The photophysics of nitrocarbazoles studied by using spectroscopic, photoacoustic and luminescence techniques†

Mariana Mesaros,[a] Sergio M. Bonesi,[b] Maria A. Ponce,[b] Rosa Erra-Balsells[*b] and Gabriel M. Bilmes[*c]

[a] Centro de Investigaciones Opticas (CONICET-CIC), Casilla de Correo 124, (1900) La Plata, Argentina

[b] CIHIDECAR-CONICET, Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón II,3 Ciudad Universitaria, (1428) Buenos Aires, Argentina

[c] Centro de Investigaciones Opticas (CONICET-CIC) y Universidad Nacional de La Plata, Casilla de Correo 124, (1900) La Plata, Argentina. E-mail: gabrielb@ciop.unlp.edu.ar

The photophysical behaviour of 1-nitrocarbazol and 3-nitrocarbazol in different organic solvents has been studied by using spectroscopic, luminescence and photoacoustic techniques. Absorption spectra and triplet state transient spectra were recorded and formation quantum yields and lifetimes determined. Phosphorescence emission at 77 K and laser induced luminescence in acetonitrile solution at 298 K for the nitrocarbazoles were studied. Results are discussed in terms of the optimized structure of 1-nitrocarbazole and 3-nitrocarbazole and compared with that of carbazole. The nitro group attached to the carbazole moiety induces important changes in the photophysical behavior of those compounds.

Introduction

As part of a comparative study of the photophysical processes and the photoreactivity of azacarbazoles (β-carbolines)[1,2] and carbazoles[3,4] and their potential use as matrices (photosensitizers) in matrix assisted ultraviolet laser desorption/ionization mass spectrometry (UV-MALDI-MS),[5,6] we decided to examine the behavior of carbazole derivatives. To begin with, nitrocarbazoles were chosen since for aromatic molecules the nitro group as a substituent induces strong modifications on the acid–base properties in the ground and electronic excited states and on the nature (π,π^*; n,π^*), multiplicity (singlet, S_1; triplet, T_1), lifetime (τ_{S1}; τ_{T1}) and efficiency of population (ϕ) of the electronic excited states.[7-10] Thus, after we completed the preparation and full characterization of 1-nitrocarbazole (2) and 3-nitrocarbazole (3)[11] (Scheme 1), we studied their photostability and their absorption and emission spectra under steady-state conditions.[7]

Both nitrocarbazoles were shown to be stable after irradiation in acetonitrile solution.[7] In experiments of laser desorption/ionization mass spectrometry with an N_2 laser source (λ_{exc} = 337 nm, LD-MS)[5,11] they showed a high efficient desorption/ionization process. They also behaved as efficient photosensitizers (matrix) in UV-MALDI analysis for low molecular mass proteins and for carbohydrates.[5] 1-Nitrocarbazole 2 showed a phosphorescence emission which was weaker than that of 3-nitrocarbazole 3, while neither compound showed any detectable fluorescence emission in steady-state experiments. Experiments were then coducted by comparing absorption and emission spectroscopy, laser flash photolysis, photoacoustic and laser induced luminescence properties of 2 and 3 relative to 1.

The results described in the present report show that the presence of the nitro group as a substituent in the carbazole moiety induces different photophysical behaviors in nitrocarbazoles 2 and 3 compared with that of carbazole 1. Besides, they also show that not only is the presence of the nitro group critical but also its location in the carbazole moiety.

Experimental

Chemicals and instrumentation

Materials. Spectrograde and HPLC grade cyclohexane, carbon tetrachloride, ethyl acetate, acetonitrile, methanol and acetic acid were purchased from J. T. Baker and were used without further purification.

2-Hydroxybenzophenone, 1-cyanonaphthalene, carbazole and Cresyl Violet were purchased from Aldrich and were recrystallized from ethanol. Ceric ammonium nitrate ($Ce(NH_4)_2(NO_3)_6$; CAN), ammonium ferric(II) sulfate hexahydrate (($NH_4)_2Fe(SO_4)_2$·6H_2O, Mohr salt), EDTA, copper(II) nitrate trihydrate ($Cu(NO_3)_2$·3H_2O), sodium nitrite and nitric acid were purchased from Aldrich. Solvents for chromatography and recrystallization were carefully purified and dried before use.[12] Thin layer chromatography (TLC) analysis was performed with aluminium silica gel sheets (0.2 mm layer thickness, silica-gel 60 F254). Products were isolated by preparative thick layer chromatography and column chromato-
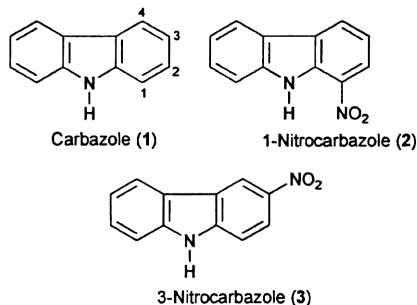
Scheme 1 Structure of the carbazoles studied.

---

† Dedicated to Professor Silvia Braslavsky, to mark her great contribution to photochemistry and photobiology particularly in the field of photothermal methods.

graphy which was carried out using silica gel 200–400 mesh 60 Å and ethyl acetate and ethyl acetate–ethanol as solvents. Melting points are uncorrected.

Equipment and experimental set-ups. UV absorption spectra were recorded on a Shimadzu UV-1203 UV-visible spectrophotometer and with a Beckman DU 65 spectrophotometer. All the measurements were made with 1 cm stoppered quartz cells at 298 K. Phosphorescence measurements were performed on a Hitachi F-500 spectrofluorometer whose output is automatically corrected for instrumental response by means of a Rhodamine B quantum counter and equipped with a Hamamatsu R 928 photomultiplier tube. The spectra at 77 K were recorded in solid matrices produced by freezing the ethyl ether–isopropanol (1 : 1) solution contained in a cylindrical cell (2 mm path length) with liquid N_2. The concentration of the substrates were 5.0×10^{-5} mol dm^{-3} and the solutions freshly prepared in the solvent mixture at 298 K and degassed with Ar during 10 min before freezing at 77 K. The electronic phosphorescence emission spectra were recorded in phosphorescence mode from 350 to 650 nm at 77 K. The selected excitation wavelength was 320 nm.

The phosphorescence lifetime values (τ_p) were measured in the same apparatus at the maximum phosphorescence emission wavelength. The monoexponential decay curves were acquired on a PC that was interfaced to the spectrofluorometer. Then, the phosphorescence lifetimes were determined by fitting the phosphorescence decay curves with a monoexponential function using the Origin 3.5 program.

The phosphorescence quantum yields (ϕ_p) of the nitrocarbazoles were measured relative to that of carbazole $(\phi_p = 0.24)$,[7] which was used as a reference. A simple comparison of the integrated areas under the phosphorescence spectra of the nitrocarbazoles and carbazole yields the ϕ_p values.

Laser flash photolysis experiments were performed by using the third harmonic of a pulsed Nd:YAG laser (Edinburg Laser Flash Photolysis System). The energy of a single 355 nm pulse was monitored with a beam splitter and a pyroelectric energy meter (Laser Precision Corp.). Laser induced transient transmission changes were monitored, perpendicular to the laser beam, by using a Xe arc lamp (ILC UV 33P). The analysing light passed through a 2 nm wide section of the excited sample and was then focused at the entrance slit of a 0.25 mm, doubled grating monochromator (PTI f/4, spectral resolution 3 nm). A photomultiplier (Hamamatsu R 936) and a Tektronix R-7912 transient digitizer interfaced to a PC IBM Asyst. Programs were used to acquire and process the signals. The electronic absorption spectrum of the triplet transient of 3-nitrocarbazole was obtained in Ar degassed acetonitrile solution (substrate concentration: 5.0×10^{-5} mol dm^{-3}) at 298 K. The triplet transient lifetime value (τ_T) of 3-nitrocarbazole was measured with the same apparatus at the maximum absorption wavelength $(\lambda = 575 \text{ nm})$.

The triplet quantum yield (ϕ_T) values were measured by laser flash photolysis in acetonitrile at 298 K. Benzophenone was selected as the triplet energy donor and as a reference $(\phi_T = 1.0)$. 1-Cyanonaphthalene was selected as the triplet energy acceptor. The absorbance of the triplet transient of 1-cyanonaphthalene at 500 nm obtained by photosensitization at 355 nm in the presence of benzophenone was meassured; 1-cyanonaphthalene itself does not absorb at 355 nm. Similarly, the absorbance of the triplet transient of 1-cyanonaphthalene was measured at 500 nm in the presence of the nitrocarbazoles. Taking into account a 100% efficiency of triplet–triplet energy transfer between the triplet energy donors (benzophenone and nitrocarbazoles) and the triplet energy acceptor (1-cyanonaphthalene), a simple ratio of the absorbance values of 1-cyanonaphthalene measured at 500 nm in the presence of the nitrocarbazoles and benzophenone yields the ϕ_T values of nitrocarbazoles.

Photoacoustic measurements were performed by using a Q-switched Nd:YAG laser (Surelite II, Continuum, 7 ns FWHM) operating at the third harmonic $(\lambda = 355 \text{ nm})$. The diameter of the laser beam was controlled with a focussing lens and a variable pinhole. The laser energy was attenuated using a polarizer and a half wave plate and measured with a pyroelectric detector (RjP-765, Laser Precision Corp.) using a quartz glass as beam-splitter. Sample solutions were contained in a spectrophotometric 1 cm quartz cell. For the detection of the acoustic signals two different piezoelectric transducers were used: a home-made ceramic PZT (4×4 mm) attached to a rear wall of the cell and a PVF_2 film of 25 μm width, attached to the bottom of the cell. In both cases the detection was perpendicular to the direction of the excitation beam. Selecting the proper value for the frequency response of the transducers and for the diameter of the beam with the lens-pinhole, the time resolution range for the acoustic measurements was 150 ns to 1.5 μs. The detected acoustic signals were amplified and processed by a storage digital oscilloscope (TDS 3032, Tektronix). Measurements were performed averaging the signals generated by 64 laser shots for better signal to noise ratio. The absorbances of the solutions were checked before and after each set of laser shots.

2-Hydroxybenzophenone was used as a calorimetric reference.[13] For the experiments, sample and reference solution concentrations were matched to absorbance values between 0.1 and 0.2 at the laser wavelength. Signals were also processed mathematically using deconvolution methods, combined with an appropriate kinetic model. Experiments were performed at open air and under controlled atmosphere, bubbling N_2 or O_2 in the solution, during 15 min.

Laser induced luminescence experiments were conducted using the same excitation set-up described for photoacoustic experiments. The spectrum emitted by the sample was recorded by means of an optical fiber attached to a cross dispersion spectrograph (Mechelle Multichannel Instruments, AB) with a CCD incorporated camera. The data was sent to a computer and processed with appropriate software that gives the whole spectra covering the 200 to 1100 nm region with a 0.3 nm spectral resolution. The emission lifetime was measured at the maximum intensity wavelength of the spectrum with a 10 ns resolution photomultiplier.

^{1}H- and ^{13}C-NMR spectra were run in dimethyl sulfoxide-d_6 at 500 MHz. Chemical shifts are reported in ppm values, using tetramethylsilane as internal standard.

Synthesis of nitrocarbazoles

Olah's method. A mixture of copper(II) nitrate trihydrate (200 mg, 0.83 mmol) and acetic anhydride (1.5 ml) was stirred at room temperature for 1.5 h. After that the carbazole (0.72 mmol) was added to the mixture, and stirring was continued for 24 h. Additional copper(II) nitrate trihydrate (100 mg, 0.83 mmol) was added, and stirring was continued for another 24 h. Then methanol (10 ml) was added. After 30 min of stirring volatiles were evaporated *in vacuo*, 20 ml of water were added to the remaining solution, and the mixture was stirred for 30 min. A pH of 14 of the aqueous solution was then set using sodium hydroxide. The aqueous solution was washed with dichloromethane (3×15 ml). The combined organic extracts were washed with water (100 ml), and the organic layer was dried over sodium sulfate, filtered and evaporated *in vacuo* to give a solid residue. The residue was separated by flash column chromatography with ethyl acetate–hexane mixtures as eluent.

1-Nitrocarbazole (2). Yellow needles from ethanol, mp 195 °C (lit.[11] 197–198 °C); ^{1}H NMR (dimethyl sulfoxide-d_6): δ 12.15 (br s, 1H, NH), 8.62 (d, 1 H, 4-H, $J = 7.3$ Hz), 8.41 (d, 1 H, 8-H, $J = 8.4$ Hz), 8.31 (dd, 1H, 5-H, $J = 1.1, 7.8$ Hz), 8.24 (d, 1 H,

Table 1 Spectroscopic data of carbazoles in acetonitrile at 298 K under inert atmosphere (Ar) together with the calculated spectroscopic data

Carbazole	λ_{max}(abs)/nm (ε/dm^{-3} mol^{-1} cm^{-1})			λ_{max}(abs)^a/nm ($f(S_2-S_0)^a$)	$\Delta\mu^a$/D	λ_{max}(abs)^a/nm ($f(S_1-S_0)^a$)	$\Delta\mu^a$/D
1	260 (90000)	292 (75000)	334 (7800)	274 (0.458)	5.17	288 (0.014)	0.93
2	290 (80000)	300 (100000)	404 (48698)	336 (0.110)	2.81	365 (0.182)	3.76
3	279 (100000)	306 (60000)	366 (45714)	321 (0.292)	2.77	326 (0.111)	2.44

^{a} Calculated using the semiempirical ZINDO/S method after HF/3-21G geometrical optimization.

2-H, J = 8.0 Hz), 7.51 (dd, 1 H, 7-H, J = 7.3, 8.4 Hz), 7.35 (dd, 1 H, 3-H, J = 7.3, 8.0 Hz), 7.29 (dd, 1 H, 6-H, J = 1.1, 7.3, 7.8 Hz); ^{13}C NMR (dimethyl sulfoxide-d$_6$): δ 140.6 (1-C), 132.8 (4-C), 131.6 (9a-C), 130.9 (4a-C), 127.9 (3-C), 127.1 (7-C, 8a-C), 121.6 (2-C), 121.4 (4b-C), 120.5 (5-C), 118.2 (6-C), 112.6 (8-C).

3-Nitrocarbazole (3). Yellow needles from ethanol, mp 215 °C (lit.[11] 215–216 °C); ^{1}H NMR (dimethyl sulfoxide-d$_6$): δ 12.02 (br s, 1H, NH), 9.15 (d, 1 H, 4-H, J = 1.8 Hz), 8.36 (d, 1H, 5-H, J = 8.0 Hz), 8.29 (dd, 1 H, 2-H, J = 1.8, 8.8 Hz), 7.65–7.58 (m, 2 H, 1-H and 8-H), 8.51 (dd, 1 H, 6-H, J = 6.9, 8.0 Hz), 7.29 (dd, 1 H, 7-H, J = 6.9, 7.7 Hz); ^{13}C NMR (dimethyl sulfoxide-d$_6$): δ 143.1 (3-C), 140.8 (9a-C), 139.6 (8a-C), 127.3 (7-C), 122.2 (4a-C), 121.9 (4b-C), 121.1 (2-C), 120.9 (5-C), 120.0 (6-C), 116.9 (4-C), 111.7 (1-C), 110.9 (8-C).

Computational details

The ground-state geometries were optimised by *ab initio* calculations (3-21G basis at HF level; Gaussian 98). UV-absorption spectra were calculated by using the ZINDO/S (CI, 6:6) method.

Results and discussion

Absorption, fluorescence and laser flash photolysis measurements at 298 K

The absorption spectra of carbazole 1 and nitrocarbazoles 2 and 3 were recorded in acetonitrile at 298 K and showed three bands at *ca.* 270, 300 and 350 nm (Table 1).

Previously spectroscopic studies and theoretical calculations have been carried out[7,14–16] allowing for unambiguous assignment of the bands located in the 300 and 350 nm regions for carbazole derivatives as ^1L_a (S_2-S_0) and ^1L_b (S_1-S_0) electronic transitions, respectively.

Also, we observed that the absorption spectra of nitrocarbazoles 2 and 3 recorded in acetonitrile at 298 K showed a noticeable bathochromic shift of the ^1L_b band of 70 and 32 nm, respectively, compared to that of carbazole 1, whereas the ^1L_a band showed a small bathochromic shift of *ca.* 10 nm. These red shifts are a result of the in-plane conjugation of the nitro groups bonded to the carbazole moiety and can be interpreted by the mesomeric effect induced by the nitro group. The oscillator strength $f(S_1-S_0)$ and $f(S_2-S_0)$ values and the dipole moment ($\Delta\mu$) of the ^1L_b and ^1L_a electronic transitions were calculated from the HF/3-21G optimised ground-state structures of carbazoles using the semiempirical ZINDO/S method and these values are shown in Table 1. The oscillator strength $f(S_1-S_0)$ associated to the ^1L_b electronic transition of nitrocarbazoles 2 and 3 are higher than that of carbazole 1 and it may be attributed to an important change in the charge transfer character in the ^1L_b electronic transition and to a noticeable increase of the transition dipole moment ($\Delta\mu$), as can be seen from the predicted ($\Delta\mu$) values of carbazoles 1, 2 and 3 shown in Table 1. In the case of the S_2-S_0 electronic transition of the nitrocarbazoles 2 and 3 we obtained oscillator strength and transition dipole moment values lower than that of the carbazole 1. Therefore, we concluded that a smaller change occurred in the charge transfer character in the ^1L_a electronic transition of the nitrocarbazoles 2 and 3 compared to that of the carbazole 1.

The solvent effect on the absorption spectra of 1-nitrocarbazole and 3-nitrocarbazole was studied and the spectra obtained are shown in Fig. 1. A small bathochromic shift on going from nonpolar to polar solvents was observed. Thus, we concluded that for compounds 2 and 3 the nature of the lowest singlet excited state is most likely to be π,π^* as in the case of carbazole 1.[7]
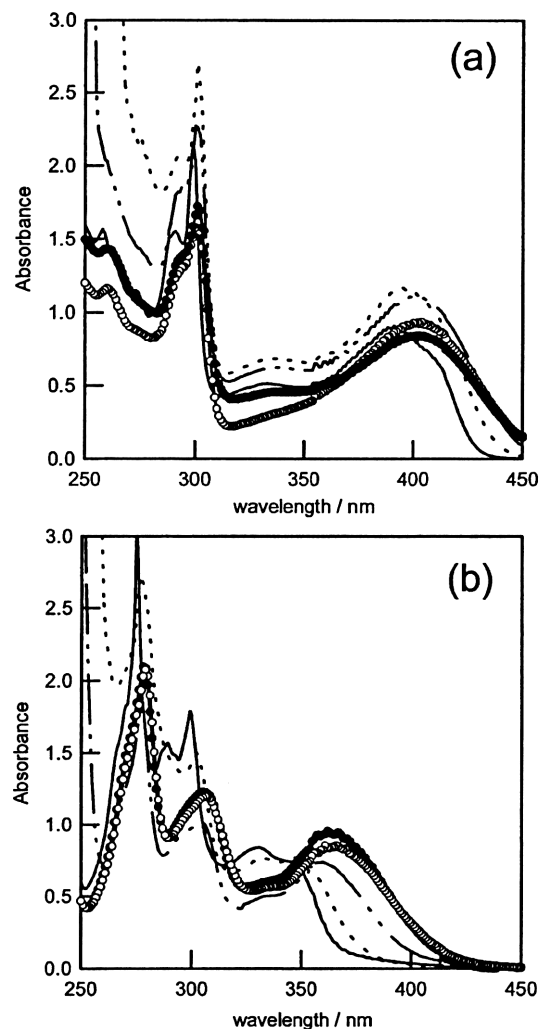
Fig. 1 Electronic absorption spectra of (a) 1-nitrocarbazole (2) and (b) 3-nitrocarbazole (3) in different solvents: (—) cyclohexane (C$_6$H$_{12}$), (···) carbon tetrachloride (CCl$_4$), (— —) ethyl acetate (CH$_3$CO$_2$C$_2$H$_5$), (O) acetonitrile (CH$_3$CN), (●) methanol (MeOH).

Carbazole 1 was a good fluorescent chromophore in acetonitrile at 298 K with ϕ_f = 0.62 and τ_f = 15.1 ns, whereas 1-nitrocarbazole (2) and 3-nitrocarbazole (3) did not show any fluorescent emission uner similar experimental conditions. Thus, from the electronic excited singlet state one or two radiationless deactivation processes could be operating: (i) an efficient intersystem crossing process, and/or (ii) an efficient release of heat to the medium.

We measured the intersystem crossing quantum yield (ϕ_{isc} or ϕ_T) of the nitrocarbazoles by laser flash photolysis at

Table 2 Intersystem crossing quantum yield (ϕ_T) and triplet lifetime (τ_T) of carbazoles in acetonitrile at 298 K[a]

Carbazole	ϕ_T	τ_T/ns
1	0.38[b]	–
2	0.40 ± 0.04	<10
3	0.50 ± 0.05	500

[a]Measured by laser flash photolysis at λ_{exc} 355 nm under Ar atmosphere. [b] From ref. 7.

λ = 355 nm in acetonitrile, under Ar atmosphere at 298 K. Benzophenone was selected as a reference and as a triplet energy donor, whose ϕ_T value is known (ϕ_T = 1.00).[17-19] 1-Nitrocarbazole (2) and 3-nitrocarbazole (3) were also selected as triplet energy donors whose ϕ_T values are unknown and 1-cyanonaphthalene was selected as a triplet energy acceptor for which a triplet energy value of 2.32 eV had been reported.[18] It is noteworthy to mention that the triplet–triplet energy transfer process between the donors and the acceptor occurs with a quantum efficiency of 1.[19] Table 2 shows the ϕ_T values obtained for carbazole (1), 1-nitrocarbazole (2) and 3-nitrocarbazole (3). The high ϕ_T values obtained indicates that ca. 50% of the initial electronic excited S_1 population is involved in the intersystem crossing process $S_1 \Rightarrow T$.

Taking into account that the nitrocarbazoles 2 and 3 are not fluorescent chromophores, the other ca. 50% of the absorbed photons should be released to the medium as heat through a radiationless internal conversion pathway from the S_1 state.

In order to characterise the triplet excited state of the nitrocarbazoles 2 and 3, we recorded the electronic absorption spectra of the triplet transients by laser flash photolysis at λ = 355 nm in acetonitrile, under Ar atmosphere at 298 K. Fig. 2 shows the electronic absorption spectra of the 3-nitrocarbazole (3) triplet transient.
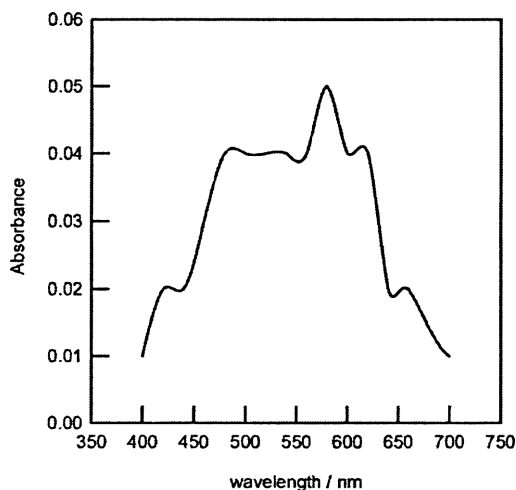

Fig. 2 Electronic absorption spectra of the triplet transient of 3-nitrocarbazole (3) obtained by laser flash photolysis. Solvent: acetonitrile; T = 298 K; atmosphere: Ar; λ_{exc} = 355 nm.

The triplet lifetime (τ_T) of 3-nitrocarbazole was also measured in similar experimental conditions at λ = 500 and 650 nm. At both absorption wavelengths, the triplet transient of 3-nitrocarbazole showed monoexponential decays giving the same τ_T value (Table 2, 500 ns). We also attempted to characterise the triplet transient of 1-nitrocarbazole (2) by laser flash photolysis experiments but no electronic absorption spectra could be detected.

Photoacoustic measurements at 298 K

The peak-to-peak amplitude of the first acoustic pulse (H) detected by the piezoelectric transducers was used to measure the prompt heat released to the medium by the sample after excitation.

Fig. 3 shows the photoacoustic signal amplitude (H) of 1-nitrocarbazole (2) and the calorimetric reference, 2-hydroxybenzophenone, as a function of the excitation fluence (F) measured in different organic solvents at 298 K. In these experiments, the sample and the reference absorbances were matched to the same value.
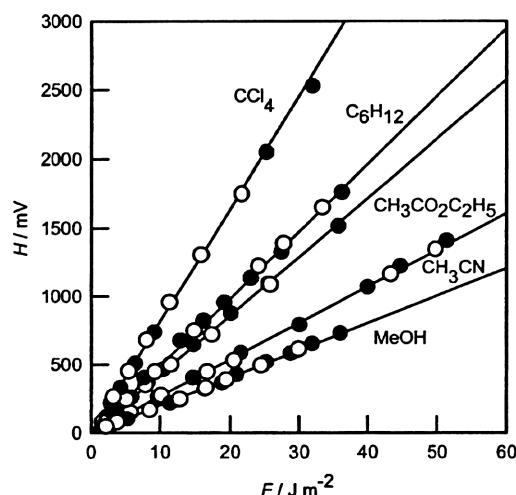

Fig. 3 Amplitude of the photoacoustic signal H as a function of the laser fluence F measured in different solvents; CCl_4 (A = 0.168), C_6H_{12} (A = 0.164), $CH_3CO_2C_2H_5$ (A = 0.151), CH_3CN (A = 0.117), MeOH (A = 0.110); τ_R = 1 μs; (●) 1-nitrocarbazole (2), (○) 2-hydroxybenzophenone (reference).

Linear correlations and good reproducibility of the experimental data were obtained in all the used solvents. No changes in the relationship between sample and reference were observed changing the resolution time of the experiments between 150 ns and 1.5 μs. As can be seen, the same slopes were obtained for the samples and the reference in all cases. These results can be interpreted in terms of the well known eqn. (1) for the photoacoustic signal amplitude:

$$H/F = Ka(1 - 10^{-A})\qquad(1)$$

where K is an experimental constant containing the thermoelastic properties of the solution and instrumental factors, A is the sample absorbance value and a is the fraction of energy released in the medium as prompt heat within the time resolution of the experiment.

Taking into account that for the calorimetric reference, 2-hydroxybenzophenone, a_R = 1 and that the measurements for sample and reference were performed in the same experimental conditions (K is a constant in eqn. (1)), the ratio of the H/F values obtained for sample and reference yields the sample a value. Thus, for the 1-nitrocarbazole (2) a = 1 was obtained when the experimental time resolution ranged from 1.5 μs to 150 ns. The same a value was obtained in the different solvents used (Fig. 3, carbon tetrachloride, cyclohexane, ethyl acetate, acetonitrile and methanol). Then, we assume that 1-nitrocarbazole (2) releases to the medium all the absorbed energy as heat in a time shorter than 150 ns. This result agrees with those obtained by laser flash photolysis experiments and suggests that the triplet transient of 1-nitrocarbazole (2) is short-lived and, after its formation, it decays to the ground state rapidly. Thus, we have roughly estimated for the triplet transient of 1-nitrocarbazole (2) a τ_T value <10 ns (the resolution limit of the laser flash photolysis experiments conducted is 10 ns).

Fig. 4 shows the photoacoustic signal amplitude (H) as a function of the excitation fluence (F) for the case of
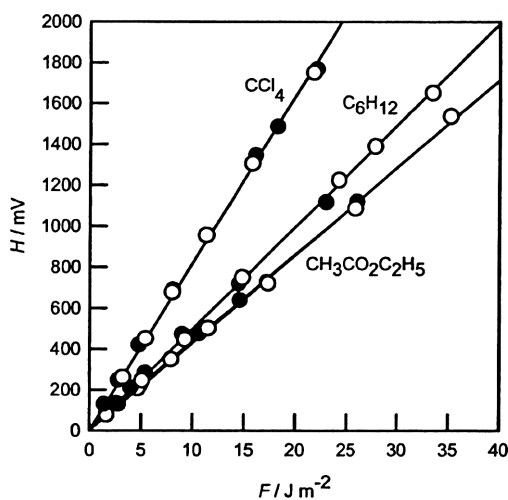
Fig. 4 Amplitude of the photoacoustic signal H as a function of the laser fluence F measured in different solvents; CCl_4 ($A = 0.168$), C_6H_{12} ($A = 0.164$), $CH_3CO_2C_2H_5$ ($A = 0.151$); $t_R = 1$ μs; (●) 3-nitrocarbazole (3), (○) 2-hydroxybenzophenone (reference).

3-nitrocarbazole (3) by using again 2-hydroxybenzophenone as reference, in cyclohexane, carbon tetrachloride and ethyl acetate solutions, at 298 K. Measurements were conducted under the same experimental conditions described for 1-nitrocarbazole (2). As can be seen, good linear correlations were obtained yielding $a = 1$ for the three solvents used. It was concluded that when cyclohexane, carbon tetrachloride and ethyl acetate were used as solvents (Fig. 4), 3-nitrocarbazole (3) showed a similar behavior to 1-nitrocarbazole (2) (Fig. 3) releasing to the medium all the absorbed energy as heat in a time shorter than 150 ns.

A comparative study of H as a function of F for 3-nitrocarbazole (3) and for the calorimetric reference in acetonitrile and nethanol, was conducted by using two different piezoelectric transducers. Similar behaviors were observed in both solvents. Fig. 5(a) shows the results obtained when a PVF_2 film with a resolution time (τ_R) of 150 ns was used and Fig. 5(b) shows those obtained with a PZT crystal with a resolution time of 1.5 μs. As it can be seen, in both cases the sample releases to the medium less energy as heat than the reference, showing a quite different behavior than those observed in the other solvents (Fig. 4, carbon tetrachloride, cyclohexane and ethyl acetate). Taking into account eqn. (1), a different value for the H_S/H_R ratio between sample (S) and reference (R) is obtained, depending on the resolution time of the experiment ($H_S/H_R = 0.77$ for $\tau_R = 150$ ns, and $H_S/H_R = 0.88$ for $\tau_R = 1.5$ μs). These results can be explained assuming that a transient species with a lifetime between 150 ns and 1.5 μs is formed and it stores part of the absorbed energy. No effect on the 3-nitrocarbazole (3) photoacoustic behavior was observed when the experiments were conducted under different atmospheres (O_2, air, N_2) (see Fig. 5). The absence of an effect due to oxygen in these measurements can be explained taking into account the short lifetime of the involved singlet and triplet states. Then, any possible quenching effect would be of low efficiency and the sensitivity of the photoacoustic method is not sufficient to detect any possible change.

In order to determine the lifetime of the transient storing species and the value of a consistent with this lifetime value, we used a deconvolution method. As it was previously demonstrated,[20,21] when the lifetime of the transient species τ is $\tau_R/5 \leq \tau \leq 5\tau_R$, the observed energy normalised acoustic wave $S(t)$ is a convolution of the system response $R(t)$ and the rate of heat evolution $q(t)$ as shown in eqn. (2):[22]

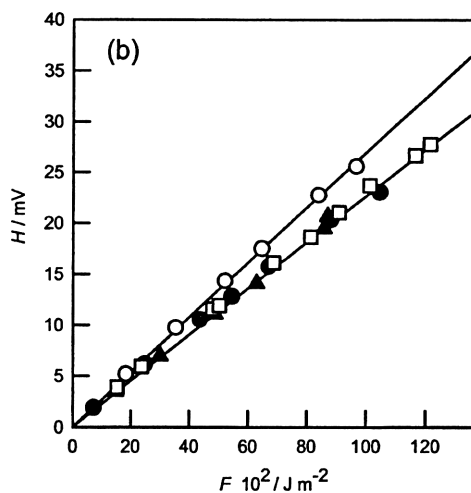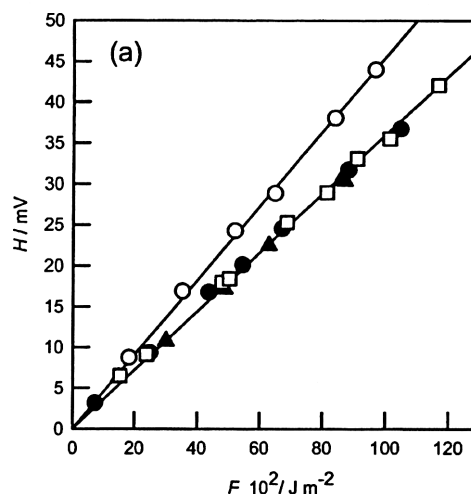$$S(t) = H(t)/E(1 - 10^{-A}) = R(t) \oplus q(t) = \int_0^t R(u)q(t - u)du \quad (2)$$

Fig. 5 Amplitude of the photoacoustic signal H as a function of the laser fluence F in acetonitrile and in methanol solutions (absorbance = 0.110); (○) 2-hydroxybenzophenone (reference), (●) 3-nitrocarbazole (3) under air atmosphere, (▲) 3-nitrocarbazole (3) under N_2 atmosphere, (□) 3-nitrocarbazole (3) under O_2 atmosphere. (a) Time resolution $t_R = 150$ ns, $H_S/H_R = 0.77$, (b) time resolution $t_R = 1.5$ μs, $H_S/H_R = 0.88$.

where $H(t)$ is the observed waveform of the sample and $R(t)$ is the system response which can be determined experimentally by using the calorimetric reference.

Assuming a kinetic decay model with a fast decay and one storing species, and performing the deconvolution by an iterative deconvolution program based on the Lavenberg-Marquardt χ^2 minimisation procedure[22] the values of τ and a can be calculated according to eqn. (3):

$$C(t) = R(t) \oplus ((a/\tau)e^{-t/\tau}) \quad (3)$$

The deconvolution method is best for treating cases where a clear phase shift between the observed waveform for the sample and reference exists. This is the case for 3-nitrocarbazole (3) in acetonitrile and in methanol solutions (see Fig. 6). Resolution of eqn. (3) by deconvolution yielded very good fits for values of τ in the range $350 \leq \tau \leq 650$ ns giving values of a in the range $0.65 \leq a \leq 0.74$. These ranges of values were obtained using sets of waveforms measured with resolution times of 150 ns (see Fig. 6), 1 μs and 1,5 μs. The range of the calculated values for the lifetime of the 3-nitrocarbazole (3) transient species (τ) is in complete agreement with the triplet state value $\tau_T = 500$ ns determined by laser flash photolysis experiments (see Table 2).
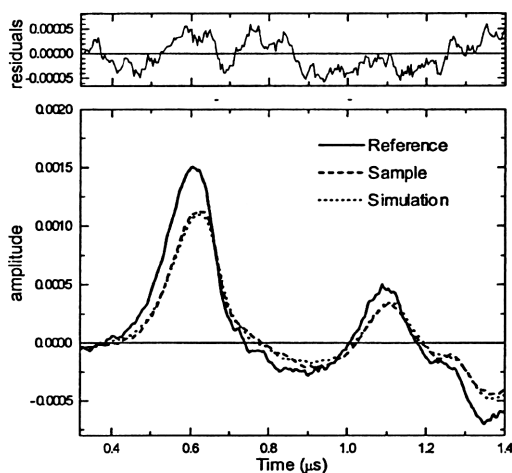
197

Fig. 6 Acoustic waveforms for 3-nitrocarbazole (3) (sample) and 2-hydroxybenzophenone (reference) measured with a piezoelectric PVF$_2$ film in acetonitrile. Simulation is the best-fit convolution according to eqn. (3). Residuals of the fit are also shown.

A simple energy balance equation[23] can be used to estimate a range for the energy content of the triplet state ($\Delta E(T_1-S_0)$) of 3-nitrocarbazole (3) in acetonitrile and in methanol, taking into account that this compound did not show any fluorescence at 298 K:

$$\Delta E(T_1-S_0) = ((1 - a)/\phi_T)E_a \qquad (4)$$

where $\phi_T = 0.50 \pm 0.05$ (see Table 2) is the quantum yield of the triplet formation determined by laser flash photolysis (298 K); the range $0.65 \le a \le 0.74$ was determined by photoacoustic measurements and E_a is the absorbed energy at $\lambda = 355$ nm. From eqn. (4) we calculated that, at 298 K, the energy content of the triplet state of 3-nitrocarbazole (3) is in the range 1.7 eV $\le \Delta E(T_1-S_0) \le 2.8$ eV, leading to a phosphorescence maximum emission in the range $450 \le \lambda_p(\text{max}) \le 750$ nm.

Phosphorescence measurements at 77 K

The phosphorescence spectrum of 1-nitrocarbazole (2) and 3-nitrocarbazole (3) were measured in isopropanol–diethyl ether (1 : 1, v/v) at 77 K. These compounds exhibited structured phosphorescence emission spectra with excitation into the S$_1$ level (see Fig. 7).
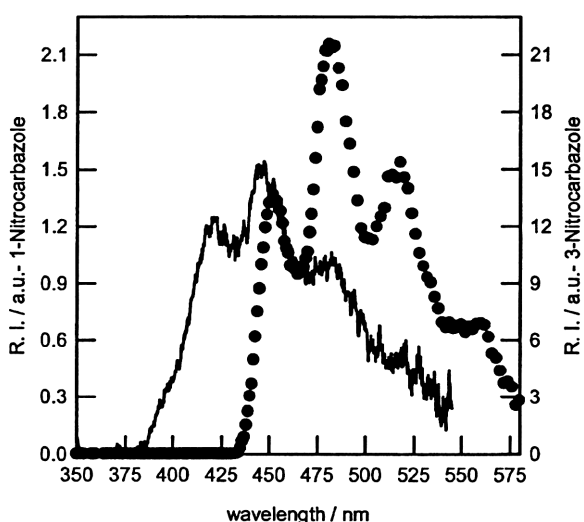

Fig. 7 Phosphorescence spectra of 1-nitrocarbazole (2) (—) and 3-nitrocarbazole (3) (●) in isopropanol–diethyl ether (1 : 1, v/v) at 77 K.

It is interesting to note that the shape and the intensity of both phosphorescence spectra are very similar showing three broad bands which are quite different than those observed for carbazole.[7] Moreover, the structure and the shape of the phosphorescence spectra of compounds 2 and 3 resemble that of the "benzophenone-like" molecules.[9] The experimentally obtained highest relative intensity radiative triplet transition ($\lambda_p(\text{max})$) of the nitrocarbazoles 2 and 3 are shown in Table 3 together with that of carbazole 1.

Comparing these data, a noticeable red shift of the $\lambda_p(\text{max})$ is observed for compounds 2 and 3 which is due to the important mesomeric effect of the nitro group, a strong electron withdrawing substituent group, on the lowest triplet excited state. For 3-nitrocarbazole (3) the $\lambda_p(\text{max}) = 480$ nm measured in this experiment ($T = 77$ K), fit in the $\lambda_p(\text{max})$ range predicted by eqn. (4), where data obtained in photoacoustic and laser flash photolysis experiments ($T = 298$ K), are used (see Discussion section above). It is interesting to point out that due to the influence of the solvent, a red Stokes shift for $\lambda_p(\text{max})$ can be expected, when the temperature is increased from low values (77 K) to 298 K. Thus, at 298 K the $\Delta E(T_1-S_0)$ value of 2.6 eV would be the upper limit for the energy content of the lower excited triplet state of 3-nitrocarbazole (3).

We also measured the phosphorescence lifetime (τ_p) and the phosphorescence quantum yields (ϕ_p) of nitrocarbazoles 2 and 3 in solid matrices at 77 K and the values obtained are shown in Table 3. Therefore, the dynamic properties of the lowest triplet excited states of these compounds were easily calculated and the photophysical parameters obtained, k^e_p and k_{nr}, are also shown in Table 3. Finally, the calculated values for the oscillator strength $f(T_1-S_0) = 1.5k^o_p v^{-2}$, where v is the wavenumber of the phosphorescence emission, are also included.

At 77 K the deactivation processes of the triplet state (T$_1$) of carbazole 1, 1-nitrocarbazole 2 and 3-nitrocarbazole 3 are different. As shown in Table 3, the ϕ_p value of 3 is double (0.47) that of carbazole (0.24) which reflects a greater efficiency of emission from T$_1$. Thus, the k^e_p value accounts for this behaviour and the lowest triplet excited state deactivates preferentially through the phosphorescence emission process while the radiationless process (k_{nr}) occurs competitively to a lesser extent. For 1-nitrocarbazole 2, the phosphorescence quantum yield (ϕ_p) is very low (0.04) and hence, the deactivation process of the T$_1$ state occurs preferentially through a radiationless pathway, as can be seen from the k_{nr} value.

This particular behavior observed for the 1-nitrocarbazole 2 can be rationalized as follows. The nitro group is attached to the *ortho* position of the carbazole moiety (C-1) and it is spatially vicinal to the N–H group. Therefore, an intramolecular hydrogen bond is easily formed between the nitro group and the N–H group of compound 2 as shown in Scheme 2(a). The optimized geometry obtained at the HF/3-21G level clearly shows that this
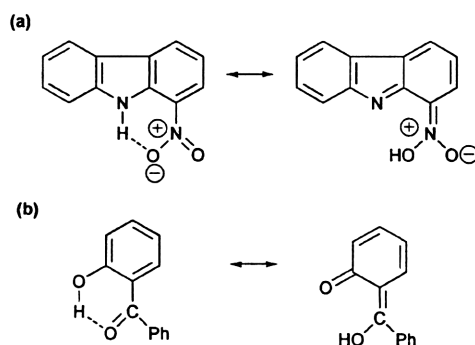
Scheme 2 (a) Intramolecular hydrogen bonding of 1-nitrocarbazole in the ground state (shown left) as the origin of a probable keto-like structure (shown in the right) and a keto–enol-like equilibrium of 1-nitrocarbazole in the electronic excited state. (b) The well known keto–enol-like equilibrium of 2-hydroxybenzophenone.

Carbazole	$\lambda_p(max)^a$/nm	$f(T_1\text{-}S_o)^b$	ϕ_p	τ_p/s	k^e_p ^{c}/s^{-1}	k_{nr} ^{d}/s^{-1}
1	406	1.36×10^{-9}	0.24	7.73	0.055	0.074
2	450	0.53×10^{-9}	0.04	9.0×10^{-4}	105.8	1005.3
3	480	4.0×10^{-9}	0.47	0.159	5.68	0.61

^{a} $\lambda_p(max) = \lambda$ value at highest relative intensity. ^{b} Calculated according to the following equation: $f(T_1\text{-}S_o) = 1.5k^e_p v^{-2}$, where v is the wavenumber of the phosphorescence emission. ^{c} $k^e_p = \phi_p k_p/\phi_p$ ^{d} $k_{nr} = k_p - k^o_p$, where $k_p = \tau_\pi^{-1}$.

hydrogen bond is possible because of the distance between the involved groups (ca. 2.4 Å). This out-of-plane fixed position of the nitro group with respect to the plane of the carbazole moiety could cause the triplet excited state to favour radiationless decay over the competitive phosphorescence emission during its short phosphorescence lifetime (τ_p = 900 μs). This intramolecular hydrogen bond is similar to the well known 2-hydroxybenzophenone intramolecular hydrogen bond and both would be operating, in the electronic excited state, in a similar manner. In Scheme 2 the keto-enol-like equilibrium for 1-nitrocarbazole 2 (a) and for 2-hydroxybenzophenone (b) are represented in a comparative manner. Of course, this intramolecular hydrogen bond is not possible for 3-nitrocarbazole 3 since the nitro group is attached to a different position of the carbazole moiety (C-3).

It is known that oscillator strength $f(T_1\text{-}S_0)$ values ranging from 10^{-5}-10^{-9} are characteristic of spin forbidden transitions.[9] Furthermore, electronic transitions of the type T_1 (n, π^*) $\Longrightarrow$ S_0 show $f(T_1\text{-}S_0)$ values which lie between 10^{-7} and 10^{-8}, k^e_p values greater than 1 s^{-1} and k_{isc} values in the range 10^{10}-10^{11} s^{-1}. Organic molecules which show these spectroscopic and photophysical parameters are classified as "benzophenone-like" molecules.[9] It is interesting to mention that the shape and the intensity of the bands in the phosphorescence spectrum is another feature to be taken into account.[9]

As a consequence the comparative analysis of the photophysical parameters (k^e_p and τ_p), the shape of the phosphorescence spectra and the oscillator strength values ($f(T_1\text{-}S_0)$) allow us to conclude that the lowest triplet excited state of 1-nitrocarbazole 2 and 3-nitrocarbazole 3 is an n,π^* electronic state. On the contrary the same analysis for carbazole 1 suggests that the lowest triplet excited state is a π,π^* electronic state.

Laser induced luminescence measurements at 298 K

During laser induced optoacoustic experiments (λ_{exc} = 355 nm) in acetonitrile solution at 298 K, the nitrocarbazoles 2 and 3 showed a weak luminescence emission. This luminescence was not observed under the same experimental conditions with carbazole 1. The spectra registered for both compounds, desplayed in Fig. 8, were measured at the same value of solution absorbance. As can be seen, they are quite similar, with a broad band ranging from 500 to 800 nm with λ_{max} centered at 570 nm. No luminescence emission spectrum of 3-nitrocarbazole (3) in cyclohexane, ethyl acetate, carbon tetrachloride or methanol solution was detected. 1-Nitrocarbazole 2 showed the same behavior except for weak luminescence emission in ethyl acetate. This latter spectrum was similar in shape and λ_{max} as that obtained in acetonitrile solution.

Experiments were repeated several times with fresh solutions in purified acetonitrile.[12] The carbazole 1 and the nitrocarbazoles 2 and 3 used were recrystallized, fully characterized and purity carefully controlled by chromatographic methods (see details in the Experimental section).

By adding small amounts of methanol to acetonitrile solutions of compounds 2 and 3 quenching of the luminescence was observed in agreement with the result obtained in methanol solution.
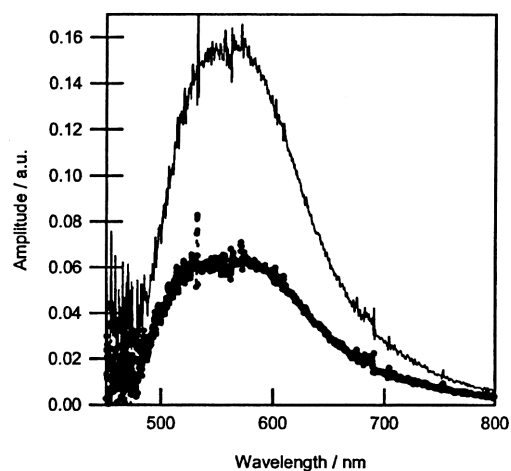

Fig. 8 Laser induced luminescence spectra of 1-nitrocarbazole (2) (—) and 3-nitrocarbazole (3) (●) obtained using solutions with the same absorbance. Solvent: acetonitrile: λ_{exc} = 355 nm.

Quantum yield values $\phi_L \leq 10^{-3}$ for the luminescence of nitrocarbazoles 2 and 3 in acetonitrile were estimated, using Cresyl Violet as a fluorescent reference. The same ϕ_L values were estimated under air or N_2 atmosphere.

Experiments were also performed to measure the lifetime of the luminescent species. In all the cases the decay value measured was limited by the resolution time of the detection system used. The lifetime of the luminescent species for compounds 2 and 3 was estimated as <10 ns.

As to the origin of the luminescence observed for compounds 2 and 3 at 298 K, the following considerations must be taken into account: the fluorescent process $S_1 \Longrightarrow S_0$ can be discarded owing to that in the same solvent, the λ_{max} of the luminescence emission is located ca. 300 nm away (red shifted) from the location of the corresponding λ_{max} in the absorption spectrum. The radiative process $S_2 \Longrightarrow S_1$ can also be discounted as being responsible for the luminescence because under our experimental conditions, λ_{exc} = 355 nm, population of the upper state, S_2, from the energetic point of view is not possible. On the other hand, if we assume that triplet states are involved in this luminescence process ($T_n \Longrightarrow T$), the heavy atom effect (HAE) should be observed.[9,10] The fact that any luminescence was observed when experiments were conducted in carbon tetrachloride solution, strongly suggests that triplet states would not be involved in these radiative processes. This suggestion is also supported by the estimated lifetime of the luminescent excited states of compounds 2 and 3 (<10 ns) and the fact that these luminescence emissions were observed for both compounds in solution, at 298 K. By the same reason, the radiative process $T_1 \Longrightarrow S_0$ (phosphorescence) as well as a delayed fluorescence process can be discarded as the mechanisms accounting for the observed luminescences at room temperature. On the other hand, for compound 2 the value of its T_1 lifetime (τ_T) is of similar magnitude or lower than the laser pulse duration (τ_{exc}). For compound 3 τ_T is ca. 50 times higher than τ_{exc}. Thus, the radiative emission process $T_2 \Longrightarrow T_1$, after population of T_2 by absorption of photons at λ = 355 nm, through a $T_1 \Longrightarrow T_2$ process, can be also discarded. If these processes were the cause of the observed

luminescences, the relative intensity of the 3-nitrocarbazole (**3**) emission would be higher than that of 1-nitrocarbazole (**2**), in contrast to the results shown in Fig. 8.

The above considerations suggest that the luminescence observed for compounds **2** and **3** in solution at 298 K, are radiative $S_{1R} \rightarrow S_0$ processes where S_0 is the ground state of the intact nitrocarbazole compounds and S_{1R} is the lowest singlet excited state of one of the resonance hybrid structures of the same compound whose tentative structure is shown in the Scheme 3. The high permanent dipole created on going from structure (**a**) to structure (**b**), would account for the fact that this very low efficiency process is observed only in a highly polar non-protic solvent such as acetonitrile, while methanol quenches it completely because of its protic character. The lack of luminescence in cyclohexane and in carbon tetrachloride solution as well as the very poor luminescence observed in ethyl acetate (for compound **2**) support the highly polar structures asigned to the luminescent species (Scheme 3, (**b**)). Furthermore, this result agrees with the fact that the polar character is higher for compound **3** than for compound **2** (Scheme 3, compare structures (**b**) for compounds **2** and **3**). The above mentioned lack of emission in methanol solution as well as the quenching of the luminescence of nitrocarbazoles **2** and **3** in acetonitrile solution when methanol was added, would account for the very low efficiency photochemical reduction of nitroaromatic compounds in alcoholic-acid mixtures described in the literature.[24,25]

2

3
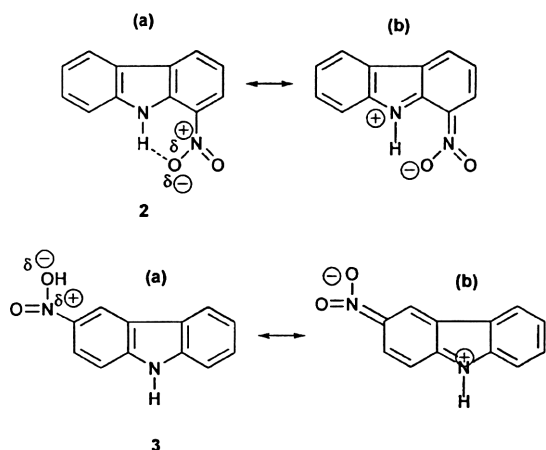
Scheme 3 Structures of nitrocarbazoles **2** and **3** (shown left; structures (**a**)) and structures of one the corresponding resonance hybrids (shown right; structures (**b**)).

Finally, it is important to note that due to the extremely low quantum yield of the luminescence emission and its high λ_{max} value, it does not affect too much the results obtained in the present work, particularly those obtained by optoacoustic experiments.

Conclusions

The results obtained in the present work clearly show that the nitro group attached to the carbazole moiety induces changes in the photophysical behavior of the nitrocarbazoles **2** and **3** compared to that of carbazole **1**. These results also show that not only the presence of the nitro group itself modifies the photophysical behavior of the nitrocarbazole but the substituent effect depends also on the location of the nitro group in the carbazole ring.

Thus, after excitation of the nitrocarbazoles **2**, **3** and carbazole **1** with UV radiation ($\lambda_{exc} = 355$ nm) in acetonitrile solution, the lowest singlet excited state S_1 likely of π,π^* nature, is populated (Table 1). From the S_1 state of compounds **1-3**, intersystem crossing process $S_1 \Rightarrow T_1$ takes place with an

efficiency of *ca.* 50% (Table 2). While in compound **1** the remaining 50% of the absorbed energy is re-emitted as fluorescence, in the case of compounds **2** and **3**, the mechanism is a radiationless internal conversion pathway to the S_0 state. From the T_1 state, compound **1** deactivates by phosphorescence and heat through processes of similar efficiency (Table 3, compound **1**, $k^e_p = 0.055$ s^{-1} and $k_{nr} = 0.074$ s^{-1}). In the case of nitrocarbazoles **2** and **3** the energy is released to the medium through both processes, but with different efficiency (see Table 3).

The measured lifetime of the lowest triplet state of 3-nitrocarbazole **3** ($\tau_T = 500$ ns) is *ca.* 50 times higher than that of 1-nitrocarbazole **2** (<10 ns). This difference is due to the different location of the nitro group as substituent in the carbazole moiety, that allows the formation of an intramolecular hydrogen bond only in compound **2**. As shown in Scheme 2, this structural characteristic allows compound **2** to show a keto–enol-like equilibrium similar to that for benzophenone. Then, it is easy rationalized, as for 2-hydroxybenzophenone, that the preferential deactivation pathway for the T_1 state of compound **2** is through radiationless mechanisms. On the contrary, as is shown in Tables 2 and 3, and in Figs. 3 and 7, for the T_1 state of the 3-nitrocarbazole **3**, radiative deactivation through phosphorescence emission is a quite efficient process.

Finally the presence of the nitro group in the carbazole moiety would account for the low efficiency luminescence observed in acetonitrile solutions of compounds **2** and **3** at room temperature (298 K) and the absence of luminescence for carbazole **1** under the same experimental conditions. As shown in Scheme 3, for compounds **2** and **3**, the formation of a singlet excited state with the structure of a resonance hybrid with highly polar character explains the results obatined in organic solvents with different polar and protic character.

References

1 M. C. Biondic and R. Erra-Balsells, Photochemical behavior of β-carbolines. Part 4. Acid-base equilibria in the ground and excited states in organic media, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1323–1328.

2 M. C. Biondic and R. Erra-Balsells, Photochemical behaviour of β-carbolines. Part 5. Ground and excited state interactions between nor-harmane and harmane with alcohols and ethers, *J. Chem. Res., (S)*, 1998, 114–115.

3 S. M. Bonesi and R. Erra-Balsells, Product Study of the Photolysis of N-Acetyl Carbazole in Ethanol and in Dichloromethane Solution. I, *J. Photochem. Photobiol., A: Chem.*, 1991, 56, 55–72.

4 S. M. Bonesi and R. Erra-Balsells, Outer-Sphere Electron Transfer from Carbazoles to Halomethanes. Reduction Potentials of Halomethanes Measured by Fluorescence Quenching Experiments, *J. Chem. Soc., Perkin Trans. 2*, 2000, 1583–1595.

5 H. Nonami, S. Fukui and R. Erra-Balsells, β-Carboline Alkaloids as Matrices for Matrix-assisted Ultraviolet Laser Desorption Time-of-flight Mass Spectrometry of Proteins and Sulfated Oligosaccharides: A Comparative Study Using Phenylcarbonyl Compounds, Carbazoles and Classical Matrices, *J. Mass Spectrom.*, 1997, 32, 287–296.

6 H. Nonami, K. Tanaka, Y. Fukuyama and R. Erra-Balsells, β-Carboline Alkaloids as Matrices for UV-Matrix-assisted Laser Desorption/Ionization Time-of-flight Mass Spectrometry in Positive and Negative Ion Modes. Analysis of Proteins of High Molecular Mass, and of Cyclic and Acyclic Oligosaccharides, *Rapid Commun. Mass Spectrom.*, 1998, 12, 285–296.

7 S. M. Bonesi and R. Erra-Balsells, Electronic spectroscopy of carbazole and N- and C-substituted carbazole in homogeneous media and in solid matrix, *J. Lumin.*, 2001, **93**, 51–74.

8 S. M. Bonesi and R. Erra-Balsells, Electronic spectroscopy of N- and C-substituted chlorocarbazoles in homogeneous media and in solid matrix, *J. Lumin.*, 2002, **97**, 83–101.

9 N. J. Turro, *Modern Molecular Photochemistry*, The Benjamin Cummings Publishing Company, Inc., CA, 1978.

10 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley Interscience, New York, 1970.

11 M. A. Ponce and R. Erra-Balsells, Synthesis and Isolation of Nitro-β-carbolines Obtained by Nitration of β-Carboline Alkaloids, *J. Heterocycl. Chem.*, 2001, **38**, 1071–1082.

12 D. D. Perrin and W. L. F. Amarego, in *Purification of Laboratory Chemicals*, Pergamon Press, New York, 3rd edn., 1988.

13 Ph. Van Haver, L. Viaene, M. Van der Auweraes and F. C. De Schyver, References for laser-induced optoacoustic spectroscopy using UV excitation, *J. Photochem. Photobiol., A: Chem.*, 1990, **63**, 265–277.

14 N. Mataga, Y. Toriashi and K. Ezumi, Electronic structure of carbazole and indole, and the solvent effects on the electronic spectra, *Theor. Chim. Acta*, 1964, **2**, 158–167.

15 J. R. Huber and J. E. Adams, Effect of the molecular geometry on the electronic structure of aromatic amines. Diphenylamine, iminodibenzyl, acridan and carbazole, *Ber. Bunsenges. Phys. Chem.*, 1974, **78**, 217–233.

16 S. C. Chakravorty and S. C. Ganguly, Polarized absorption spectra of carbazole single crystal, *J. Chem. Phys.*, 1970, **52**, 2760–2762.

17 S. P. Mc Glyn, T. Azumi and M. Kinoshita, in *Molecular Spectroscopy of the Triplet State*, Prentice – Hall Inc., Englewood Cliff, New York, 1969, ch. 6, p. 251.

18 S. L. Murov, I. Carmicheal and G. L. Hug, in *Handbook of Photochemistry*, Marcel Dekker Inc., New York, 2nd edn., 1993.

19 K. Snadros, Transfer of triplet state energy in fluid solutions, *Acta Chem. Scand.*, 1969, **23**, 2815–2829.

20 M. Terazima and T. Azumi, A time-resolved photoacoustic method widht pulsed laser excitation in the condensed phase: the relation between signal intensity and decay-rate constant, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 741–745.

21 C. Martí, O. Jurgens, O. Cuenca, M. Casals and S. Nonell, Aromatic ketones as standards for singlet molecular oxygen photosensitization. Time resolved photoacoustic and near-IR emission studies, *J. Photochem. Photobiol., A: Chem.*, 1996, **97**, 11–18.

22 J. R. Small, L. J. Libertini and E. W. Small, Analysis of photoacoustic waveforms using the nonlinear least squares method, *Biophys. Chem.*, 1992, **42**, 29–48.

23 S. E. Braslavsky and G. E. Heibel, Time resolved photothermal and photoacoustic methods applied to photoinduced processes in solution, *Chem. Rev.*, 1992, **92**, 1381–1410.

24 W. Trotter and A. C. Testa, Photoreduction of 1-nitronaphthalene by protonation in the excited state, *J. Phys. Chem.*, 1970, **74**, 845–847.

25 A. Cu and A. C. Testa, Photochemistry of the nitro group in aromatic heterocyclic molecules, *J. Phys. Chem.*, 1975, **79**, 644–646.