Published in final edited form as:

J Phys Chem A. 2011 January 20; 115(2): 152–160. doi:10.1021/jp108652p.

A comparative photophysical and photochemical study of nitropyrene isomers occurring in the environment

Rafael Arce*, Eduardo F. Pino†, Carlos Valle, Ideliz Negrón-Encarnación, and María Morel

Department of Chemistry, University of Puerto Rico, Rio Piedras Campus, San Juan, Puerto Rico, 00931-3346

Abstract

Ground state absorption, first excited-singlet state, and properties of reactive intermediates of mononitropyrene isomers encountered in the atmospheric aerosol have been studied under different conditions that could mimic the environment. The nitro group can present different orientation relative to the pyrene ring depending on its geometric location and could induce differences in the photochemistry of the isomers. The 2-NO₂Py isomer has the largest red shift and lowest oscillator strength in the UV-visible band associated with the nitrogroup. The isomers show very low fluorescence yields (10^{-3} – 10^{-4}). Only 1-NO₂Py and 4-NO₂Py have phosphorescence emission ($\Phi_p \approx 10^{-4}$), indicating that the lowest triplet state decays mainly through effective radiationless channels. Laser photolysis produces a low lying triplet state ($\tau_T = 10^{-5}$ – 10^{-6} s), a long-lived pyrenoxy radical, and a PyNO₂H radical in solvents in which the triplet can abstract a hydrogen atom. Similar triplet yields were calculated (0.1–0.6) for the isomers while significant differences in the relative yield of the long-lived species were determined. Differences in the quenching rate constants of the triplet by water and phenols suggest a strong hydrogen bond interaction with the nitro group in the C-2 position, which provides for radiationless deactivation routes.

Keywords

nitropyrenes; photochemistry; transient intermediates; triplet yields; quenching rate constants; quenching effects of phenols; and water

Introduction

Most nitropolycyclic aromatic hydrocarbons (nitro-PAHs), a class of genotoxic environmental pollutants, are formed by incomplete combustion processes and emitted from diesel engine vehicles, wood stoves, fire places, and kerosene heaters.^{1,2} These can be also encountered in urban air particles, coal fly ash, and grilled foods. Nitropyrenes exist almost entirely in the particle phase under ambient conditions.³ In air and diesel particulate, the three nitropyrene isomers (1-NO₂Py, 2-NO₂Py and 4-NO₂Py, Scheme 1) are found at levels of ng/g, the 1-NO₂Py level (155 ng/g) being at least 3 to 10 times higher than for 2-NO₂Py and 4-NO₂Py.⁴ Of these isomers, 2-NO₂Py, can be formed through heterogeneous or homogeneous reactions of the parent pyrene with OH radicals and nitrogen oxides under

*To whom correspondence should be addressed: Department of Chemistry, University of Puerto Rico, Rio Piedras Campus, P.O. Box 23346, San Juan, Puerto Rico. 00931-3346, rarce@uprr.pr.

†Present address: Facultad de Química y Biología, Universidad de Santiago de Chile, Chile

Supporting Information Available: Fluorescence excitation (2-NO₂Py and 4-NO₂Py) and phosphorescence emission spectra (4-NO₂Py). This material is available via free of charge via the Internet at <http://pubs.acs.org>.

photochemical conditions, and detected in ambient air and not in direct combustion emissions.⁵ The reactions and fate of the four ring nitroaromatics continues to be a topic of high interest due to their mutagenic and possible carcinogenic properties.

The nitro group in these nitro-PAHs can have different orientations relative to the arene moiety depending upon its geometric location. The orientation can be described as parallel, if the torsion or dihedral angle, C-C-N-O, is coplanar with the aromatic ring or perpendicular when the group is in an out-of plane rearrangement. Intermediate angles are possible. For the three nitropyrenes, PM3 and density functional calculations have predicted that in 2-NO₂Py the nitro group is coplanar with the rings,^{6,7} while for 1-NO₂Py angles of 55,⁶ 23.15⁷ and 27.5⁸ degrees have been reported. Torsion angles of 12.7⁶ and 26⁷ were reported for 4-NO₂Py. More recently, using density functional level theory, Reichardt et. al.⁹ have demonstrated that at room temperature a distribution of nitroaromatic torsion angles is available for nitronaphthalenes. This orientation of the nitro group has been correlated with direct acting mutagenicity and tumorigenicity^{10,11} and the photochemical reactivity of these molecules.^{12,13} In the development of these correlations different structural, spectroscopic, and electronic properties associated with the orientation of the nitro group such as half-wave potentials,¹⁴ calculated energy of the lowest unoccupied molecular orbital,¹⁵ MS,⁶ high resolution proton NMR data,^{15,16} and Raman depolarization spectral data¹⁷ have been used to predict the biological activity of nitro-PAHs. A general observation is that nitro-PAHs, with a nitro group planar to the arene moiety are more mutagenic than their isomers; although in the case of the nitropyrenes this is not sustained.⁷

The photochemical reactivity of the nitropyrene isomers has been reported in methanol solutions.¹³ The 1-NO₂Py showed a rapid conversion, 4-NO₂Py was three times more stable than 1-NO₂Py in terms of the irradiation time, while 2-NO₂Py did not show a clear reaction. Some products were identified¹³, and from those it was proposed that 1-NO₂Py undergoes the Chapman nitro-nitrite rearrangement,¹⁸ typical of nitroarenes, leading to 1-hydroxypyrene in 88% and 1-hydroxy-2-nitropyrene in a 7% yield. For 4-NO₂Py, pyrene was the major photoproduct observed.¹³ More recently, Warner et al.¹² demonstrated that some nitro-PAHs showed an association between the torsion angle and photoreactivity in solution while when adsorbed on a surface, there was no correlation. Some photophysical and photochemical properties of 1-NO₂Py were reported by us.¹⁹ Low temperature phosphorescence and room temperature transient absorption spectra showed the presence of a low energy ³(π,π^*) state decaying with lifetime in the 10⁻⁵–10⁻⁴ s range depending on the solvent. Reactions of this triplet state with known quenchers and with substances with hydrogen donor abilities were also informed. A long lived transient absorption with maximum at 420 nm was assigned to the pyrenoxy radical.

In this work, we have studied the ground, excited singlet, triplet states, and the reactive intermediates and their reactions for the three isomers of nitropyrene in order to understand their photochemical differences and to determine if these can be associated with the nitro group orientation. In addition, because of the intermediates formed in the photochemical processes can transform into intermediates that participate in the nitro reduction or ring oxidation reactions, produced by the metabolic activation of nitro-PAHs into genotoxic agents,¹¹ it was of interest to compare the reactivity and yield of these intermediates.

Experimental Section

Reactants and solvents

Ferrocene, laboratory grade, perylene 99+%, anthracene, benzophenone 99+%, 1-hydroxynaphthalene (1-naphthol) 99%, 2, 6-dimethoxyphenol (syringol) 99%, 4-hydroxy-3-

methoxybenzoic acid (vanillic acid) 99% were from Sigma-Aldrich Chemical Co. and used as received.

1-Nitropyrene 99% (Aldrich Chemical Co.), 2-nitropyrene 99.2% (Chiron AS), and 4-nitropyrene 99.5% (Chiron AS) were purified. 1-nitropyrene was recrystallized three times from methanol,¹⁹ while 2-nitropyrene and 4-nitropyrene, due to the small quantities available and high cost, were purified by dissolving them on acetonitrile and passing the solution through a short activated silica gel column contained in a Pasteur pipette. Their purity was assessed from the emission-excitation and UV-visible absorption spectra. The acetonitrile was evaporated with a nitrogen flow and the bright yellow solids were then used to prepare solutions in other solvents.

Hexane 99%, cyclohexane 99%, 3-methylpentane 99+%, 2-propanol 99.5%, n-propanol 99%, methylcyclohexane 99+% were from Aldrich Chemical Co. Methanol and acetonitrile were obtained from Fisher Scientific. The purity of the solvents was verified by HPLC. Non-polar solvents were purified by passing these through an activated silica gel column and the purification was corroborated by recording the fluorescence and UV-visible spectra of the fractions collected from the column. Other solvents were used as received.

Methods

Absorption spectra of the isomers in different solvents were recorded with a Varian Cary IE UV-visible spectrophotometer. Solutions were purged with N₂ for 30 min before the spectrum was recorded. Molar absorption coefficients, oscillator strengths, bandwidths at half-peak height were calculated as previously described.¹⁹ Fluorescence spectra were recorded with a Varian Cary Eclipse fluorescence spectrophotometer. Plots of the area under the emission spectrum as a function of $1-10^{-A}$ where A is the absorbance at the excitation wavelength, were prepared to determine quantum yields. For these, fluoranthene in cyclohexane ($\Phi_f = 0.35$)²⁰ was used as the standard for 1-nitropyrene and biacetyl in cyclohexane (0.27×10^{-3})²¹ for the other isomers, to facilitate the matching of the absorbance of both solutions at the excitation wavelength.

Phosphorescence spectra of 1-nitropyrene and 4-nitropyrene in 3-methylpentane, n-propanol, ethanol, and methylcyclohexane glasses were recorded in a Varian Cary Eclipse spectrophotometer in the phosphorescence mode. Phosphorescence yields were calculated from plots of the areas under the emission spectra as a function of $1-10^{-A_v}$, where A_v is an average absorbance of the solution in a 4 mm i.d. diameter quartz tube. Biacetyl in n-propanol ($\Phi_p = 0.23$)²² was used as a standard to calculate the relative quantum yield.

The transient absorption spectrokinetic system has been described elsewhere.^{19,23} It consists of a Continuum Surelite II Nd: YAG Q switched laser delivering up to 70 mJ at 266 nm and 150 mJ at 355 nm. Time resolved absorption measurements were made perpendicular to the excitation beam by using a conventional Xe-300 W arc lamp (Oriel Co.), a monochromator and an R 928 five stage wired photomultiplier. The output signal was recorded on a digital oscilloscope (Le Croy 9360, 600 MHz, 5 Gs/s) and transferred to a personal computer. Signals were averaged to improve the signal to noise ratio. The N₂ degassed solutions were changed after 300 laser shots to avoid for the excitation of photoproducts and photodegradation of the sample. The energy of the laser was measured with a Newport 1835 high power meter or using benzophenone as an actinometer.

The molar absorption coefficients of the triplet-triplet absorption of the isomers were measured by the energy transfer method.²⁴ Perylene was used as a triplet energy acceptor in the cases of 1-NO₂Py and 4-NO₂Py, while anthracene was used for the determination of the molar absorption coefficient of 2-NO₂Py. Briefly, a solution of the nitropyrene isomer in the

specific solvent was excited in the absence and in the presence of the energy acceptors. Kinetic corrections were applied for less than 100% energy transfer and decay of the triplets.²⁵ Using the molar absorption coefficient of the triplet state of the isomers and benzophenone as an actinometer, triplet quantum yields were obtained from power dependence plots of the triplet absorption signals for the isomers and of the benzophenone at the wavelength, where the molar absorption coefficients are known, and using optically matched solutions at the excitation wavelengths.²⁶

In quenching experiments using phenols, the concentration of the isomer was in the range of 10^{-5} M, while of the co-solute was in the range of 10^{-3} – 10^{-4} M.

Results and Discussion

Ground state properties

The UV-visible spectra of the three nitropyrene isomers show three major bands typical of other nitro-PAHs (Figure 1). The long wavelength band observed in the region of 345 to 475 nm, depending on the isomer and solvent, and extending the absorption of these molecules into the visible, thus increasing the possibility of photochemical transformation in the environment, is typical of nitropyrenes and has contributions from π, π^* transitions from the NO_2 group and the pyrene's ring system.^{8,13,27} The intensity of this band decreases in the order $1\text{-NO}_2\text{Py} > 4\text{-NO}_2\text{Py} \gg 2\text{-NO}_2\text{Py}$ and the oscillator strengths associated to this band are 0.2–0.3, 0.09–0.15, and 0.01–0.07, respectively (Table 1). Vibronic structure on this band is more clearly observed in non-polar solvents and it is more clearly seen in the 1- NO_2Py band. Larger bandwidths and red shifts (5–10 nm) were observed in polar solvents.

For comparison the absorption spectrum of pyrene, the parent PAH compound, is included in Figure 1. It has four absorption bands in the 26,000 (384.6) to $47,000\text{ cm}^{-1}$ (212.8 nm) wavelength region. On the basis of theoretical calculations, absorption, and fluorescence spectral data, the first band (very weak, not seen in Figure 1) has been attributed to a short-axis polarized transition, the second ($\sim 30,000\text{ cm}^{-1}$, 333.3 nm) to a long-axis polarized, the third ($37,500\text{ cm}^{-1}$, 266.7 nm) to a short-axis, while the fourth has been associated with a transition dipole moment polarized to a long-axis.²⁸ In general, the substitution of an electron-withdrawing nitro-group is known to have a particularly strong stabilizing resonance effect, inducing a red shift in the pyrene bands,²⁹ as observed in Figure 1. Furthermore, a significant loss of the vibronic structure in each pyrene band is also induced. Substitution in the C-2 position with a nitro group, which would affect the long axis transition moment of pyrene, shows the largest bathochromic shift and effect on the intensity of the third band of pyrene ($37,500\text{ cm}^{-1}$). This substitution also induces a significant reduction in the intensity of the first and third bands of the nitro-PAH. Other C-2 substituted pyrene derivatives with electron donating or withdrawing groups show similar effects.^{29,30} These observations have been explained in terms of a poor interaction between the substituent at the C-2 position and the pyrene's orbitals, which results in a UV-visible absorption spectrum that closely resembles the parent's spectrum.¹³ Substitution at the C-1 or C-4 positions should perturb the short-axis polarized transition to a larger extent than the long-axis. In this case, minor effects are seen on the fourth band of pyrene, while the third band decreases in intensity and is red shifted in both 1- NO_2Py and 4- NO_2Py relative to pyrene.

Singlet excited state

The three isomers show a broad very low intensity band with maximum in the 425–585 nm wavelength region depending on the solvent (Figure 2). A singlet state energy, ranging from 250 to 290 kJ/mol, was calculated from the intersection of the excitation and emission

spectra. In general, the 1-NO₂Py fluorescence state is stabilized to a greater extent than for the other two isomers in polar solvents and the energy of this state is approximately 15 to 20 kJ/mol higher. The largest Stokes shifts were observed for 4-NO₂Py followed by 2-NO₂Py and 1-NO₂Py (Table 2). These shifts increased with solvent polarity, suggesting a large dipole moment in the excited state and its π,π^* character. Indeed, plots of the Stokes shifts as a function of the normalized scale of $E_T(30\text{-betain dye})^{31}$ resulted in a $\Delta\mu$ of 8 to 20 D between the singlet excited and ground state dipole moment's, implying a significant charge transfer character for this transition.

Very low fluorescence quantum yields of the order of 10^{-3} – 10^{-4} were measured (Table 2), which follow the trend 4-NO₂Py > 2-NO₂Py > 1-NO₂Py in acetonitrile. Excluding benzene and toluene, in the other non-polar solvents tested, the fluorescence yields were less than 10^{-4} for the three isomers. In comparison to the parent PAH (Φ_f pyrene = 0.88³²), the nitro-isomers show a significant reduction in the fluorescence yield which can be interpreted in terms of a high charge transfer character of the singlet excited state, to a high rate of intersystem crossing, and/or to the photodissociation of the nitropyrene into a NO and a pyrenoxy radical.^{8,33,34}

The fluorescence of 2-NO₂Py is quenched by alcohols such as methanol (Figure 3), ethanol, 2-propanol, n-propanol, and 1-naphthol, a feature not observed for 1-NO₂Py or 4-NO₂Py, except in methanol. From these plots quenching constants of 3.0 ± 0.1 (2-propanol) to 15 ± 1 M⁻¹ (1-naphthol) in acetonitrile were calculated using a Stern-Volmer analysis. Except for a small displacement of the wavelength of maximum absorption, no changes in the UV-visible spectrum of 2-NO₂Py were observed upon addition of the alcohols that could provide evidence of ground state complex. The fluorescence yield did not change with increasing temperature in the range of 25 to 55 °C, suggesting a static quenching process mediated by the formation of a weak ground state complex. Thus, this decrease in fluorescence can be rationalized in terms of nitropyrene forming a hydrogen bond with the alcohols which provides a pathway for radiationless deactivation of the fluorophore through new vibronic dissipation modes which can couple the excited and ground states.³⁵ The fact that this effect is more noticeable in the C-2 substituted pyrene could indicate that in this position, hydrogen bonding interactions are more favorable due to less steric effects caused by the hydrogen atoms (peri H, Scheme 1) in the ring which for 2-NO₂Py are inexistent. The similarity in some of the properties of the singlet excited state of the isomers can be interpreted in terms that even if there are differences in the NO₂ group orientation in the ground state, the excited singlet state relaxes through an ultra fast rotation of the nitro group resulting in a relaxed planar state as suggested by theoretical calculations.⁸

Lowest triplet state at 77 K

Only 1-NO₂Py,^{19,27} and 4-NO₂Py showed low intensity phosphorescence emission spectra at 77 K in the polar and non-polar organic glasses tested. The phosphorescence spectra of these showed two distinct maxima, the one with the largest intensity in the wavelength region of 630–640 nm and another with maximum around 700 nm, and a shoulder around 750–755 nm. From the first maximum, a triplet energy of 187 kJ/mol was calculated. Phosphorescence quantum yields of the order of 10^{-4} were calculated for 4-NO₂Py (9.2×10^{-4}) and 1-NO₂Py (3.1×10^{-4}) in a 3-methylpentane glass, and lifetimes of 40 to 50 ms were obtained from mono-exponential fits to the phosphorescence decay curves. Pyrene also shows a small phosphorescence yield of 2×10^{-3} in 3MP glass.³² For 1-NO₂Py and 4-NO₂Py this low energy triplet state has been assigned to a $^3(\pi,\pi^*)$ state. In the case of 4-NO₂Py in a 3MP glass, a band with maximum at 550 nm, and a shorter lifetime of 5 ms has been attributed to a triplet aggregate because the intensity of this band shows a strong concentration dependence.

The absence of a phosphorescence emission for 2-NO₂Py could imply a larger n,π^* character for the lowest energy triplet state which would result in a shorter lifetime³⁶ and lower phosphorescence yield. Furthermore, such low emission yields for these isomers suggest very effective radiationless decay routes for the lowest triplet state.

Transient absorption spectra

Lowest triplet state (short-lived intermediate)—The three isomers show transient absorptions above 300 nm and up to 700 nm (Figure 4A, B). Two distinct absorption bands are identified, one in the wavelength region of 350–475 nm with maximum around 440–465 nm for 1-NO₂Py, 430–450 nm for 4-NO₂Py, and remarkably blue shifted (415–425 nm) for 2-NO₂Py, and another band with maximum at 510–520 nm for 1-NO₂Py, 550–600 nm for 4-NO₂Py, and at 510–525 nm for 2-NO₂Py. The intensity ratio of these bands is different, being three for 2-NO₂Py, two for 4-NO₂Py, and close to one for 1-NO₂Py. Noticeably, the transient absorption spectra for 2-NO₂Py and 4-NO₂Py resemble more the parent pyrene's transient absorption^{24,37} than for 1-NO₂Py.

Decay curves for the transient absorbance, most notably for 1-NO₂Py and 4-NO₂Py, recorded in the short wavelength band show the presence of at least two transient species, while at the longer wavelengths the decay curves fitted to a mono-exponential decay. In addition, plots of the initial absorbance at the maxima of these bands as a function of the laser energy show different slopes. The larger slopes for these plots at the shorter wavelength band are indicative of the presence of different species. These plots show an initial linear dependence, which depending on the solvent polarity, saturates at different laser energies. In polar solvents, a small red shift of 10 nm was observed for the long wavelength band for 1-NO₂Py and 4-NO₂Py, but not for 2-NO₂Py (see below, water effect).

Oxygen, perylene, azulene, anthracene, and ferrocene, acting as triplet quenchers, induced an increase in the decay rate of the short lived species contributing to the two major absorption bands. Thus, one of the species contributing to the transient spectra, was assigned to a $^3(\pi,\pi^*)$ state. The band with maximum in the 510–600 nm region is assigned to a $T_1 \rightarrow T_m$ transition, while the band with maximum in the 400–470 nm region presents contributions from a $T_1 \rightarrow T_n$ transition and other reactive species, discussed below. A quenching process of the triplet state by the ground state nitropyrene was observed for the isomers. A summary of the natural decay, k_0 , and quenching rate constants for the triplet state of the isomers in some polar and non-polar solvents is presented in Table 3.

The triplet decay time constants (10^{-5} – 10^{-6} s) for 4-NO₂Py and 2-NO₂Py decreased by a factor of 2 or 3 in going from a non-polar to a polar protic environment, while for 1-NO₂Py was the opposite. This instability in polar protic solvents can be explained in terms of hydrogen bonding interactions that could lead to quenching either by vibronic coupling to the ground state or a hydrogen abstraction reaction (see below). Quenching rate constants were of the order of 10^9 – 10^{10} M⁻¹ s⁻¹ for ferrocene, perylene, anthracene, and O₂ for all the isomers suggesting diffusion controlled processes, and indicating an energy transfer mechanism from the lowest triplet state of the nitropyrene isomer to the quencher. This was corroborated, for example, when perylene, azulene or anthracene were used as quenchers that a growth of an absorption signal was observed in the region where the triplet of these molecules absorb. No significant differences were observed for the quenching reactions of the different triplet isomers with the same quencher. Nonetheless, self quenching rate constants were larger for 4-NO₂Py, and 1-NO₂Py than for 2-NO₂Py, a possible ring position effect for this reaction.

A similar lowest triplet state energy of 187 kJ/mol was calculated from the phosphorescence spectra of 1-NO₂Py and 4-NO₂Py. Because the excited singlet state energy is in the range of

270–290 kJ/mol, this high energy gap (~ 100 kJ/mol) between the excited singlet and the lowest triplet state suggests the possibility of other triplet states, as demonstrated from computational results for 1-NO₂Py,⁸ into which the excited singlet state can intersystem cross with a high rate constant into a higher triplet $^3(n,\pi^*)$ state. Although, this intermediate was not observed⁸ for 1-NO₂Py, recent results from Peón and coworkers³⁸ for the case of 1-nitronaphthalene provide evidence of decaying absorption signals below 400 nm in picoseconds timescale assigned to an (n,π^*) state which acts as a receiver in the intersystem-crossing process and as the precursor of the lowest triplet state.

A significant decrease in the triplet molar absorption coefficient in the 500–600 nm region, and in the intersystem crossing yields were observed in going from 3 1-NO₂Py to 3 4-NO₂Py (Table 4). This trend can be correlated to the observed increase in the fluorescence yield observed for 4-NO₂Py, compared to the other isomers.

It is interesting to single out the similarity, in terms of the position of the absorption bands and their relative intensity, of the triplet absorption spectra of 2-NO₂Py and of pyrene^{24,37} which could indicate a weak interaction of the nitro at the C-2 position with the pyrene ring π system, resulting in an absorption spectrum that resembles that of pyrene.

Pyrenoxy radical (long-lived transient)—At observation times longer than 5×10^{-5} s a long-lived transient absorption was observed with maximum in the wavelength region of 400 to 450 nm depending on the solvent. Figure 5 shows the transient spectra for the isomers recorded at these long observation times. The species associated with this absorption grows within the laser pulse and then slowly decays persisting up to times when the triplet or other transient species have disappeared. This species decays, assuming a first order process, with a decay rate constant of the order of 10^{-3} s⁻¹, close to a hundred times smaller than for the triplet state.

In the interest of establishing the identity and precursor of this species, the effects of solvents and quenchers on its yield and decay rate were examined. The latter were measured at times when the triplet state has completely decayed and in nitropyrene isomer solutions exhibiting the same initial absorbance at the excitation wavelength. The formation of this transient is favored in polar protic solvents and at laser energies above 30 mJ, although at lower energies (10 mJ) the absorption signal is still seen. For 1-NO₂Py and 4-NO₂Py the relative yield increases in the order: cyclohexane $\approx$ acetonitrile $<$ CCl₄ $<$ methanol (Figure 6). This intermediate, in the case of 2-NO₂Py, is only observed in CCl₄ and methanol, at a yield one fifth of that observed for 4-NO₂Py. For 1-NO₂Py the yield is close to two times higher than for 4-NO₂Py in CCl₄ and methanol, while in acetonitrile similar yields were observed. For all isomers, the decay rate of the long-lived transient in the presence of ferrocene (10^{-4} M) and in O₂ saturated solutions (10^{-3} – 10^{-2} M) is not affected. In the presence of these additives and for the cases of the 4-NO₂Py and 2-NO₂Py isomers the yield is barely affected, although a noticeable decrease (40%) was observed for 1-NO₂Py.¹⁹ On the basis of these observations and comparing the spectra (Figure 5) with that generated in the laser flash photolysis of 1-hydroxypyrene in methanol under N₂ and O₂ atmospheres,¹⁹ and the reported spectra of the pyrenoxy (PyO) radical,^{39,40} the long-lived transient is assigned to this species.

It has been suggested that the pyrenoxy radical can decay by abstracting a hydrogen atom from the solvent to form hydroxypyrene,^{13,19,41} thus experiments to further characterize the kinetic properties of this radical were performed in CCl₄ to avoid reactions with the solvent and the interference from the radical formed from the reaction of the nitropyrene triplet with the solvent (see below). In O₂ saturated solutions, total quenching of the PyO absorption was observed in the case of 1-NO₂Py and 2-NO₂Py, while for 4-NO₂Py only a 50%

decrease was noticed. The presence of 1-naphthol (10^{-4} M) resulted in a 40–50% decrease in the yield of the radical for the three isomers (Figure 7A) and a very slight increase in its decay rate, from a hydrogen abstraction reaction of the PyO radical with the phenol hydrogen. Also, in the naphthol containing solutions an increase in absorbance at wavelengths in the 400 nm region was noticed due to the formation of a PyNO_2H radical (see below, reactions with phenols).

The precursor of the PyO radical is still in dispute. As argued before,¹⁹ the radical was postulated to originate from the corresponding nitro-nitrite rearrangement¹⁸ of $^3(\text{n},\pi^*)$ and/or $^3(\pi,\pi^*)$ states. A $^3(\text{n},\pi^*)$ state, formed in a few picoseconds (7 ps)⁸ which decays by internal conversion into a $^3(\pi,\pi^*)$ state in an ultrafast time scale could explain that this radical is generated within the laser pulse, that its yield is not affected by diffusion controlled quenching reactions by O_2 or ferrocene, and the much smaller yield for the 2- NO_2Py isomer due to a less favorable orientation of the nitro group to form the proposed cyclic intermediate in the nitro-nitrite rearrangement.¹⁸ Nonetheless, a $^3(\pi,\pi^*)$ precursor with a lifetime of 10^{-5} – 10^{-6} s could account for the effect of quenchers on the yield. Because the triplet quenchers affect differently the yield of this radical for the nitropyrene isomers, this could suggest differences in reactivity of the triplet excited states or reactive intermediate (cyclic intermediate¹⁸) precursors of this species.

Recently, Reichardt et. al.⁹ have proposed a non-radiative decay channel from the S_1 state of nitronaphthalene competing with intersystem crossing into a $^3(\text{n},\pi^*)$ state. They suggested that in 200 fs lifetime the S_1 state can relax to a dark charge transfer state from which an aryloxy radical can be formed. In our experiments we observed a possible hydrogen effect on the yield of the pyrenoxy radical and this could shed light on the properties of the precursor of this intermediate.

Intermediate lifetime transient, PyNO_2H —When methanol and 2-propanol were used as solvents, and at intermediate observation times (5×10^{-5} to 2×10^{-4} s), the transient absorbance in the wavelength region of 390 to 430 nm was either totally quenched, as is the case in 2-propanol or decreased significantly (80%) in methanol, in the presence of triplet quenchers. For example, in the presence of ferrocene (10^{-4} M), the yield of the intermediate lifetime species in 4- NO_2Py irradiated solutions is reduced to a third of its value in the absence of ferrocene, while in O_2 saturated solutions this intermediate was not observed (Figure 7B). Similar effects were observed for the other isomers. Because the intermediate lifetime species was quenched in the presence of known triplet quenchers and it appeared in solvents where there is a possibility of hydrogen abstraction reaction, this intermediate has been assigned to a PyNO_2H radical formed through a hydrogen atom abstraction reaction of the $^3(\pi,\pi^*)$ state with the solvent. The PyNO_2H radical further reacts to form a nitrosopyrene product. Indeed, our unpublished results⁴¹ demonstrate that in solvents such as 2-propanol and methanol the yield of 1-nitrosopyrene is as high as 10% of the total photodestruction yield in N_2 saturated solutions, while in the presence of O_2 the product is not observed.

Quenching of the $^3(\pi,\pi^*)$ state by phenols—Phenolic compounds, ArOH , have been identified in the atmospheric aerosols. These result from incomplete combustion processes or from the slow oxidation of compounds in the aerosol. It has been shown that in their presence, the photodegradation rate of polycyclic aromatics and nitroaromatics increases.^{42–46} Recently, we reported that the $^3(\pi,\pi^*)$ state of 1- NO_2Py is quenched by several phenolic compounds.¹⁹ Quenching rate constants for this process were large (10^7 – $10^9 \text{ M}^{-1}\text{s}^{-1}$) and fitted a Rehm–Weller plot of $\log k_q(\text{ArOH})$ versus the oxidation potential of the phenolic compounds. Moreover, the transient absorption spectra did not provide evidence for a complete electron transfer because transient bands corresponding to the radical anion of 1- NO_2Py or the radical cation of the phenolic compound were not observed. Thus, it was

proposed that the quenching occurs via a hydrogen atom abstraction reaction that goes through an electron transfer within a hydrogen-bonded triplet exciplex followed by a proton transfer mechanism.^{19,47–49}

In a similar manner, we have observed an increase in the triplet decay rate of the $^3(\pi,\pi^*)$ state of the other isomers with an increase in ArOH concentration. The triplet decay curve fitted to a mono-exponential function. Quenching rate constants were calculated from Stern-Volmer plots and are of the order of magnitude of 10^7 – 10^9 M⁻¹ s⁻¹ for the three isomers (Table 5). Although the rate constants are similar, in the case of 4-NO₂Py and 2-NO₂Py, the transient spectra in acetonitrile at different observation times showed distinct features (not shown). At short observation times (10^{-7} s), the spectra presented bands having contributions from the triplet state (410 nm), the PyNO₂H radical (390–430 nm), the aryloxy (ArO) radical (370–390 nm), and the pyrenoxy radical (420–450 nm).⁵⁰ At intermediate observation times, after the triplet state has completely decayed ($t > 10^{-5}$ s), the spectra showed contributions from the other species, while at long-observation times only the residual absorption from the pyrenoxy radical was detected. In contrast, for 1-NO₂Py, the absorption bands associated to the PyNO₂H radical and the aryloxy radical grew after the pulse with a rate constant similar to the calculated decay rate constant of the triplet state.¹⁹ These differences can be accounted if the 4-NO₂Py and 2-NO₂Py isomers form stronger ground state complexes with the ArOH in acetonitrile than the 1-NO₂Py isomer, allowing for a rapid initial hydrogen-bonded triplet exciplex formation reaction with the corresponding triplet states of those isomers. A transient absorption signal, assigned to a ArNO₂H radical, was reported by Göerner⁵⁰ in the triplet quenching of nitronaphthalenes by amines in benzene.

For the 1-NO₂Py and 4-NO₂Py isomers a higher reactivity toward hydrogen atom abstraction from 1-naphthol and 2,6-dimethoxyphenol was observed in non-polar versus polar solvent, while the opposite was observed for 2-NO₂Py. In general, for the same hydrogen donating substrate (ArOH) higher rates in non-polar solvents are anticipated. This is because in highly polar acetonitrile, strong interactions between the H atom in the OH group and polar acetonitrile molecules are expected which through solvation effects can difficult the triplet exciplex formation between PyNO₂ and the ArOH. Thus, in the case of 2-NO₂Py, the position of the NO₂ group, less hindered by peri-H atoms, can allow for this interaction despite the solvation effects of the acetonitrile molecules with ArOH.

The lowest reaction rate was observed for 4-hydroxy-3-methoxybenzoic acid in which steric effects can impede the formation of the triplet exciplex. Interestingly, in this case the highest rate constant corresponds to the 2-NO₂Py isomer, again showing a location effect (a less hindered NO₂ position).

Effect of water—It has been demonstrated that a significant amount of water can be incorporated into automobile exhaust and wood smoke particles at a high relative humidity.^{43,51} The water content of the organic layer in which PAHs are associated can affect the photodegradation rates of PAH in these particles.^{43,51} Because the mechanism of the effect of water on these phototransformations is not fully understood, this motivated us to study the effect of water on the ground state, first excited singlet, and reactive intermediates produced during the photolysis of nitropyrene isomers.

The addition of water to solutions of the nitropyrene isomers in acetonitrile induced a small red shift in the absorption band associated to the nitro-group. For the 2-NO₂Py and 4-NO₂Py isomers larger shifts were observed (3–7 nm) as the water percent increased from 0 to 15 % by volume, while above this percentage the shifts were smaller in magnitude (<1 nm). This behavior suggests a solvent specific interaction such as the formation of hydrogen bonds

with the NO₂ group. In the case of 1-NO₂Py the red shifts increased continuously with increasing water content. This observed red shifts with increasing solvent polarity also corroborated the π,π^* character of this transition.

Red shifts in the emission spectra for 1-NO₂Py (10 nm) and 4-NO₂Py (25 nm) were also observed with increasing addition of water, while for 2-NO₂Py an instant quenching effect was seen (from 0.5 to 2 %) at a very low fraction of water. The shifts in the emission bands were larger than those observed for the absorption band and are the result of the increase in solvent polarity which stabilizes the first excited singlet state. A larger stabilization effect was observed for 4-NO₂Py compared to 1-NO₂Py. From Stern-Volmer plots fluorescence quenching constants by water were determined for the isomers ($0.22 \pm 0.02 \text{ M}^{-1}$ for 1-NO₂Py, $2.83 \pm 0.01 \text{ M}^{-1}$ for 4-NO₂Py, and $8.7 \pm 0.4 \text{ M}^{-1}$ for 2-NO₂Py). The quenching constant for 2-NO₂Py by water is about three times higher than for aliphatic alcohols, reflecting differences in the strength of the hydrogen bonds.

In terms of the transient intermediates, red shifts of 8–15 nm in the bands associated to the T-T absorption were observed for 1-NO₂Py and 4-NO₂Py. This red shift is consistent with the π,π^* nature of the lowest triplet state. An increase in the lifetime from 4.3 to 6.4 μs (at 60%) was observed for the 1-NO₂Py triplet suggesting a stabilization of this state in the presence of water. This agrees with the increase in the triplet lifetime observed for this isomer in polar solvents. A decrease in the initial triplet yield with increasing water content was noticed, which is interpreted in terms of either a decrease in the triplet molar absorption coefficient or in the intersystem crossing yield. Although no shifts in the absorption bands of the 2-NO₂Py triplet were detected, suggesting a greater n,π^* character of this state, a drastic increase in the triplet decay rate constant from 4.2×10^4 to $3.7 \times 10^5 \text{ s}^{-1}$ in 45% water was observed.

Conclusions

The reactions and fate of the nitroaromatic continues to be a topic of high interest due to their mutagenic and possible carcinogenic properties. In this work, we demonstrate that the geometric location of the nitro group in the pyrene ring of the mononitropyrene isomers, detected in direct combustion (1-NO₂Py and 4-NO₂Py) and in ambient air (2-NO₂Py), determines the absorption, fluorescence quenching properties, and reactivity of the lowest triplet state with constituents of the aerosol such as water and phenols. The less hindered C-2 position in the pyrene ring allows for stronger hydrogen bond interactions which facilitates fluorescence quenching and formation of a triplet exciplex which participates in the quenching process of the lowest triplet state. The absence of phosphorescence emission and water effects on the T-T absorption bands suggest a large n,π^* character for the lowest triplet state of the 2-NO₂Py isomer.

In general (Scheme 2), the absorption of light by these nitropyrene isomers induces a transition into a singlet excited state, which emits with yields of the order of 10^{-3} – 10^{-4} . Large Stokes shifts were observed (~ 4800 – 7900 cm^{-1}) which increased with solvent polarity, suggesting a large dipole moment in the excited state and its π,π^* character. The low fluorescence yield, the high energy gap between the singlet excited and lowest triplet state, femtosecond broad band transient results and theoretical calculations⁸ predict a strong spin-orbit coupling and rapid intersystem crossing ($<10 \text{ ps}$) into a dark $^3(n,\pi^*)$ state. An additional decay channel for the S₁ state of nitronaphthalene has been recently postulated⁹ in which this state transforms into a species with charge-transfer characteristics which dissociates into a pyrenoxy radical. According to our results the formation of this radical is favored in polar protic solvents and for some of the isomers its precursor can be quenched by triplet quenchers. This radical reacts with the solvent and with phenols through a

hydrogen atom abstraction to form a hydroxypyrene product. The low lying triplet state reacts at diffusion controlled rates with quenchers which include other PAHs, ground state nitropyrene isomers, and by a hydrogen abstraction reaction with phenols that goes through an electron-transfer within a hydrogen bonded triplet exciplex followed by a proton transfer mechanism. In solvents in which the energetic favors a hydrogen atom abstraction by the triplet state, the triplet forms a PyNO_2H radical which eventually leads to nitrosopyrene product.

A large difference in photoreactivity of the nitropyrene isomers has been reported in methanol¹³ and quantified by us in this and other solvents.⁴¹ For example, in methanol⁴¹ the $\Phi(1\text{-NO}_2\text{Py})$ is $(1.2 \pm 0.1) \times 10^{-3}$ while for $4\text{-NO}_2\text{Py}$ is $(0.4 \pm 0.1) \times 10^{-3}$. Initially, one could try to explain this difference in terms of the differences in the triplet quantum yields, assuming that the lowest triplet state is the reactive state, but this argument will not follow for $2\text{-NO}_2\text{Py}$ which is very unreactive, although its $^3(\pi,\pi^*)$ yield is similar. Furthermore, this triplet state shows similar reactivity toward quenching and hydrogen atom abstraction reactions for all isomers, thus the reactivity of this excited state cannot account for the differences in the photoreactivity. Therefore, the differences possibly arises from differences in reactivity of the precursor $^3(n,\pi^*)$ state to form the nitro-nitrite cyclic intermediate, and on the yield of the pyrenoxy radical which results from this rearrangement.

In terms of the atmospheric transformations of these contaminants, our results suggest that constituents and composition of the atmospheric aerosol can affect their photochemical degradation. In specific, phenols and substances from which a hydrogen atom can be abstracted will accelerate the rate of transformation of the lowest triplet state and of the pyrenoxy radical to yield a PyNO_2H radical which can transform into a nitroso or amino substituted pyrene. On the other hand, incorporation of water into the aerosol can either stabilize the triplet state or quench the excited singlet and lowest triplet state.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The project described was supported by Award Number SC1ES017352 from the National Institute of Environmental Health Sciences. The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institute of Health Sciences or the National Institutes of Health. The authors thank Miss Melanie Burgos for her technical assistance and Dr. Carlos Crespo-Hernández of Case Western Reserve University for his helpful comments.

Abbreviations

1-NO₂Py	1-nitropyrene
2-NO₂Py	2-nitropyrene
4-NO₂Py	4-nitropyrene
ArOH	phenols

References

1. Hayakawa K, Murahashi T, Butch M, Miyazaki M. *Environ Sci Technol.* 1995; 29:928.
2. Tang N, Hattori T, Taga R, Igarashi K, Yang X, Tamura K, Kakimoto H, Mishukow VF, Toriba A, Kizu R, Hayakawa K. *Atmos Environ.* 2005; 39:5817.

3. Ciccioli P, Cecinato A, Brancaleoni E, Frattoni M, Zacchei P, Miguel AH, Vascocellos PdeCJ. *Geophys Res.* 1996; 101:19567.
4. Bamford HA, Bezabeth DZ, Shantz MM, Wise SA, Baker JE. *Chemosphere.* 2003; 50:575. [PubMed: 12685733]
5. Arey J, Zielinska B, Atkinson R, Winer AM, Ramdahl T, Pitts JN. *Atmos Environ.* 1986; 20:2339.
6. Lin ST, Jih YF, Fu PP. *J Org Chem.* 1996; 61:5271.
7. Onchoke KK, Hadad CH, Dath PK. *Polycyclic Aromat Compd.* 2004; 24:37.
8. Crespo-Hernández C, Burdzinski G, Arce R. *J Phys Chem A.* 2008; 112:6313. [PubMed: 18572893]
9. Reichardt C, Aaron Vogt R, Crespo-Hernandez CE. *J Chem Phys.* 2009; 131:224518. [PubMed: 20001068]
10. Fu PP, Tungal LSV, Chiu LH, Zhan DJ, Deck J, Bucci T, Wang CJ. *Chem Res Toxicol.* 1998; 11:987.
11. Purohit V, Basu AK. *Chem Res Toxicol.* 2000; 13:673. [PubMed: 10956054]
12. Warner SD, Farant JP, Butler IS. *Chemosphere.* 2004; 54:1207. [PubMed: 14664850]
13. Van den Braken-van Leersum AM, Tintel C, van't Zelfde M, Cornelisse J, Lugtenberg J. *Recl Trav Chim Pays-Bas.* 1987; 106:120.
14. Jung H, Shaikh AU, Heflich RH, Fu PP. *Environ Mol Mutagen.* 1991; 17:169. [PubMed: 2022194]
15. Fu P, Chou MW, Miller DW, White GL, Heflich RH, Beland FA. *Mutat Res.* 1985; 143:173. [PubMed: 3892279]
16. Miller DW, Evans FE, Fu PP. *Spectrosc Int.* 1985; 4(2):91.
17. Li YS, Fu PP, Church JS. *J Mol Struct.* 2000; 550:217.
18. Chapman OL, Heckert DC, Reasoner JW, Thackaberry SP. *J Am Chem Soc.* 1996; 88:5550.
19. Arce R, Pino EF, Agreda J. *J Phys Chem A.* 2008; 112:10294. [PubMed: 18800782]
20. Gusten H, Heinrich G. *J Photochem.* 1982; 18:9.
21. Almgren M. *Mol Photochem.* 1972; 4(3):327.
22. Murov, SL.; Carmichael, I.; Hug, GL. *Handbook of photochemistry.* Marcel Dekker, Inc; New York: 1993. p. 136
23. Arce R, García C, Oyola R, Piñero L, Nieves I, Cruz N. *J Photochem Photobiol A Chem.* 2003; 154:245.
24. Benssason RV, Land EJ. *Trans Faraday Soc.* 1971; 67:1904.
25. Benssason, RV.; Land, EJ.; Truscott, TG. *Excited states and free radicals in biology and medicine, contributions from flash photolysis and pulse radiolysis.* Vol. Chapter 5. Oxford University Press; New York: 1993.
26. Cosa G, Scaiano JC. *Photochem Photobiol.* 2004; 80:159. [PubMed: 15307807]
27. Wolfbeis OS, Posch W, Gubitz G, Tritthart P. *Anal Chem Acta.* 1983; 147:405.
28. Becker RS, Singh IS, Jackson EA. *J Chem Phys.* 1963; 38:2144.
29. Jaffé, HH.; Orchin, M. *Theory and application of ultraviolet spectroscopy.* Vol. Chapters 12, 13. Wiley; London: 1962.
30. Jones RN. *J Am Chem Soc.* 1945; 67:2127. [PubMed: 21005681]
31. Valeur, B. *Molecular fluorescence, principles and applications.* Vol. Chapter 7. Wiley; Weinheim: 2002.
32. Kanamura N, Bhattacharjee HR, Lim EC. *Chem Phys Lett.* 1974; 26:174.
33. Guilbault, G. *Practical Fluorescence.* Marcel Dekker; New York: 1970. p. 97
34. Morales-Cueto R, Esquivelzeta-Rabell M, Saucedo-Zugazagoitia J, Peón J. *J Phys Chem A.* 2007; 111:552. [PubMed: 17249742]
35. Biczók L, Bérces T, Linschitz H. *J Am Chem Soc.* 1977; 119:1107.
36. Turro, NJ. *Modern molecular photochemistry.* Vol. chapter 5. Benjamin Cumings; Menlo Park: 1978.
37. Thomas JK, Richards JT, West G. *J Phys Chem A.* 1970; 74:4137.
38. Zugazagoitia JS, Collado-Fragoso E, Plaza-Medina EF, Peón J. *J Phys Chem A.* 2009; 113:805. [PubMed: 19140711]

39. Milosavljevic BH, Thomas JK. Photochem Photobiol Sci. 2002; 1:100. [PubMed: 12659124]
40. Mori Y, Shinoda H, Nakano T, Takasu R, Kitagawa T. J Photochem Photobiol A Chem. 2006; 182:168.
41. García Z, Arce R. unpublished results.
42. McDow SR, Sun Q, Vartiainen M, Hong Y, Yao Y, Fister T, Yao R, Kamens RM. Environ Sci Technol. 1994; 28:2147.
43. McDow SR, Vartiainen M, Sun Q, Hong Y, Yao Y, Kamens RM. Atmos Environ. 1995; 29:791.
44. Jang M, Mc Dow RS. Environ Sci Technol. 1995; 29:2654.
45. Feilberg A, Nielsen T. Environ Sci Technol. 2000; 34:789.
46. Feilberg A, Nielsen T. Environ Sci Technol. 2001; 35:108. [PubMed: 11351991]
47. Das PK, Encinas MV, Scaiano JC. J Am Chem Soc. 1981; 103:4154.
48. Leigh WJ, Lathioor EC, Pierre MJSt. J Am Chem Soc. 1996; 118:12339.
49. Yoshihara T, Yamaji N, Itoh T, Shikuza H, Shimokage T, Tero-Kubota S. Phys Chem Chem Phys. 2000; 2:993.
50. Göerner HJ. Chem Soc, Perkin Trans. 2002; 2:1778.
51. Kamens RM, Guo Z, Fulcher JN, Bell DA. Environ Sci Technol. 1988; 22:103.

Figure 1. Absorption spectra of 1-NO₂Py (—), 2-NO₂Py (—), 4-NO₂Py (—) and pyrene (—) at room temperature in (A) hexane; and (B) acetonitrile.

Figure 2. Normalized fluorescence spectra of (1) 1-NO₂Py, (2) 2-NO₂Py, and (3) 4-NO₂Py in acetonitrile.

Figure 3.
Quenching of the 2-NO₂Py fluorescence in acetonitrile by methanol.

Figure 4. Normalized transient absorption spectra of 1-NO₂Py (■), 2-NO₂Py (△), and 4-NO₂Py (○) at short ($t = 2 \mu\text{s}$) observation times in (A) cyclohexane; and (B) methanol.

Figure 5. Transient absorption spectra of 1-NO₂Py (■), 2-NO₂Py (△), and 4-NO₂Py (○) at long observation times (10^{-4} s) in methanol.

Figure 6. Relative yield of the long-lived intermediate of 4-NO₂Py in different solvents: (a) methanol, (b) CCl₄, (c) cyclohexane, and (d) acetonitrile. Inset: Effect on 1-NO₂Py in: (a) methanol, and (b) CCl₄.

Figure 7. (A) Intermediate lifetime species: effect of triplet quenchers on the intermediate lifetime species (5×10^{-5} – 2×10^{-4} s). a) N₂ saturated, b) O₂ saturated, 4-NO₂Py (10^{-5} M in methanol). (B) Effect of 1-naphthol on the intermediate lifetime: (a) CCl₄, and (b) 1-naphthol (7×10^{-4} M in CCl₄).

Scheme 1.
Nitropyrene isomers

Scheme 2.

Some mechanistic steps in the photodegradation of nitropyrene isomers.

TABLE 1

Ground State Properties Associated to the Long Wavelength Band of Nitropyrenes, at Room Temperature.

nitropyrene	solvent	$\lambda_{\text{max}}/\text{nm}$	$\epsilon_{\text{max}}/\text{M}^{-1}\text{cm}^{-1}$	$f_{\text{n-m}}$	Γ/cm^{-1}
1-NO ₂ Py		347 ^s , 370	8,986 ^s /13,226	0.322	4833
		389, 405	11,565/9,692		
2-NO ₂ Py	Hexane	378, 399, 421	1,928/2,324/2,135	0.0608	4500
4-NO ₂ Py		347, 370, 389 ^s , 405	6,433/6,375	0.107	5613
			4,478 ^s /2,925		
1-NO ₂ Py		347 ^s , 371	8,207 ^s /12,630	0.240	4833
		391, 407	11,392/9,348		
2-NO ₂ Py	Cyclohexane	381, 401, 424	857/1,231/1,045	0.0214	4500
4-NO ₂ Py		347, 371, 391 ^s , 407	8,715/8,829	0.150	5581
			6,494 ^s /4,509		
1-NO ₂ Py	2-propanol	375, 397	11,494/11,572	0.227	4750
		410	1010	0.0249	5000
		375, 397	5,656/4,663	0.089	5670
1-NO ₂ Py		375, 399	10,511/10,698	0.265	4750
2-NO ₂ Py	Methanol	410	1155	0.0249	5000
		375, 399	7,474/6,143	0.132	6390
1-NO ₂ Py		377, 402	10,276/10,834	0.249	4750
2-NO ₂ Py	Acetonitrile	415	807	0.0167	7500
4-NO ₂ Py		377, 402	5,556/4,632	0.107	6390

TABLE 2
Comparison of 1-NO₂Py, 2-NO₂Py and 4-NO₂Py First Singlet Excited State Parameters in Solution.

nitrotyrene	solvent	λ_{max}/nm	*Stoke shifts/cm ⁻¹	$E_0/kJ\ mol^{-1}$	$\Phi_{fluor}/10^{-3}$
1-NO ₂ Py		425	1041	291	< 0.1
2-NO ₂ Py	Cyclohexane	-	-	-	< 0.1
4-NO ₂ Py		-	-	-	< 0.1
1-NO ₂ Py		465	3681	277	0.26
2-NO ₂ Py	2-Propanol	-	-	-	< 0.1
4-NO ₂ Py		550	8845	271	1.38
1-NO ₂ Py		500	4876	275	0.24
2-NO ₂ Py	CH ₃ CN	585	7000	254	0.99
4-NO ₂ Py		570	7456	258	2.11

TABLE 3
Natural Decay and Quenching Rate Constants of the π,π^* Triplet State of Nitropyrenes.

nitropyrene/solvent	k_0^a	k_{sq}^b	k_b (ferrocene) ^b	k_q ^b	k_q (O ₂) ^b
1-NO ₂ Py/Cyclohexane	1.0 ± 0.3	1.6 ± 0.2	9.5 ± 0.1	6.4 ± 0.4 ^c	1.6 ± 0.1
1-NO ₂ Py/Methanol	0.3 ± 0.1	1.5 ± 0.1	22 ± 1	4.4 ± 0.4 ^c	1.5 ± 0.2
4-NO ₂ Py/Cyclohexane	5.6 ± 0.9	1.0 ± 0.1	8.5 ± 0.9	4.4 ± 0.4 ^c	1.3 ± 0.2
4-NO ₂ Py/Methanol	9.9 ± 0.1	0.17 ± 0.03	13 ± 1	1.1 ± 0.2 ^c	1.0 ± 0.1
2-NO ₂ Py/Cyclohexane	0.87 ± 0.03	0.76 ± 0.08	8.0 ± 0.6	7.1 ± 0.9 ^d	1.7 ± 0.1
2-NO ₂ Py/Methanol	2.5 ± 0.6	0.25 ± 0.01	9.8 ± 0.2	7.5 ± 0.9 ^d	1.6 ± 0.4

^a10⁵ s⁻¹,

^b10⁹ M⁻¹ s⁻¹,

^ck_q (perylene),

^dk_q (anthracene)

TABLE 4

Nitropyrene Isomers Triplet State Parameters in Cyclohexane and Methanol at Room Temperature.

nitropyrene	solvent	$\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$	Φ_{ISC}	$E_T/\text{kJ mol}^{-1}$
1-NO ₂ Py	cyclohexane	7.8 ± 0.9 (530nm)	0.6 ± 0.1	187
	methanol	6.5 ± 0.9 (570nm)	0.5 ± 0.1	
4-NO ₂ Py	cyclohexane	2.9 ± 0.5 (550nm)	0.26 ± 0.05	187
	methanol	2.3 ± 0.5 (550nm)	0.10 ± 0.05	
2-NO ₂ Py	cyclohexane	2.4 ± 0.3 (520nm)	0.49 ± 0.03	---
	methanol	1.7 ± 0.02 (520nm)	0.33 ± 0.02	

TABLE 5

Quenching Rate Constants for the $^3(\pi, \pi^*)$ State of Nitropyrene Isomers by ArOH.

reactants	solvent	1-NO ₂ Py/10 ⁹ M ⁻¹ s ⁻¹	2-NO ₂ Py/10 ⁹ M ⁻¹ s ⁻¹	4-NO ₂ Py/10 ⁹ M ⁻¹ s ⁻¹
1-naphthol	cyclohexane	6.1 ± 0.2	0.14 ± 0.01	3.5 ± 0.5
	acetonitrile	0.32 ± 0.02	0.28 ± 0.05	a
2,6-dimethoxyphenol	cyclohexane	0.25 ± 0.02	0.12 ± 0.04	0.19 ± 0.03
	acetonitrile	0.20 ± 0.01	0.58 ± 0.02	0.14 ± 0.01
4-hydroxy-3-methoxybenzoic acid	acetonitrile	0.016 ± 0.009	0.040 ± 0.004	0.022 ± 0.009

^a
not measured