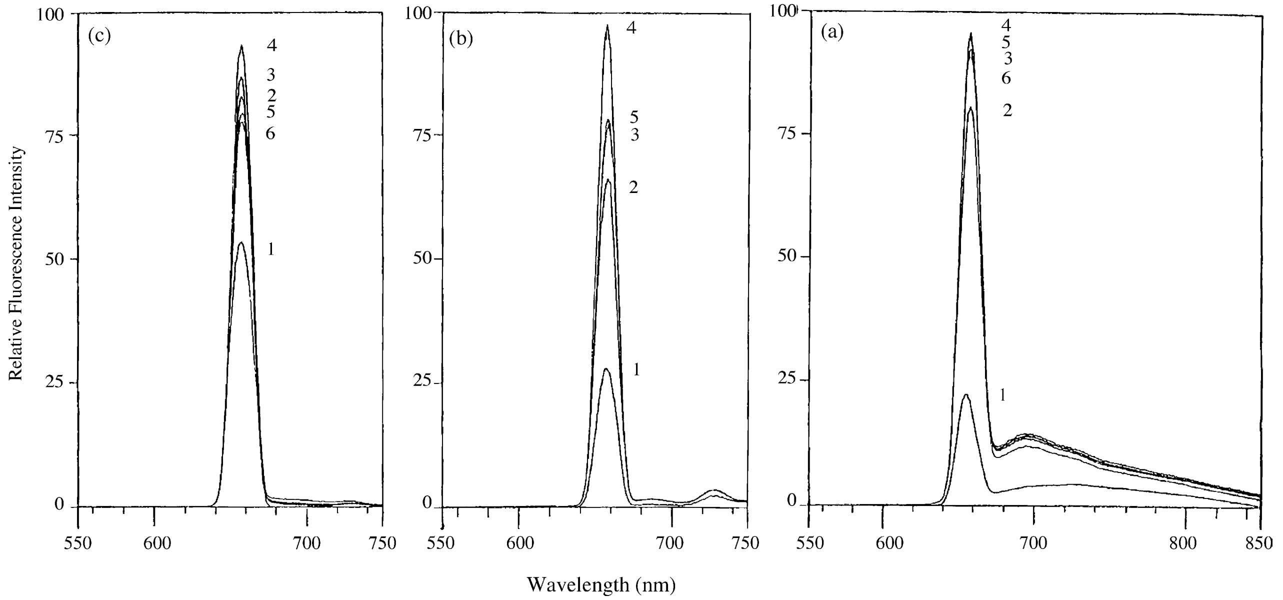


Fig. 3. Self-quenching of α-*p*-methoxyphenyl-*N*-phenylnitrone **1b** in: (a) acetonitrile, (b) ethanol and (c) methylene chloride at **1**: 4.84×10^{-5} M, **2**: 4.84×10^{-6} M, **3**: 4.84×10^{-7} M, **4**: 4.84×10^{-8} M and **5**: 4.84×10^{-9} M of nitrone **1b**.

band with a maximum around 597–660 nm appears. Table 3 shows the maximum emission of nitrones **1a**–**1g** in different solvents.

The dependence of fluorescence intensity to nitrone concentration illustrates the self-quenching phenomenon. By decreasing the nitrone concentration to a specific concentration (ideal concentration), the fluorescence intensity increases and after that, by decreasing the nitrone concentration the fluorescence intensity decreases too. The spectra obtained from the nitrone systems vary in intensity, but no change is observed in the shape or the position of the band maxima (Fig. 3).

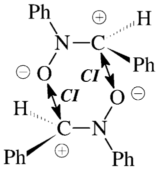
The presence of a methoxy group as an electron-releasing substituent in compound **1b**, increases the delocalization via increasing the conjugation system and consequently affects to lower the energy level of the π^* orbital and gives it less antibonding characteristics. In contrast, replacement of the phenyl group with a *t*-butyl group in nitrone **1c** decreases the conjugation system and as a result the distance between π and π^* levels increases. Therefore, in comparison with nitrone **1a,** a bathochromic shift (or red shift) is observed for compound **1b** and a reverse trend (hypsochromic or blue shift) is seen for nitrone **1c**. In ketonitrone **1d** and **1e**, conjugation of chromophores has a profound effect on the spectral properties. It is observed that the nitrones **1d** and **1e** have strong emission bands, which are shifted to longer wavelengths (about 20 nm) as compared with the similar peak for an unconjugated nitrone **1a**. In nitrones **1f** and **1g** two parameters act in opposite directions. Electronic density due to the presence of methyl ester group cause a bathochromic shift and electron-withdrawing properties of this substituent makes a hypsochromic shift. The interference of these two contrary effects shifts the emission wavelength of nitrone **1f** and **1g** to a similar region of nitrone **1a** accidentally.

Table 3
Maximum fluorescence wavelength of nitrones **1a**–**1g** in various solvents

Nitrone	λ_{max} (em) (nm)		
	Acetonitrile	Ethanol	Methylene chloride
1a	618	617	618
1b	660	659	660
1c	597.6	597	597.6
1d	638	636	638.8
1e	638	637	639
1f	618	618	618
1g	620	620	620

The solvent nature did not exert any change on the shape and the position of the band maxima, and only affect the relative fluorescence intensity. A typical diagram of the relative fluorescence intensity versus nitrone concentration in different solvents has been shown in Fig. 4.

In all above plots the relationship between the relative fluorescence intensity and nitrone concentration before and after ideal concentration were linear. In aldonitrones **1a**–**1c**, the maximum fluorescence intensity was observed in acetonitrile. The intensities in methylene chloride were less than acetonitrile and also in ethanol were less than methylene chloride. This sequence is due to the dipole–dipole interaction between 1,3-dipoles of nitrone molecules as shown bellow:



CI = Coulombic Interaction

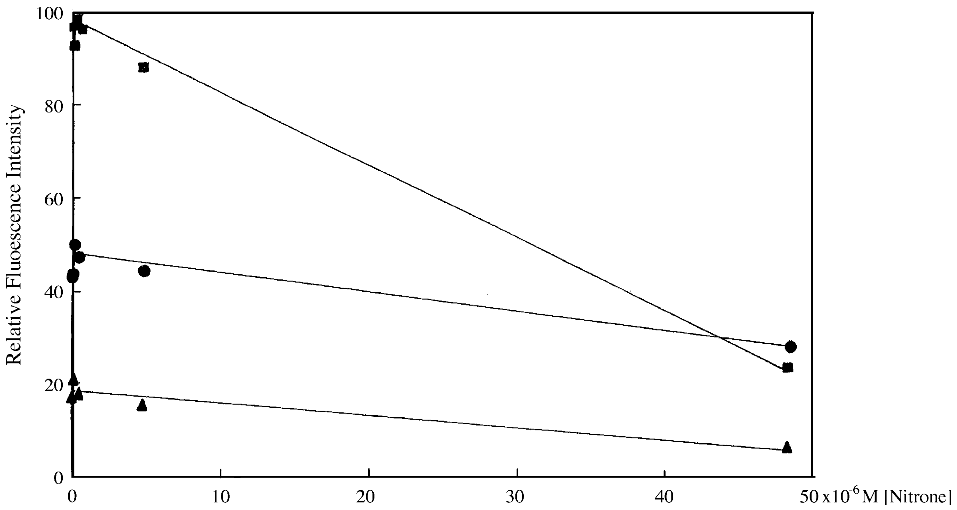
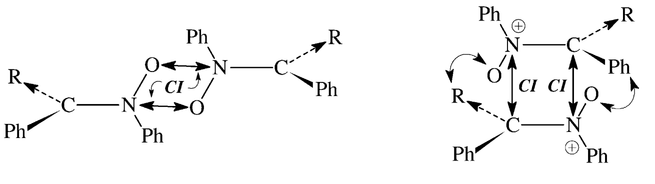


Fig. 4. Plots of relative fluorescence intensity vs. α-*p*-methoxyphenyl-*N*-phenyl nitrone (**1b**) concentration in: acetonitrile (■), ethanol (▲) and methylene chloride (●).

It is better to investigate the interaction between the nitrone molecules in the ground state with another one in the excited state. As the singlet excited state lifetime is very short, the corresponding dipole moment from excitation changes rapidly. So, there is no much time for two molecules in the ground and excited states to find each other. By increasing the dielectric constant of solvent, separation between these molecules is increased and consequently self-quenching of a nitrone with another one will be decreased. Therefore, the relative fluorescence intensity increases. According to this hypothesis, it is expected that the relative fluorescence intensities will follow the trend based on dielectric constant i.e. acetonitrile > ethanol > methylene chloride. The fluorescence intensity in acetonitrile was maximum but according to the protic characteristic of ethanol, the excitation becomes difficult due to solvation of nitrone via hydrogen bonding. As a result, the relative fluorescence intensity decreased progressively even less than methylene chloride. The presence of electron-withdrawing group on the carbon atom of ketonitrones **1d**, **1e**, **1f** and **1g** caused a new charge distribution in nitrone systems. Because of delocalization of the negative charge throughout the nitrone molecules, nitrogen poses a whole positive charge. On the other hand, oxygen and carbon will bear two partial negative charges. By changing molecule structure or substituent groups, the amount of partial negative charges on each center varies. Consequently, instead of an interaction between 1,3 center a 1,2 interaction would be observed as below:



CI = Coulombic Interaction

According to high steric hindrance, which occurred in the above cases these interactions will not be important and it is influenced by the other parameters such as polarity, diffusion coefficient of solvent and effective volume of molecule. Thus no specific trend could be observed. To investigate the self-quenching phenomena in nitrone systems, the equation for determination of the relative fluorescence yields can be written as below:

$$I^0/I = 1 + K_q\tau[Q] \qquad (1)$$

where I^0 and I are the fluorescence intensities in an ideal and a typical sample of nitrones with definite concentration respectively, $[Q]$ the quencher concentration (here is nitrone) and τ is the fluorescence lifetime of the excited nitrone. The relative fluorescence intensity data measured at 597–660 nm for nitrone solutions **1a**–**1f** in acetonitrile, ethanol and methylene chloride were used to plot Eq. (1). Plots of I^0/I versus nitrone concentration gave straight lines in good accordance with the theoretical equation and supporting the simple nature of self-quenching of the nitrone fluorescence. As well as, the intercept values close to unity and standard deviations within the range of 0.99–1.00 were found in all cases. Strickler–Berg equation usually gives the relationship between fluorescence lifetime (τ) to absorption intensity with some approximation

Table 4
τ-Values of nitrones **1a**–**1g** in various solvents

Nitrone	τ (s)		
	Acetonitrile	Ethanol	Methylene chloride
1a	6.12×10^{-9}	4.99×10^{-9}	6.05×10^{-9}
1b	4.29×10^{-9}	4.77×10^{-9}	4.27×10^{-9}
1c	6.62×10^{-9} (E2)	5.82×10^{-9} (E2)	5.86×10^{-9} (E2)
1d	5.58×10^{-9}	5.64×10^{-9}	5.62×10^{-9}
1e	1.37×10^{-8}	1.23×10^{-8}	0.90×10^{-8}
1f	8.10×10^{-9}	7.12×10^{-9}	7.97×10^{-9}
1g	7.77×10^{-9}	6.91×10^{-9}	7.55×10^{-9}

Table 5
Singlet-state properties of nitrones **1a**–**1g** in various solvents

Nitrone	Acetonitrile		Ethanol		Methylene chloride	
	$K_q\tau$	K_q	$K_q\tau$	K_q	$K_q\tau$	K_q
1a	9.36×10^{4}	1.53×10^{13}	9.18×10^{4}	1.84×10^{13}	9.16×10^{4}	1.51×10^{13}
1b	6.80×10^{4}	1.59×10^{13}	4.82×10^{4}	1.01×10^{13}	1.47×10^{4}	3.44×10^{12}
1c	3.48×10^{4}	5.26×10^{12}	5.07×10^{4}	8.71×10^{12}	7.39×10^{4}	12.6×10^{12}
1d	4.28×10^{4}	7.67×10^{12}	4.19×10^{4}	7.43×10^{12}	7.46×10^{4}	1.33×10^{13}
1e	3.77×10^{4}	2.75×10^{12}	9.55×10^{3}	7.76×10^{11}	4.22×10^{4}	4.69×10^{12}
1f	3.08×10^{4}	3.80×10^{12}	5.47×10^{3}	7.68×10^{11}	5.40×10^{4}	6.78×10^{12}
1g	2.29×10^{4}	2.95×10^{12}	4.71×10^{3}	6.81×10^{11}	4.23×10^{4}	5.64×10^{12}

[32]. With this modified formula, the τ values were calculated. The obtained results are given in Table 4.

No significant changes in the value of τ were investigated, especially in **1b**, **1d** and **1e**. K_q i.e. the self-quenching rate constant for the association reaction in the excited state could be obtained from slope of the lines by knowing τ values (Table 5).

In our system, the calculated value of K_q corresponds to the value of bimolecular rate constant for the diffusion-controlled process of quenching (Eq. (2))

$$M^* + M \xrightarrow{K_q} 2M \quad \text{(self-quenching of } M^* \text{ by } M) \qquad (2)$$

Rate of unimolecular deactivation of the excited species (Eq. (3)) is comparable with the rate of Eq. (2)

$$M^* \xrightarrow{K_1} \text{product} \quad \text{(unimolecular decay of } M^*) \qquad (3)$$

At constant temperature, the diffusion rate constant has reciprocal relationship with viscosity. So, the following trend is expectable for self-quenching phenomena in different solvents: acetonitrile > methylene chloride > ethanol. Fluorescence lifetime of nitrones **1a**, **1c**, **1f** and **1g** obeyed the above trend but nitrones **1b**, **1d** and **1e** showed more complication in their behavior. This complicated behavior might come from: (i) the interaction of nitrones with protic solvents such as ethanol, which is different for each compound, (ii) the mechanism of energy transfer. Coulombic and exchange interactions are two spin-allowed mechanisms for singlet–singlet energy transfer (Eq. (4))

$$M^*(S_1) + M(S) \rightarrow M(S_0) + M^*(S_1) \qquad (4)$$

This energy transfer occurs for coulombic interactions when M^* and M are far from each other and for exchange interactions if M^* and M are near to each other. So, the structure of nitrones is an important factor to determine the energy transfer process.

4. Conclusion

N,α-Diphenylnitrone derivatives were synthesized and their solvent dependency were fully characterized by UV spectrophotometer in several solvents. The photochemical irradiation of nitrones in ethanol under argon and oxygen atmosphere using high pressure mercury vapor lamp was unchanged after 30 s irradiation, suggesting that the transition state of nitrones was singlet. To investigate the fluorescence behavior of nitrones, emission spectra of all nitrones were recorded in several solvents by fixing the excitation wavelength at 310 nm. The dependency of fluorescence intensity on nitrones concentration illustrates the self-quenching phenomenon, which has been discussed here.

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