

H-bonding assisted intramolecular charge transfer in 1-aminopyrene derivatives

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Abstract

The electronic spectroscopy and photochemical properties of new derivatives of pyrene-1-aminovinylene containing strong electron withdrawing groups are reported. 2-((Pyren-8-ylamino)methylene) malononitrile (I) ethyl 2-cyano-3-(pyren-8-ylamino) acrylate (II), and diethyl 2-((pyren-8-ylamino)methylene) malonate (III) were prepared. These molecules show excited-state intramolecular charge transfer (ESICT). The carbonyl in II and III gives rise to a solvent dependent intramolecular H-bond interaction which not only enhances the mixing between $\pi-\pi^*$ and $n-\pi^*$ states but also influences the ESICT dynamics.

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1. Introduction

Pyrene and 1-aminopyrene are fluorescent probes often used for solvent polarity studies in several different media [1–3]. Likewise, very interesting photophysical properties have been investigated using some of their derivatives [4–6]. For instance, in donor–acceptor-substituted tetrahydropyrene, and phenyl and biphenyl pyrene derivatives, excited-state intramolecular charge transfer (ESICT) has been observed [6]. Such process, which is present in a large number of donor–acceptor systems [7], has been also observed when pyrene or 1-aminopyrene is attached to biomolecules [8–11]. Pyrene derivatives such as aminopyrene and pyrenecarboxaldehyde have their photophysics influenced by the mixing of $\pi-\pi^*$ and $n-\pi^*$ states [2,3]. Although only a few examples of pyrene derivatives with photo-induced electron transfer or ESICT properties have been described [12], several other probes with charge transfer have been used as fluorescent chemosensors [13]. More recently, specific solute-solvent interaction by H-bonding

has been a topic of research in ICT systems [14,15], in particular with aminocoumarin dyes in protic solvents [16–18].

In this work, the photochemical properties of three new derivatives of pyrene-1-aminovinylene (*vide* Scheme 1 for molecular structures) containing strong electron-withdrawing groups: two CN in compound I, 2-((pyren-8-ylamino)methylene) malononitrile, CN and COOEt in compound II, ethyl 2-cyano-3-(pyren-8-ylamino) acrylate, and two COOEt in compound III, diethyl 2-((pyren-8-ylamino)methylene) malonate, are reported. The crucial difference among these new fluorescent probes is the possible intramolecular H-bond capacity of compounds II and III, which influences their photophysical properties.

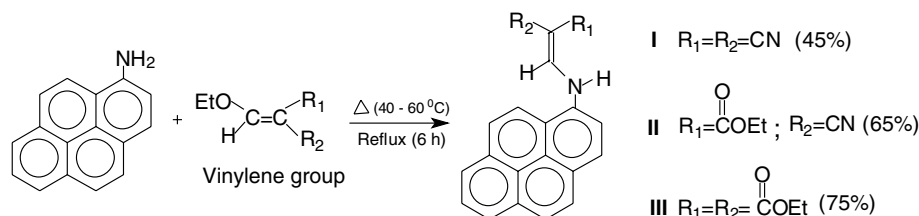
2. Experimental section

2.1. Synthesis of the 1-aminopyrene derivatives

Derivatives of 1-aminopyrene with vinylene group were obtained from reaction with ethoxymethylene malononitrile, ethyl(ethoxymethylene) cyanoacetate, and diethylethoxymethylene malonate (Acros Organic, 98%), resulting in compounds I–III, respectively, as shown in Scheme 1 above.

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Scheme 1. Aminopyrene derivatives.

A sample, 1.2 mmol, of each vinylene reactant was added to 1.0 mmol of 1-aminopyrene, both dissolved in treated ethanol. The system was gently heated under reflux for 6 h, cooled, and solvent evaporated under low pressure. The crude compound was purified through flash chromatography using a concentration gradient of hexane/acetone, affording a net yield of 45%, 65%, and 75% for the compounds I–III, respectively. Compound I: $\text{C}_{20}\text{H}_{11}\text{N}_3$ (293.3). Mp = 231 °C. Calculated: C 82.00, H 4.00, N 14.00. Found: C 81.96, H 4.05, N 13.60. FTIR (cm^{-1}): 3192 (NH), 2215 (CN), 1654 (C=C). ^1H NMR (DMSO- d_6): 11.70 (d, NH), 7.35 (d, $-\text{CH}=\text{C}-\text{R}$), 8.25 (m, 9H, Py). LC–MS: $m/z = 292.3$.

Compound II: $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_2$ (340.4). Mp = 199 °C. Calculated: C 77.65, H 4.71, N 8.24. Found: C 77.40, H 4.80, N 8.05. FTIR (cm^{-1}): 3190 (NH), 2210 (CN), 1674 (C=O), 1628 (C=C). ^1H NMR (CDCl_3): 11.90 (d, NH), 7.83 (d, $-\text{CH}=\text{C}-\text{R}$), 4.42 (q), 1.45 (t), OCH_2CH_3 , 8.18 (m, 9H, Py). LC–MS: $m/z = 339.4$.

Compound III: $\text{C}_{24}\text{H}_{21}\text{NO}_4$ (387.4). Mp = 181 °C. Calculated: C 74.34, H 5.42, N 3.61. Found: C 73.90, H 5.52, N 3.55. FTIR (cm^{-1}): 3210 (NH), 1691 (C=O), 1637 (C=C). ^1H NMR (CDCl_3): 11.90 (d, NH), 7.83 (d, $-\text{CH}=\text{C}-\text{R}$), 4.42 (q), 1.45 (t), OCH_2CH_3 , 8.18 (m, 9H, Py). LC–MS: $m/z = 386.4$.

2.2. Instrumentation

The FTIR and ^1H NMR spectra were obtained using a Bomem MB 102 and a Bruker DRX 400 spectrometers, respectively. LC–MC mass spectrum was performed in a Micromass Quattro LC–MS spectrometer, using electron spray interface with a voltage up to 25 V. Absorption measurements were performed on a Cary 5G – Varian spectrophotometer, and the corrected steady-state fluorescence spectra were recorded on a CD-900 Edinburgh spectrofluorimeter at $T = 298$ K. The samples were conditioned in a 1×1 cm quartz cuvette, thermostated by circulating fluid through a jacketed cuvette-holder, and in air-equilibrated conditions. Total emission quantum yields (ϕ_{em}) were calculated using quinine sulfate in 1 N H_2SO_4 ($\phi_{\text{em}} = 0.546$) as standard. Fluorescence decays in solution were measured by time-correlated single photon counting technique using a homemade ps spectrometer equipped with Glan-Laser polarizers in magic angle, a Peltier-cooled PMT-MCP (Hamamatsu R3809U-50) as photon detector, and Tennelec-Oxford counting electronics. The light pulse was

provided by frequency doubling the 200 fs laser pulse of Mira 900 Ti – sapphire laser pumped by Verdi 5 W Coherent laser, and the pulse frequency was reduced down to 800 kHz by using a Conoptics pulse picker [19,20]. The system provides an instrument response function (irf) of about 40 ps at fwhm. Decay traces were collected with 2–12 ps/channel over 1 kB data points. The fluorescence decays were analyzed by a reconvolution procedure with multiexponential decay models.

3. Results and discussion

3.1. Steady state measurements

The absorption and emission spectra of I in organic solvents, cyclohexane (CH, apolar), 2-propanol (2-PrOH, polar protic), and *N,N*-dimethylacetamide (DMA, polar aprotic), are shown in Fig. 1. Absorption and emission of I in CH (emission quantum yield $\phi_{\text{em}} = 0.140$) is similar to that of 1-aminopyrene, with a clear structured emission band with main peaks at $\lambda_{\text{em}} = 400, 406$ and 420 nm. The small Stokes shift and the presence of structured band suggest that its emission is mainly from the locally excited ($S_1 \rightarrow S_0$) of $\pi-\pi^*$ character, and, therefore, ICT does not occur in this apolar solvent as usual. In polar protic solvent like 2-propanol ($\phi_{\text{em}} = 0.180$), compound I shows a red shifted and weak absorption band (indicated by a shoulder at 400 nm) when compared with 1-aminopyrene, besides the strong absorption at 350 nm. This is a first clue that some ICT contribution appears in the optical transition of the extended π -system due to the presence of the amino vinyl group, similar to what has been observed in aromatic or in polyene systems with electron donor and acceptor groups [21,22]. In DMA ($\phi_{\text{em}} = 0.095$), this effect is much more evident, and a strong absorption band appears at 414 nm, with a redshift of about 64 nm when compared with the absorption of 1-aminopyrene (data not shown) in the same solvent.

The fluorescence of I in polar solvents (see Fig. 1B) is dominated by a strong and red shifted emission band, particularly in alcohols, which suggests an ICT character also in the emission. In agreement with ICT character in absorption measurements, the change in IR frequency of the CN withdrawing group from 2229 cm^{-1} (of the ethoxymethylene malononitrile) to 2205 cm^{-1} in I corroborates to the assumption of partial charge transfer already in ground state, similar to what has been observed in tetra-

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