Toward the Photostability Mechanism of Intramolecular Hydrogen Bond Systems. 4.[1] 3(5)-(1′-Hydroxy-2′-naphthyl)pyrazoles and 3(5)-(2′-Hydroxy-1′-naphthyl)pyrazoles

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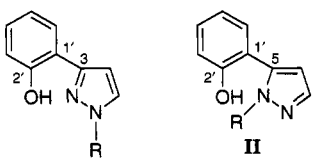
Two new families of compounds, the 3(5)-(1′-hydroxy-2′-naphthyl)pyrazoles (**a** series) and the 3(5)-(2′-hydroxy-1′-naphthyl)pyrazoles (**b** series), have been synthesized and fully characterized. The use of NMR (^{1}H and ^{13}C) and UV (absorption and emission) spectroscopies in different solvents led us to determine the major tautomers, the coplanarity of both rings (naphthyl and pyrazolyl) if present, and the existence of hydrogen bonds. The photostability of a representative set of such derivatives was also determined, showing that the existence of an intramolecular hydrogen bond (IMHB) is not an essential condition for providing UV stability. Moreover when such an IMHB is present in the molecule, the photostability is not dependent on whether the proton is transferred or not.

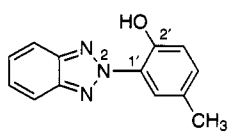
Introduction

In a previous paper[2] we studied the photophysics and photostability of 3- and 5-(2′-hydroxyphenyl)pyrazoles **I** and **II**, concluding that some of such derivatives are as photostable as 2-(2′-hydroxy-5′-methylphenyl)benzotriazole or Tinuvin P, **III**, which is regarded as the archetype of photostability. Attention must be paid to the fact that



I

II



III

these compounds present in their structure a carbon–carbon bond, between the pyrazolyl ring and the phenol group $C_{1'}$–C_3 or $C_{1'}$–C_5, which has a tendency to increase its bond order with electronic excitation contrary to the nitrogen–carbon linkage $C_{1'}$–N_2, still a single bond in the excited electronic state, which appears in Tinuvin P; interannular torsional motions are proposed as responsible for the dissipative energy mechanism in the latter type of systems.[3–8]

The photostabilities of **I** and **II** are similar to that of Tinuvin P, but they are only useful in protecting light-sensitive materials from UV radiation of wavelength below 310 nm, different from Tinuvin P which absorbs UV light up to 340 nm.

With the aim of avoiding this disadvantage, we have synthesized the homologous derivatives, namely 3- and 5-(1′-hydroxy-2′-naphthyl)pyrazoles **2a–7a** and 3- and 5-(2′-hydroxy-1′-naphthyl)pyrazoles **2b–7b** (see Schemes 1 and 2), which have an enlarged aromatic structure susceptible to absorption in the spectral range of 310–340 nm.

The main structural difference between the 3- and 5-(2′-hydroxyphenyl)pyrazoles **I–II** and the 3- and 5-(1′-hydroxy-2′-naphthyl)pyrazoles **2a–7a** or 3- and 5-(2′-hydroxy-1′-naphthyl)pyrazoles **2b–7b** lies in the fact that in the naphthyl derivatives the *peri* effect[9] of the hydrogen in the 8′ position will hinder the torsional freedom of the hydroxy and methoxy groups in **series a** and of the pyrazolyl ring about the carbon–carbon bond in **series b**.

The photophysical study of such compounds will enable us to discuss the proposed models that account for the photostability mechanism in systems containing a phenolic hydroxyl group which is intramolecularly hydrogen bonded to a neighboring nitrogen atom.

Experimental Section

General Methods. Melting points are uncorrected. Nuclear magnetic resonance spectra were obtained on a Bruker AC-200 spectrometer. Chemical shifts and coupling constants

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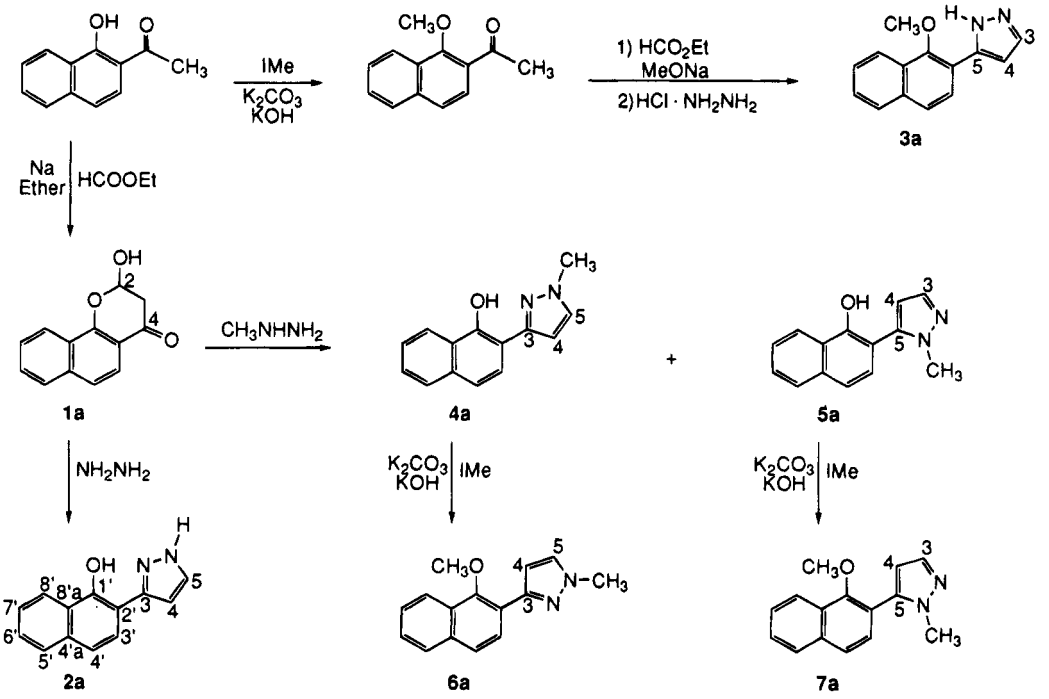
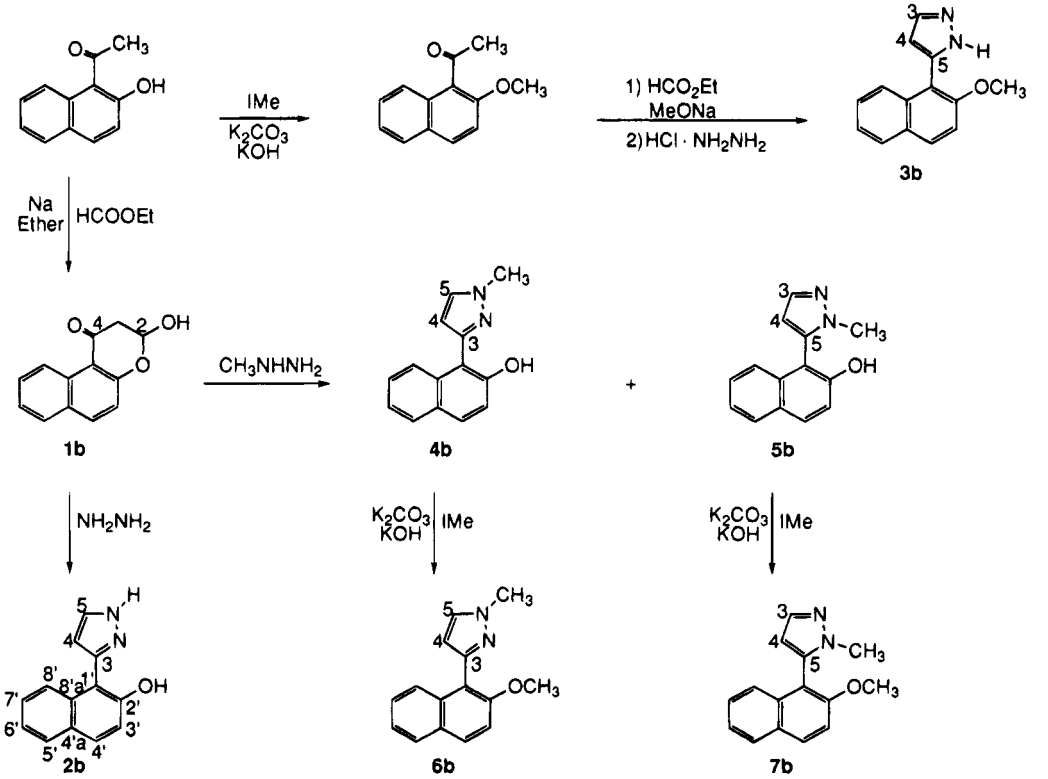
Scheme 1



Scheme 2



were measured in deuteriochloroform or hexadeuteriodimethyl sulfoxide with tetramethylsilane as internal standard. ^1H (10^{-2} M solutions) and ^{13}C (10^{-1} M solutions) chemical shifts are accurate to 0.01 and 0.1 ppm, respectively; coupling constants are accurate to ±0.2 Hz (^1H NMR) and to ±0.6 Hz (^{13}C NMR). The data acquisition parameters for the heteronuclear ($^1H-^{13}C$) correlation experiment were set as follows: F_1 domain (SI1, 512 W; SW1, 1403.7 Hz; relaxation delay D1, 3 s), F_2 domain (SI2, 4K; SW2, 10000 Hz), number of transients per FID, NS, 32; number of preparatory dummy transients per FID, DS, 0. The 2D experiment was processed with a sine bell window (WDW1 = WDW2 = S, SSB1 = 0, SSB2 = 2). Analytical thin layer chromatography was performed on silica gel Merck kieselgel 60 F254 with a layer thickness of 0.2 mm. Column chromatography was carried out with silica gel Merck 60 (70–230 mesh, ASTM). High resolution mass spectra (HRMS) at 70 eV using the electron impact mode were performed on a VG AUTOSPEC spectrometer.

Synthesis (see Schemes 1 and 2). 2-Hydroxybenzo[*h*]chroman-4-one (1a) and 2-Hydroxybenzo[*f*]chroman-4-one (1b). In a 100 mL three-necked flask fitted with a reflux condenser, a dropping funnel, and a stirrer are placed 1.6 g (0.07 mol) of oxide-free sodium and 20 mL of anhydrous xylene. The flask is surrounded by an oil bath which is heated until

the sodium melted. The stirrer is started, and after the sodium is powdered, the oil bath is removed. When the contents of the flask have cooled to room temperature, the stirrer is stopped, the xylene decanted, and the sodium washed twice with 20 mL of dry ether to remove traces of xylene. After, the powdered sodium was suspended in 20 mL of dry ether and a mixture of 3.7 g (0.02 mol) of 2-acetyl-1-hydroxynaphthalene or 1-acetyl-2-hydroxynaphthalene, 12 g (13.2 mL, 0.162 mol) of ethyl formate, and 30 mL of dry ether is placed in the dropping funnel. After a small amount (1–2 mL) of the mixture has been added, the flask is warmed with the hand to make sure that the reaction has started. Then, the funnel is adjusted so that the ester–ketone mixture is added over a period of 1 h. When the reaction had subsided, another 2 mL of the ester was added; then the mixture was stirred for 2 h and left overnight. Ice and water were then carefully added, and the resulting solution was extracted twice with 50 mL of ether. The separated aqueous layer was freed from ether in a vacuum and then acidified with glacial acetic acid until pH = 4–5. The resulting precipitate was collected, washed with water, and dried to give **1a** or **1b**.

2-Hydroxybenzo[*h*]chroman-4-one (**1a**) (89% yield): mp 143–145 °C; HRMS *m/e* (M^+) calcd for $C_{13}H_{10}O_3$ 214.062994, found 214.062990. ^{1}H NMR (DMSO-d_6) δ 2.79 (dd, 1 H, ^2J = −16.6, ^3J = 5.0,), 3.14 (dd, 1 H, ^2J = −16.6, ^3J = 3.4), 6.06 (dd, 1H, ^3J = 5.0, ^3J = 3.4), 7.50 (d, 1 H, ^3J = 8.7), 7.60 (ddd, 1 H, ^3J = 8.0, ^3J = 6.8, ^4J = 1.3), 7.69 (ddd, ^3J = 8.0, ^3J = 6.8, ^4J = 1.5), 7.73 (d, 1 H, ^3J = 8.7), 7.92 (d, 1 H, ^3J = 8.0), 8.25 (d, 1 H, ^3J = 8.0), 7.8–7.9 (s, OH); ^{13}C NMR (DMSO-d_6) δ 43.9 (d, ^1J = 260.9), 96.1 (dd, ^1J = 172.5, ^2J = 3.3), 115.2 (s), 120.5 (dd), 120.9 (d), 123.1 (dd), 124.7 (s), 126.4 (dd), 127.9 (ddd), 129.6 (dd), 137.0 (s), 156.2 (s), 190.8 (s).

2-Hydroxybenzo[*f*]chroman-4-one (**1b**) (85% yield): mp 148–149 °C; HRMS *m/e* (M^+) calcd for $C_{13}H_{10}O_3$ 214.062994, found 214.062760; ^{1}H NMR (DMSO-d_6) δ 2.7 (dd, 1 H, ^2J = −16.2, ^3J = 4.9), 3.15 (dd, 1 H, ^2J = −16.2, ^3J = 3.2), 5.87 (ddd, 1H, ^3J = 4.9, ^3J = 3.2, ^3J = 4.9), 7.19 (d, 1 H, ^3J = 9.0), 7.44 (ddd, 1 H, ^3J = 8.1, ^3J = 6.9, ^4J = 1.2), 7.63 (ddd, ^3J = 8.7, ^3J = 6.9, ^4J = 1.5), 7.89 (d, 1 H, ^3J = 8.1), 8.12(d, 1 H, ^3J = 9.0), 9.32(d, 1 H, ^3J = 8.7), 7.71 (d, OH, ^3J = 4.9); ^{13}C NMR (DMSO-d_6) δ 45.5 (d, ^1J = 260.8), 95.1 (dd, ^1J = 173.7, ^2J = 2.3), 111.9 (s), 119.3 (d), 124.5 (dd), 124.8 (dd), 128.6 (dd), 128.7 (s), 129.4 (dd), 130.6 (s), 137.4 (dd), 160.3 (s), 192.6 (s).

3-(1′-Hydroxy-2′-naphthyl)pyrazole (2a) and 3-(2′-Hydroxy-1′-naphthyl)pyrazole (2b). **1a** or **1b** (0.5 g, 2.34 mmol) was dissolved in 10 mL of ethanol and heated until 50 °C. Then, 0.15 g (30 mmol) of hydrazine (98%) in 3 mL of ethanol was added and the reaction mixture was stirred at 50 °C for 1 h. Then the solvent was evaporated under vacuum, and 15 mL of water was added to the crude residue. The resulting precipitate was filtered off, washed with water, dried, and recrystallized from benzene to obtain **2a** or **2b**. Compound **2a** (51% yield) had mp 144–145 °C: HRMS *m/e* (M^+) calcd for $C_{13}H_{10}N_2O$ 210.079313, found 210.079160. Compound **2b** (61% yield) had mp 135–137 °C: HRMS *m/e* (M^+) calcd for $C_{13}H_{10}N_2O$ 210.079313, found 210.079180.

5-(1′-Methoxy-2′-naphthyl)pyrazole (3a) and 5-(2′-Methoxy-1′-naphthyl)pyrazole (3b). A mixture of 3 g (16.1 mmol) of 2-acetyl-1-naphthol or 1-acetyl-2-naphthol, 6.7 g (48.5 mmol) of anhydrous K_2CO_3, 1.8 g (32.1. mmol) of KOH, and 1.2 mL (19.3 mmol) of CH_3I in 30 mL of anhydrous acetone was heated under reflux for 3 h. After cooling, the solvent and excess of CH_3I were evaporated under vacuum, and the crude residue was purified by column chromatography using as eluent hexane/ethyl acetate (7/3) to obtain the derivatives 2-acetyl-1-methoxynaphthalene (65% yield, R_f 0.83) or 1-acetyl-2-methoxynaphthalene (70% yield, R_f 0.78).

Then 2 g (10.0 mmol) of 2-acetyl-1-methoxynaphthalene or 1-acetyl-2-methoxynaphthalene, 1.13 g (15.3 mmol) of ethyl formate, and 10 mL of toluene were added in one portion with rapid stirring to a slurry of sodium methoxide (0.54 g, 10.0 mmol). The thick slurry was stirred for 4 h, and the resulting precipitate of 1-methoxy-2-acetyl-(α-sodiooxymethylene)naphthalene or 2-methoxy-1-acetyl-(α-sodiooxy-methylene)naphthalene was filtered off, washed with hot toluene followed by hexane, and then dried. To a slurry of this solid in 10 mL of ethanol was added a solution of hydrazine monohydrochloride (0.68 g, 10 mmol) in 10 mL of water. After standing overnight at room temperature, the resulting solution was extracted with dichoromethane. Removal of solvent from dried ($MgSO_4$) extract gave the derivative **3a** or **3b** which was purified by column chromatography with dichloromethane/ethanol (93/7 or 95/5) as eluent, respectively. 5-(1′-Methoxy-2′-naphthyl)-pyrazole (**3a**) (20% yield) had mp 124–125 °C: R_f (dichloromethane/ethanol 93/7) 0.49; HRMS *m/e* (M^+) calcd for $C_{14}H_{12}N_2O$ 224.094963, found 224.094830. 5-(2′-Methoxy-1′-naphthyl)pyrazole (**3b**) (26% yield) had mp 134–136 °C: R_f (dichloromethane/ethanol 95/5) 0.68; HRMS *m/e* (M^+) calcd for $C_{14}H_{12}N_2O$ 224.094963, found: 224.095020.

1-Methyl-3-(1′-hydroxy-2′-naphthyl)pyrazole (4a), 1-Methyl-5-(1′-hydroxy-2′-naphthyl)pyrazole (5a), 1-Methyl-3-(2′-hydroxy-1′-naphthyl)pyrazole (4b), and 1-Methyl-5-(2′-hydroxy-1′-naphthyl)pyrazole (5b). To a stirred and heated (50 °C) solution of 1 g (4.7 mmol) of **1a** or **1b** in 20 mL of ethanol was added a solution of 0.28 g (6.0 mmol) of methylhydrazine in 4 mL of ethanol. The mixture was left standing at 50 °C for 1 h. On cooling, the solvent was removed under reduced pressure, and the crude residue was separated into its components by column chromatography: the *N*-methylpyrazoles **4a** and **5a** with dichloromethane/ethanol (99/1) as eluent and the *N*-methylpyrazoles **4b** and **5b** with dichloromethane/ethanol (97/3). Compound **4a** (22% yield) had mp 89–91 °C: R_f (dichloromethane/ethanol 99/1) 0.93; HRMS *m/e* (M^+) calcd for $C_{14}H_{12}N_2O$ 224.094963, found 224.095260. Compound **5a** (70% yield) had mp 152–153 °C: R_f (dichloromethane/ethanol 99/1) 0.25; HRMS *m/e* (M^+) calcd for $C_{14}H_{12}N_2O$ 224.094963, found 224.094530. Compound **4b** (17% yield) had mp 51–53 °C: R_f (dichloromethane/ethanol 97/3) 0.77; HRMS *m/e* (M^+) calcd for $C_{14}H_{12}N_2O$ 224.094963, found 224.094470. Compound **5b** (63% yield) had mp 175–177 °C: R_f (dichloromethane/ethanol 97/3) 0.24; HRMS *m/e* (M^+) calcd for $C_{14}H_{12}N_2O$ 224.094963, found 224.094620.

1-Methyl-3-(1′-methoxy-2′-naphthyl)pyrazole (6a), 1-Methyl-5-(1′-methoxy-2′-naphthyl)pyrazole (7a), 1-Methyl-3-(2′-methoxy-1′-naphthyl)pyrazole (6b), and 1-Methyl-5-(2′-methoxy-1′-naphthyl)pyrazole (7b). A mixture of 0.5 g (2.23 mmol) of *N*-methylpyrazole (**4a** or **4b** or **5a** or **5b**), 0.9 g (6.70 mmol) of anhydrous K_2CO_3, 0.3 g (5.35 mmol) of KOH, and 0.17 mL (2.73 mmol) of CH_3I in 6 mL of anhydrous acetone was heated under reflux for 2 h. After cooling, the solvent and excess of CH_3I were evaporated under reduced pressure to give methoxy derivatives **6a** or **7a** or **6b** or **7b**, respectively. These compounds were purified by column chromatography using as eluent hexane/ethyl acetate (1/1) for **6a** (R_f 0.72), dichloromethane/ethanol (99/1) for **7a** (R_f 0.44), dichloromethane/ethanol (97/3) for **6b** (R_f 0.55), and dichloromethane/ethanol (97/3) for **7b** (R_f 0.52). Compound **6a** (72% yield) was isolated as an oil: HRMS *m/e* (M^+) calcd for $C_{15}H_{14}N_2O$ 238.110613, found 238.110460. Compound **6b** (73% yield) had mp 111–113 °C: HRMS *m/e* (M^+) calcd for $C_{15}H_{14}N_2O$ 238.110613, found 238.110310. Compound **7a** (70% yield) had mp 63–65 °C: HRMS *m/e* (M^+) calcd for $C_{15}H_{14}N_2O$ 238.110613, found 238.110520. Compound **7b** (60% yield) had mp 89–90 °C: HRMS *m/e* (M^+) calcd for $C_{15}H_{14}N_2O$ 238.110613, found: 238.110370.

Photophysical Measurements. Absorption spectra were recorded at 298 K on a Shimadzu UV-2100 spectrometer furnished with a matched pair of Suprasil cells of 1-cm path length.

Luminescence spectra were acquired at 298 and 77 K by using an SLM 48000S spectrofluorimeter equipped with a cooled wide-band RF housing for the R928 photomultiplier tube employed. Corrected excitation spectra were obtained at a constant excitation intensity that was controlled by means of a rhodamine B quantum counter. For phosphorescence measurements at 77 K, samples were held in sealed Suprasil quartz tubes of 3 mm diameter that were placed in the low-temperature SLM accessory.

Quantum yields and fluorescence lifetimes were measured at room temperature on freshly prepared samples with optical densities in the excitation region of ca. 0.02 and 0.1 or lower,

respectively. 2-Aminopyridine in 0.1 N H_2SO_4 ($\phi_f = 0.66$)[10] and methyl salicylate in cyclohexane ($\phi_f = 0.022$)[11] were used as quantum yield standards and refractive indexes were appropriately corrected.[12] Each ϕ_f value was determined using at least three excitation wavelengths. Fluorescence lifetimes, determined by phase and modulation measurements, were made relative to glycogen scattering solutions[13a] by using an SLM 48000S spectrofluorimeter at modulation frequencies between 1 and 250 MHz. The oxygen was not eliminated from the solutions due to the interest in obtaining data in experimental conditions close to those where photoprotectors are really used, nondegassed environments.

The analysis of experimental multifrequency data is an iterative process intended to fit an appropriately chosen model to available data by carrying the model parameters (lifetimes and fractional contributions) in a direction that minimizes deviations between the model and the data.[13b] Decisions on the suitability of the model, a linear combination of exponentials, rest on examination of the residuals deviations with frequency and the reduced χ-square value, a numerical value that reflects the overall goodness of fit.

Room-temperature photostability was determined by using a PTI system consisting of a horizontally mounted water-cooled lamp housing for a 1000 W xenon lamp furnished with an *f*/4.0 elliptical reflector that concentrated the lamp intensity 4-fold. Light reflected to the sample housing was previously passed through a water-cooled PTI 02-A002 infrared water filter, and then, through a monochromator, a wavelenght was selected for sample excitation. The photon flux reaching the sample was measured with Aberchrome 540[14] and was found to be 1.66×10^{17} photons/s. The samples used for photostability measurements had an optical density of 2.0 at the excitation wavelength and were magnetically stirred into the cell in a continuous way. Sample degradation was monitored by UV spectroscopy and was expressed as the ratio of optical densities measured at the different light exposure times and a given wavelength to that measured at zero time. The degradation products present zero absorbance at the selected wavelength. Cyclohexane (CyH), ethanol (EtOH), dimethyl sulfoxide (DMSO), and acetonitrile (ACN) were used as solvents for fluorescence and phosphorescence measurements.

Results and Discussion

Synthesis. As shown in Schemes 1 and 2, 3(5)-(1′-hydroxy-2′-naphthyl)pyrazoles (**a** series) and 3(5)-(2′-hydroxy-1′-naphthyl)pyrazoles (**b** series) and their *N*- and *O*-methyl derivatives have been prepared by standard methods.[15] Thus, 2-acetyl-1-hydroxynaphthalene and 1-acetyl-2-hydroxynaphthalene reacted with ethyl formate in the presence of powdered sodium to give the corresponding 2-hydroxybenzo[*h*]chroman-4-one (**1a**) and 2-hydroxybenzo[*f*]chroman-4-one (**1b**), which when treated with hydrazine gave 3(5)-(1′-hydroxy-2′-naphthyl)pyrazole (**2a**) and 3(5)-(2′-hydroxy-1′-naphthyl)pyrazole (**2b**), respectively. The 2-acetyl-1-methoxynaphthalene and 1-acetyl-2-methoxynaphthalene *via* the hydroxymethylene intermediates afforded by the same procedure the 5(3)-(1′-methoxy-2′-naphthyl)pyrazole (**3a**) and 5(3)-(2′-methoxy-1′-naphthyl)pyrazole (**3b**) (see Experimental Section).

Reaction of the 2-hydroxybenzo[*h*]- and 2-hydroxybenzo[*f*]chroman-4-ones (**1a** and **1b**) with methylhydrazine yielded the corresponding pairs of *N*-methyl derivatives **4a/5a** and **4b/5b**, which were conveniently separated into its components by column chromatography.

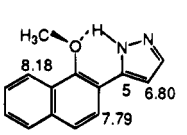
Subsequent methylation of each individual isomer with methyl iodide in a basic medium gave finally the dimethyl derivatives: 1-methyl-3-(1′-methoxy-2′-naphthyl)-pyrazole (**6a**), 1-methyl-5-(1′-methoxy-2′-naphthyl)pyrazole (**7a**), 1-methyl-3-(2′-methoxy-1′-naphthyl) pyrazole (**6b**), and 1-methyl-5-(2′-methoxy-1′-naphthyl)pyrazole (**7b**).

All compounds have been fully characterized by ^1H and ^{13}C NMR spectroscopy (see Experimental Section and Tables 1−4).

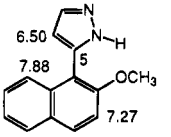
NMR Spectroscopy. In Tables 1−4 are assembled the ^1H and ^{13}C NMR spectroscopic data for compounds **2a**−**7a** and **2b**−**7b**.

The ^1H coupling constant criteria $^3J(H_3H_4) < {}^3J(H_4H_5)$ previously applied to 1,3- and 1,5-disubstituted pyrazoles[16,17] was also found to be valid for the assignment of the pyrazole protons. Thus, in $CDCl_3$ solution the parent compounds **2a** and **2b** exist mainly as 3-substituted tautomers with $^3J(H_4H_5)$ values of 2.6 and 2.5 Hz, respectively. Attention must be paid to the pairs of 1-methyl-3-substituted derivatives **4a/4b** with $^3J(H_4H_5)$ of around 2.4 Hz and 1-methyl-5-substituted derivatives **5a/5b** with $^3J(H_3H_4)$ of 1.8 Hz. As can be seen in Tables 1 and 2, in the case of the methoxy derivatives **6a/6b** and **7a/7b** the differences between $^3J(H_4H_5)$ of 2.2 Hz and $^3J(H_3H_4)$ of 1.9 Hz are less important.

Concerning **3a** and **3b** in $CDCl_3$, they are 5-substituted according to the coupling constants criteria. The preference for the 5-aryl structure in these ethers was also encountered in the 5-(2′methoxyphenyl)pyrazole[2] as a consequence of the formation of an intramolecular hydrogen bond between the NH and the ether oxygen. In the 5(3)-(1′-methoxy-2′-naphthyl)pyrazole (**3a**) the pyrazolyl group in the *ortho* position and the *peri* H-8′ can be expected to force the 1′-methoxy group out of the ring plane.[18]



3a



3b

When the ^1H NMR was run in DMSO-d_6 solution, the coupling constant values for the NH derivatives **2a** and **3b** and their *N*-methyl isomers **4a**, **5a**, **4b**, and **5b** were the same as in $CDCl_3$. The situation changed in the case of **2b**, where the presence of two tautomers, 3-(2′-hydroxy-1′-naphthyl)pyrazole (65%) and 5-(2′-hydroxy-1′-naphthyl) pyrazole (35%), was detected (cf. two broad signals corresponding to the H_4 protons at 6.55 and 6.39, two OH at 10.20 and 9.92, and two NH at 13.15 and 12.82 ppm, respectively). In compound **3a** the coupling constant value $^3J(H_3H_4)$ of 1.8 Hz in $CDCl_3$ increased, meaning that in DMSO-d_6 the tautomeric equilibrium

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Table 1. ^{1}H NMR Data (Chemical Shifts, δ in ppm, and Coupling Constants, J in Hz)

compd	H-3′	H-4′	H-5′	H-6′	H-7′	H-8′	H-3	H-4	H-5	others	solvent
2a	7.68 (d)	7.43 (d)	7.80 (m)	7.52 (m)	7.52 (m)	8.45 (m)		6.77 (d)	7.62 (d)	OH: 10.2−9.7 (s)	$CDCl_3$
	$^3J(H_3'H_4')$ = 8.6							^3J = 2.6		NH: 10.2−9.7 (s)	
	7.85 (d)	7.44 (d)	7.84 (m)	←7.53−7.46 (m)→		8.25 (m)		6.98 (d)	7.98 (d)	OH: 12.05 (s)	DMSO-d_6
								^3J = 2.5		NH: 13.33 (s)	
3a	7.79 (d)	7.66 (d)	7.85 (m)	7.51 (ddd)	7.57 (ddd)	8.18 (m)	7.73 (d)	6.80 (d)		O-CH_3: 3.89 (s)	$CDCl_3$
	$^3J(H_3'H_4')$ = 8.6; $^3J(H_5'H_6')$ = 6.9; $^3J(H_6'H_7')$ = 6.9; $^3J(H_7'H_8')$ = 6.9; $^4J(H_5'H_7')$ = 1.6; $^4J(H_6'H_8')$ = 1.7							^3J = 1.8		NH: 10.70 (s)	
	8.05 (d)	7.73 (d)	7.93 (m)	7.53 (ddd)	7.57 (ddd)	8.12 (m)	7.77 (d)	6.90 (d)		O-CH_3: 3.78 (s)	DMSO-d_6
								^3J = 2.1		NH: 13.08 (s)	
4a	7.66 (d)	7.41 (d)	7.80 (m)	7.51 (m)	7.53(m)	8.46 (m)		6.67 (d)	7.38(d)	N-CH_3: 3.94 (s)	$CDCl_3$
	$^3J(H_3'H_4')$ = 8.6							^3J = 2.5		OH: 11.60 (s)	
	7.82 (d)	7.44 (d)	7.83 (m)	7.48 (m)	7.50 (m)	8.23 (m)		6.94 (d)	7.92 (d)	N-CH_3: 3.98 (s)	DMSO-d_6
								^3J = 2.3		OH: 11.72 (s)	
5a	7.26 (d)	7.51 (d)	7.87 (m)	7.59 (m)	7.59 (m)	8.42 (m)	7.53 (d)	6.42 (d)		N-CH_3: 3.80 (s)	$CDCl_3$
	$^3J(H_3'H_4')$ = 8.5							^3J = 1.8		OH: n.o.[a]	
	7.28 (d)	7.54 (d)	7.89 (m)	←7.46−7.56 (m)→		8.29 (m)	7.49 (d)	6.32 (d)		N-CH_3: 3.69 (s)	DMSO-d_6
								^3J = 1.8		OH: 9.66 (s)	
6a	8.09 (d)	7.65 (d)	7.84 (m)	7.47 (ddd)	7.53 (ddd)	8.20 (m)		6.98 (d)	7.45 (d)	O-CH_3: 3.85 (s)	$CDCl_3$
	$^3J(H_3'H_4')$ = 8.7; $^3J(H_5'H_6')$ = 8.1; $^3J(H_6'H_7')$ = 6.8; $^3J(H_7'H_8')$ = 8.2; $^4J(H_5'H_7')$ = 1.6; $^4J(H_6'H_8')$ = 1.6							^3J = 2.2		N-CH_3: 4.00 (s)	
7a	7.36 (d)	7.66 (d)	7.88 (m)	7.56 (m)	7.56 (m)	8.25(m)	7.60 (d)	6.39 (d)		O-CH_3: 3.60 (s)	$CDCl_3$
	$^3J(H_3'H_4')$ = 8.5							^3J = 1.9		N-CH_3: 3.82 (s)	

[a] n.o. = not observable.

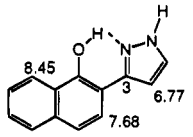
Table 2. ^{1}H NMR Data (Chemical Shifts, δ in ppm, and Coupling Constants, J in Hz)

compd	H-3′	H-4′	H-5′	H-6′	H-7′	H-8′	H-3	H-4	H-5	others	solvent
2b	7.28 (d)	7.77 (d)	7.81 (m)	7.35 (ddd)	7.48 (ddd)	8.25 (d)		6.88 (d)	7.81 (d)	OH: 4.0−5.0 (s)	$CDCl_3$
	$^3J(H_3'H_4')$ = 9.0; $^3J(H_5'H_6')$ = 8.0; $^3J(H_6'H_7')$ = 6.9; $^3J(H_7'H_8')$ = 8.4; $^4J(H_5'H_7')$ = 1.5; $^4J(H_6'H_8')$ = 1.2							^3J = 2.5		NH: 8.0−9.0 (s)	
	7.24 (d)	←7.50−8.10 (m)→		←7.26−7.42 (m)→		←7.50−8.10 (m)→		6.55 (br s)	←7.50−8.10 (m)→	OH:10.20 (s)	DMSO-d_6
								6.39 (br s)		9.92 (s)	
										NH: 13.15 (s)	
										12.82 (s)	
3b	7.27 (d)	7.86 (d)	7.79 (m)	7.34 (ddd)	7.40 (ddd)	7.88 (m)	7.62 (d)	6.50 (d)		O-CH_3: 3.82 (s)	$CDCl_3$
	$^3J(H_3'H_4')$ = 9.0; $^3J(H_5'H_6')$ = 6.9; $^3J(H_6'H_7')$ = 6.9; $^3J(H_7'H_8')$ = 6.9; $^4J(H_5'H_7')$ = 1.7; $^4J(H_6'H_8')$ = 1.5							^3J = 1.6		NH: 9.6−9.1 (s)	
	←			7.30−8.05 (m)			→	6.35 (d)		O-CH_3: 3.32 (s)	DMSO-d_6
								^3J = 1.6		NH: 12.90 (s)	
4b	7.31(d)	7.76 (d)	7.83 (m)	7.35 (ddd)	7.49(ddd)	8.33 (m)		6.78 (d)	7.52(d)	N-CH_3: 3.99 (s)	$CDCl_3$
	$^3J(H_3'H_4')$ = 8.9; $^3J(H_5'H_6')$ = 8.0; $^3J(H_6'H_7')$ = 6.8; $^3J(H_7'H_8')$ = 8.5; $^4J(H_5'H_7')$ = 1.6; $^4J(H_6'H_8')$ = 1.2							^3J = 2.3		OH: n.o.[a]	
	7.22 (d)	7.77 (d)	7.81 (d)	7.28 (ddd)	7.39 (ddd)	7.98 (d)		6.52 (d)	7.87 (d)	N-CH_3: 3.95 (s)	DMSO-d_6
								^3J = 2.1		OH: 9.98 (s)	
5b	7.31 (d)	7.87 (d)	7.83 (m)	7.39 (ddd)	7.42 (dd)	7.28 (m)	7.69 (d)	6.45 (d)		N-CH_3: 3.63 (s)	$CDCl_3$
	$^3J(H_3'H_4')$ = 9.0; $^3J(H_5'H_6')$ = 6.8; $^3J(H_6'H_7')$ = 6.8; $^3J(H_7'H_8')$ = 6.8;$^4J(H_5'H_7')$ = 1.6							^3J = 1.8		OH: 5.9−6.3 (s)	
	7.29 (d)	7.89 (d)	←	7.31−7.42 (m)	→	7.85 (d)	7.55 (d)	6.28 (d)		N-CH_3: 3.52 (s)	DMSO-d_6
						$^3J(H_7'H_8')$ = 8.8		^3J = 1.7		OH: 10.09 (s)	
6b	7.35 (d)	7.89 (d)	7.82 (m)	7.34 (ddd)	7.42 (ddd)	7.90 (m)		6.46 (d)	7.52 (d)	O-CH_3: 3.90 (s)	$CDCl_3$
	$^3J(H_3'H_4')$ = 9.0; $^3J(H_5'H_6')$ = 8.0; $^3J(H_6'H_7')$ = 6.8; $^3J(H_7'H_8')$ = 8.5; $^4J(H_5'H_7')$ = 1.6; $^4J(H_6'H_8')$ = 1.3							^3J = 2.2		N-CH_3: 4.02 (s)	
7b	7.36 (d)	7.96 (d)	7.84 (m)	7.36 (ddd)	7.41 (ddd)	7.49 (m)	7.68 (d)	6.35 (d)		O-CH_3: 3.89 (s)	$CDCl_3$
	$^3J(H_3'H_4')$ = 9.3; $^3J(H_5'H_6')$ = 6.6; $^3J(H_6'H_7')$ = 6.6; $^3J(H_7'H_8')$ = 6.6; $^4J(H_5'H_7')$ = 1.9; $^4J(H_6'H_8')$ = 2.1							^3J = 1.8		N-CH_3: 3.63 (s)	

[a] n.o. = not observable.

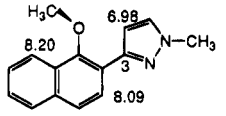
was somehow shifted to the 3-substituted form with a $^3J(H_4H_5)$ of 2.1 Hz.

From our ^1H NMR data some conclusions concerning the relative planarity of the pyrazolyl and naphthyl groups can be drawn by considering the chemical shift values of H-3′, H-8′, and H-4. In the **a** series the results are that **2a** and **4a** have a planar structure in which the pyridinic nitrogen of the pyrazole ring lies on the same side as the 1′-hydroxy group (form A). Compound **6a** shall also be planar but with the pyrazole ring on the opposite side (form B). Concerning the remaining derivatives: **3a** is more or less planar according to the previous NMR discussion; compounds **5a** and **7a** present non planar forms.



2a

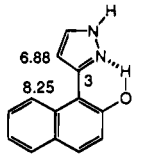
Form A



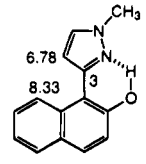
6a

Form B

In the **b** series it appears that all derivatives, except for **2b** and **4b**, exist as nonplanar conformations due to the interaction of the pyrazole substituent with the H-peri at the 8′ position. In compounds **2b** and **4b**, the ^1H NMR chemical shift values of H-8′ and H-4 support a quasi-planar situation due to the intramolecular hydrogen bond effect.



2b



4b

The same conclusions were attained by applying the ^{13}C NMR chemical shift increments criteria:[2] $\delta C3'-\delta C4'$ in **a** series, **2a** and **4a** (5.0 ppm, planar form A), **6a** (2.1 ppm, planar form B), **3a** (0.5 ppm), **5a** (6.7 ppm), and **7a** (4.5 ppm); $\delta C7'-\delta C8'$ in **b** series, **2b** (2.8 ppm), **3b** (2.1 ppm), **4b** (2.7 ppm), **5b** (3.5 ppm), **6b** (1.1 ppm), and **7b** (2.7 ppm). Here again the ^{13}C coupling constant criteria of $^2J(C_3H_4) < {}^2J(C_4H_3)$; $^3J(C_5H_3) < {}^3J(C_3H_5)$; $^2J(C_4H_5) < {}^2J(C_4H_3)$ were valid in both series, **a** and **b**, of compounds.

The influence of hydroxy and methoxy substituents[19,20] was taken into account for the assignment of the protons (see Tables 1 and 2) and carbons (see Tables 3 and 4) of the naphthyl group, together with the multiplicity of the signals and the coupling constant values.

Photophysical Studies. The ultraviolet spectra of all compounds were recorded in cyclohexane, ethanol, acetonitrile, and dimethyl sulfoxide solutions. The extinction coefficients ϵ for the first absorption maxima of derivatives of the **a** and **b** series have the following values: in CyH between 6300 and 8200 and in DMSO in the range of 3500−11500.

In order to make the discussion of the results easier, we will present the photophysics of the **a** and **b** series separately. Attention must also be paid to the established fact that the absorption spectra of 3(5)-arylpyrazoles are relatively insensitive to tautomerism but very

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Table 3. ^{13}C NMR Data (Chemical Shifts, δ in ppm, and Coupling Constants, J in Hz) in Deuteriochloroform[a]

compd	C-1′	C-2′	C-3′	C-4′	C-4a′	C-5′	C-6′	C-7′	C-8′	C-8a′	C-3	C-4	C-5	others
2a	152.0[b]	109.7 $^3J = 8.6$	124.0 $^1J = 157.9$	119.0 $^1J = 161.9$ $^3J = 4.7$	134.3	127.3 $^1J = 160.7$ $^3J = 4.9$ $^3J = 4.9$	126.6 $^1J = 160.8$ $^3J = 8.7$	125.3 $^1J = 160.2$ $^3J = 8.4$	123.0	125.6	152.5[b]	102.3 $^1J = 177.2$ $^2J = 8.4$	129.1 $^1J = 188.0$ $^2J = 8.4$	
3a	152.6	118.3 $^3J = 8.5$	125.4 $^1J = 161.1$	124.9 $^1J = 161.8$ $^3J = 4.8$	134.6	128.0 $^1J = 161.7$ $^3J = 5.2$ $^3J = 5.2$	126.63 $^1J = 163.2$ $^3J = 8.5$	126.58 $^1J = 159.2$ $^3J = 8.1$	122.3 $^1J = 161.1$ $^3J = 6.4$	128.1	138.0 $^1J = 185.4$ $^2J = 5.8$	104.3 $^1J = 176.3$ $^2J = 10.5$	141.6	O-CH_3: 61.7 ($^1J = 145.0$)
4a	151.6	109.7 $^3J = 8.6$	123.7 $^1J = 158.0$	118.7 $^1J = 161.5$ $^3J = 4.9$	133.9	127.2 $^1J = 159.0$	126.3 $^1J = 160.4$ $^3J = 8.6$	125.1 $^1J = 160.1$ $^3J = 8.3$	122.8 $^1J = 161.0$ $^3J = 5.9$	125.4	151.6	102.2 $^1J = 176.6$ $^2J = 8.6$	130.9 $^1J = 186.7$ $^2J = 8.2$ $^3J = 2.6$	N-CH_3: 38.7 ($^1J = 140.3$)
5a	150.1	109.8 $^3J = 9.0$	126.8 $^1J = 161.0$	120.1 $^1J = 162.6$ $^3J = 5.0$	134.9	127.5 $^1J = 161.4$ $^3J = 5.8$ $^3J = 5.8$	127.3 $^1J = 160.7$ $^3J = 8.6$	125.8 $^1J = 160.5$ $^3J = 8.3$	122.7 $^1J =$ n.m.[c] $^3J = 5.9$	124.6	138.7 $^1J = 186.0$ $^2J = 5.6$	106.8 $^1J = 176.3$ $^2J = 10.3$	138.7	N-CH_3: 37.0 ($^1J = 140.2$)
6a	153.1	122.1	126.2 $^1J = 160.0$	124.1 $^1J = 159.3$ $^3J = 4.7$	134.5	127.8 $^1J = 161.5$ $^3J = 5.0$ $^3J = 5.0$	125.9 $^1J = 160.2$ $^3J = 8.4$	125.9 $^1J = 160.0$	122.3 $^1J = 161.1$ $^3J = 6.5$	128.6	148.2	106.7 $^1J = 178.7$ $^2J = 9.0$	131.1 $^1J = 184.7$ $^2J = 9.6$ $^3J = 2.4$	O-CH_3: 61.1 ($^1J = 144.2$) N-CH_3: 39.0 ($^1J = 139.6$)
7a	154.1	118.7 $^3J = 8.4$	128.2 $^1J = 162.4$	123.7 $^1J = 162.4$ $^3J = 4.8$	135.0	127.8 $^1J = 161.1$ $^3J = 5.7$ $^3J = 5.7$	127.0 $^1J = 162.4$ $^3J = 8.5$	126.4 $^1J = 160.6$ $^3J = 8.5$	122.5 $^1J = 162.9$	128.1	138.5 $^1J = 184.6$ $^2J = 5.5$	106.6 $^1J = 175.9$ $^2J = 10.4$	140.3	O-CH_3: 61.7 ($^1J = 144.8$) N-CH_3: 37.6 ($^1J = 140.1$)

[a] In all of cases an heteronuclear ($^1H-^{13}C$) correlation experiment with a J value of 160 Hz confirmed the assignment. [b] These signals can be interchanged. [c] n.m. = not measurable.

Table 4. ^{13}C NMR Data (Chemical Shifts, δ in ppm, and Coupling Constants, J in Hz) in Deuteriochloroform[a]

compd	C-1′	C-2′	C-3′	C-4′	C-4a′	C-5′	C-6′	C-7′	C-8′	C-8a′	C-3	C-4	C-5	others
2b	110.2	153.5	118.7	130.2	129.0	128.6	123.1	126.7	123.9	132.2	148.4	107.1	130.2	
		^3J = 10.5	^1J = 160.7	^1J = 158.5		^1J = n.m.[b]	^1J = 160.1	^1J = 161.2	^1J = 158.7			^1J = 178.8	^1J = 187.8	
				^3J = 5.4			^3J = 8.5	^3J = 8.8	^3J = 7.2			^2J = 8.9	^2J = 8.4	
3b	113.9	154.7	113.0	130.4	128.9	127.9	123.7	126.9	124.8	133.3	135.7	107.4	139.8	O-CH_3: 56.4 (^1J = 144.3)
			^1J = 159.2	^1J = 159.7		^1J = n.m.[b]	^1J = 159.1	^1J = 160.0	^1J = 156.4		^1J = 186.0	^1J = 177.1		
				^3J = 5.3			^3J = 8.1	^3J = 8.2			^2J = 4.6	^2J = 10.8		
4b	110.2	153.4	118.7	129.8	128.8	128.5	122.8	126.5	123.8	131.8	148.6	107.3	131.3	N-CH_3: 38.9 (^1J = 140.3)
		^3J = 10.3	^1J = 159.5	^1J = 161.9	^3J = 6.5	^1J = 157.5	^1J = 159.8	^1J = 159.4	^1J = 158.8	^3J = 6.7	^3J = 8.4	^1J = 178.2	^1J = 186.5	
				^3J = 5.0	^3J = 6.5		^3J = 8.3	^3J = 8.6	^3J = 6.8	^3J = 6.7	^2J = 5.0	^2J = 8.7	^2J = 8.6	
					^3J = 6.5					^3J = 6.7			^3J = 2.4	
5b	109.2	152.8	117.8	131.4	128.6	128.2	123.6	127.3	123.8	133.5	139.1	108.2	136.5	N-CH_3: 36.7 (^1J = 140.2)
		^3J = 9.7	^1J = 161.2	^1J = 159.8		^1J = 161.0	^1J = n.m.[b]	^1J = 160.4	^1J = n.m.[b]		^1J = 185.9	^1J = 177.0		
				^3J = 5.0				^3J = 8.8			^2J = 5.8	^2J = 10.2		
6b	117.3	154.9	113.3	129.7	128.9	127.6	123.4	126.4	125.3	134.0	146.4	108.1	130.2	O-CH_3: 56.6 (^1J = 144.0)
	^3J = 3.6		^1J = 158.5	^1J = 159.4		^1J = 157.5	^1J = 158.8	^1J = 158.1	^1J = 160.4	^3J = 7.0	^3J = 8.4	^1J = 177.3	^1J = 185.1	N-CH_3: 38.9 (^1J = 139.4)
	^3J = 3.6			^3J = 5.1			^3J = 8.5	^3J = 8.6	^3J = 6.3	^3J = 7.0	^2J = 4.6	^2J = 8.6	^2J = 9.2	
										^3J = 7.0			^3J = 2.5	
7b	113.0	155.1	112.8	131.1	128.6	127.9	123.8	127.1	124.4	133.7	138.3	107.8	137.1	O-CH_3: 56.2(^1J = 144.4)
			^1J = 159.6	^1J = 160.4		^1J = 161.5	^1J = 159.9	^1J = 160.3	^1J = 161.5		^1J = 184.4	^1J = 176.2		N-CH_3: 36.6 (^1J = 139.7)
				^3J = 4.9			^3J = 8.3	^3J = 8.6	^3J = 6.6		^2J = 5.9	^2J = 10.4		

[a] In all cases a heteronuclear ($^1H-^{13}C$) correlation experiment with a J value of 160 Hz confirmed the assignment. [b] n.m. = not measurable.

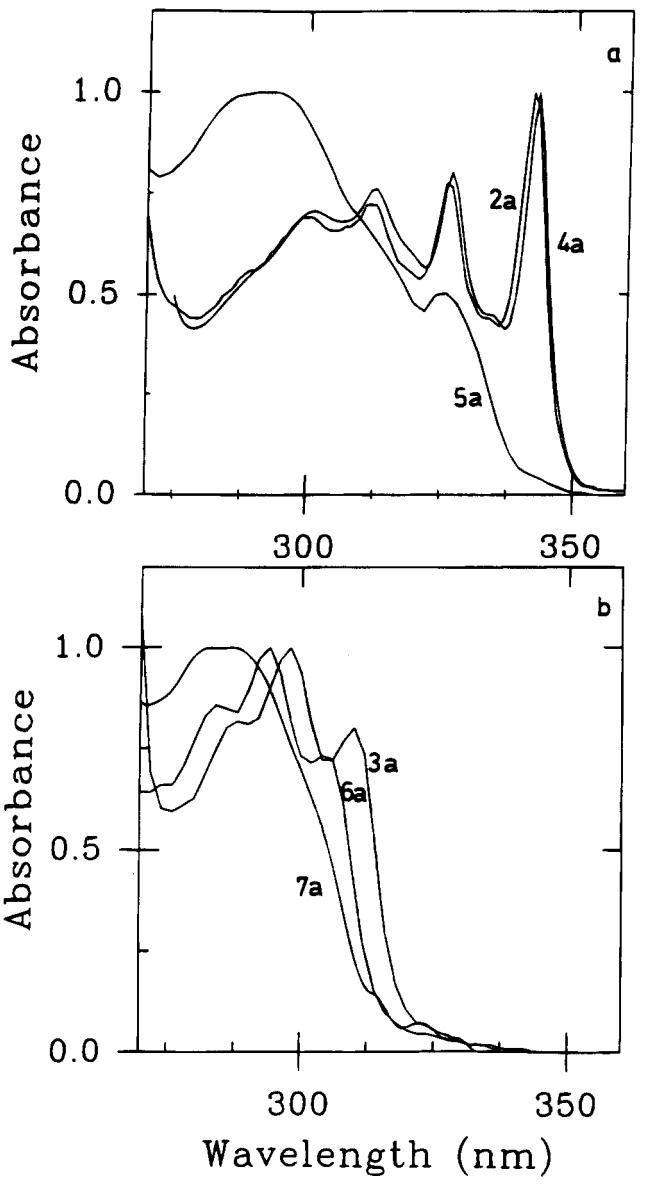


Figure 1. UV absorption spectra in CyH normalized with respect to the maximum wavelength: (a) 1′-hydroxy-2′-naphthyl derivatives **2a**, **4a**, and **5a**; (b) 1′-methoxy-2′-naphthyl derivatives **3a**, **6a**, and **7a**.

dependent on the dihedral angle between the pyrazole and the phenyl rings.[2,21]

3- and 5-(1′-Hydroxy-2′-naphthyl)pyrazoles (a Series). As shown in Figure 1a, the ultraviolet spectra in CyH of compounds **2a** and **4a** present an absorption maximum at 342 nm covering all the UV zone until 350 nm; in **5a** the maximum shifted to 325 nm and the vibrational structure disappeared. The behavior of these three 1′-hydroxy-2′-naphthyl derivatives can be explained as **2a** and **4a** being planar with an intramolecular hydrogen bond and **5a** nonplanar, in agreement with the NMR results. A similar situation was also encountered in the 3(5)-(2′-hydroxyphenyl)pyrazoles **I** and **II**.

The UV wavelengths absorption maxima of **2a** and **4a** were practically independent of the nature of the solvent, but the relative intensity of the band around 342 nm diminishes with respect to the ones in the blue region

(21) Cativiela, C.; García-Laureiro, J. I.; Elguero, J.; Elguero, E. *Gazz. Chim. Ital.* **1991**, *121*, 477.

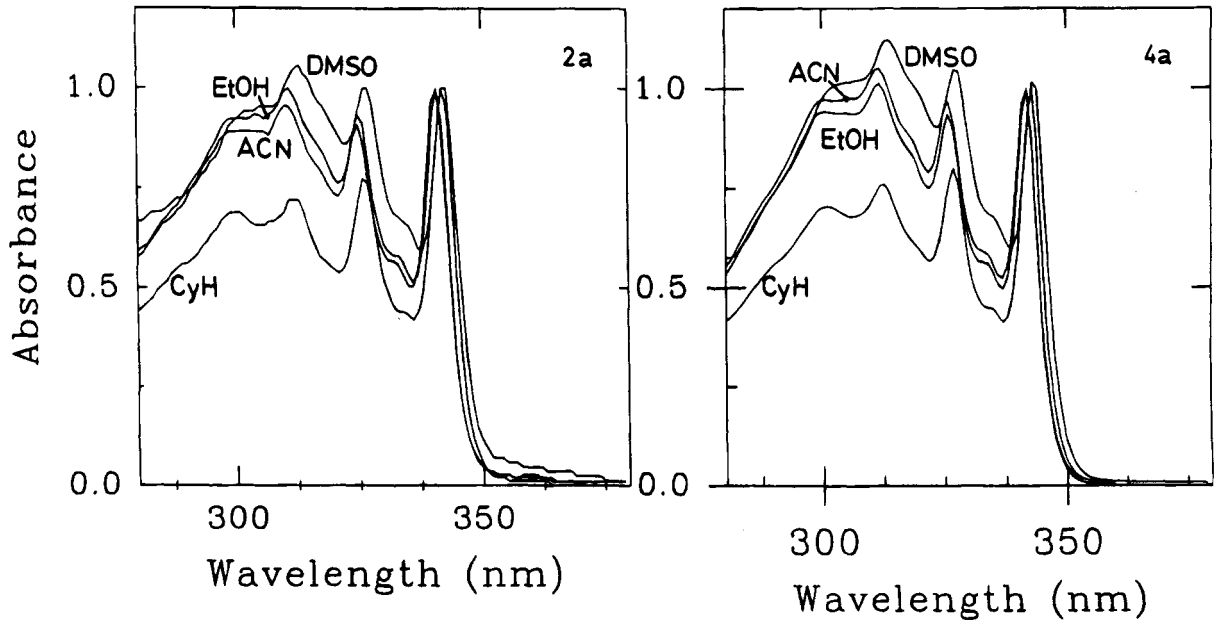


Figure 2. UV absorption spectra of **2a** and **4a** normalized with respect to the first maximum wavelength in CyH, ACN, EtOH,, and DMSO.

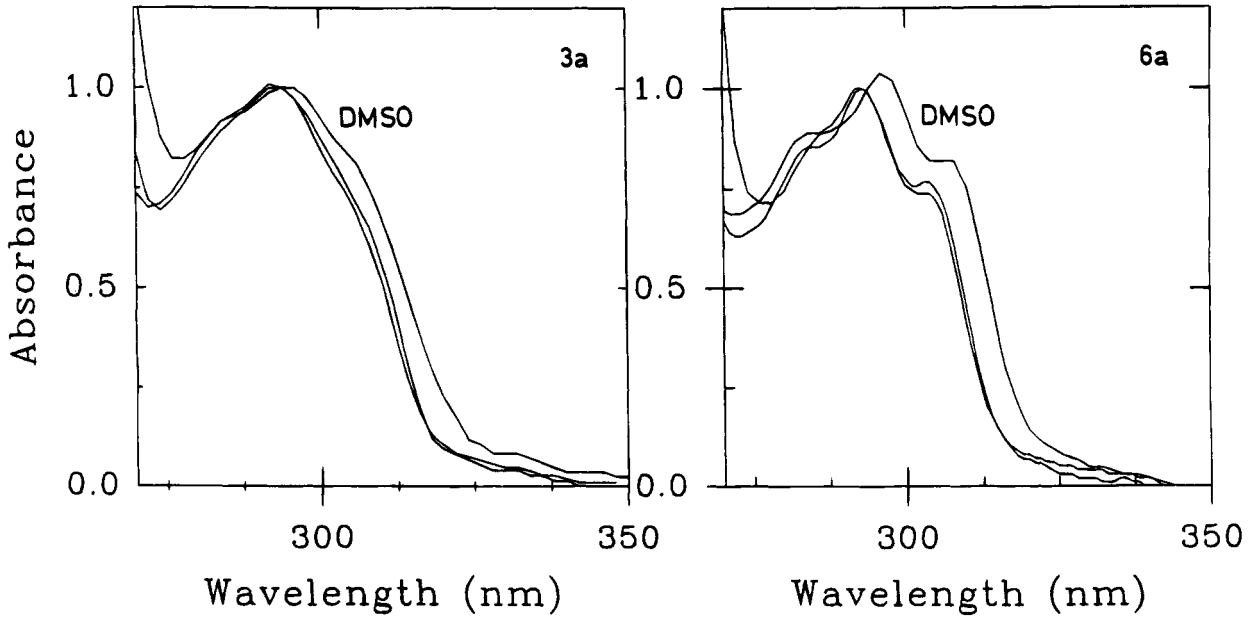
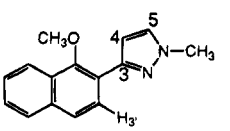


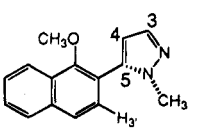
Figure 3. UV absorption spectra of **3a** and **6a** normalized with respect to the first maximum wavelength in ACN, EtOH, and DMSO.

when the basicity of the solvent increases, meaning that the intramolecular hydrogen bond is disrupted in a fraction of the total molecules (Figure 2).

In the case of the 1′-methoxy-2′-naphthyl derivatives (Figure 1b), two different spectral situations were found: for **3a** and **6a** a first band between 285 and 310 nm with vibrational structure exist but in **7a** this band had no vibrational structure and was shifted to the blue region around 285 nm. We could tentatively interpret such characteristics taking into account the NMR results: a situation of coplanarity between the two aromatic moieties, pyrazolyl and naphthyl, in **3a** and **6a** that will push the 1′-methoxy groups out of the plane[18] due to the H-8′ *peri* interaction, with **7a** existing as a mixture of various nonplanar conformations due to the steric interaction between $H_{3'}$ and the *N*-methyl group in position 1 of the 5-pyrazolyl substituent.



6a



7a

The intramolecular hydrogen bond in **3a** could also explain the following features: (i) the first absorption band in CyH is shifted to the red with respect to **6a**; (ii) basic solvents break that bond, moving the first absorption band to the blue in **3a**, but not in **6a** (Figure 3). In basic solvents the first absorption band of **3a** corresponds

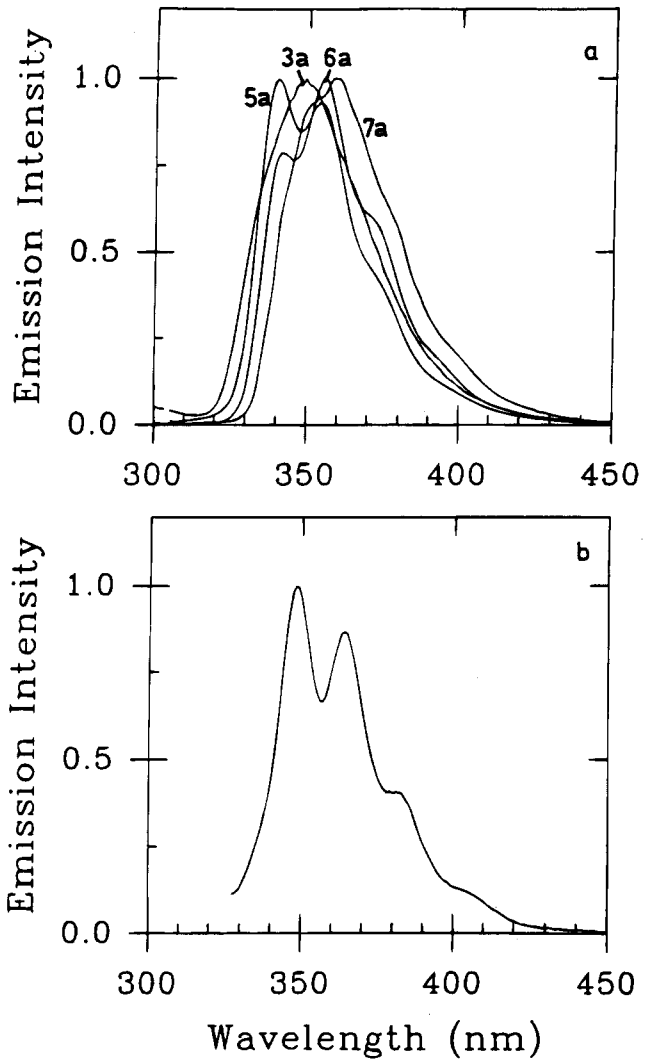


Figure 4. UV fluorescence emission spectra in CyH at room temperature: (a) **3a**, **5a**, **6a**, and **7a**; (b) **4a**.

to the sum of the spectra of **6a** and **7a**, supporting our ^{1}H NMR results about the displacement in **3a** of the tautomeric equilibrium from a 5-substituted form in CyH toward the 3-substituted one in such solvents with loss of planarity (see Table 1 for $^3J(H_3H_4)$ and $^3J(H_4H_5)$ coupling constant values).

The UV emission fluorescence spectra of 5-(1′-methoxy-2′-naphthyl)pyrazole (**3a**), 1-methyl-5-(1′-hydroxy-2′-naphthyl)pyrazole (**5a**), 1-methyl-3-(1′-methoxy-2′-naphthyl) pyrazole (**6a**), and 1-methyl-5-(1′-methoxy-2′-naphthyl)pyrazole (**7a**) in CyH at room temperature (see Figure 4a) appear in the same region with maxima around 350 nm, suggesting that these compounds emit from a common structural unit. Specular symmetry in compounds **3a** and **6a** denoted that emission occurred from planar structures very close to the ones present in the electronic ground state.

In Table 5 are gathered the fluorescence quantum yields and the lifetimes for the **a** series derivatives. The quantum yields are 10 times lower than the ones of the 3(5)-(2′-hydroxyphenyl)pyrazoles,[2] a surprising behavior if we consider that the fluorescence quantum yields for biphenyl and 1-phenylnaphthalene in CyH are of 0.18 and 0.26, respectively.[22]

(22) Berlman, I. D. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic Press: New York, 1965; pp 176 and 347.

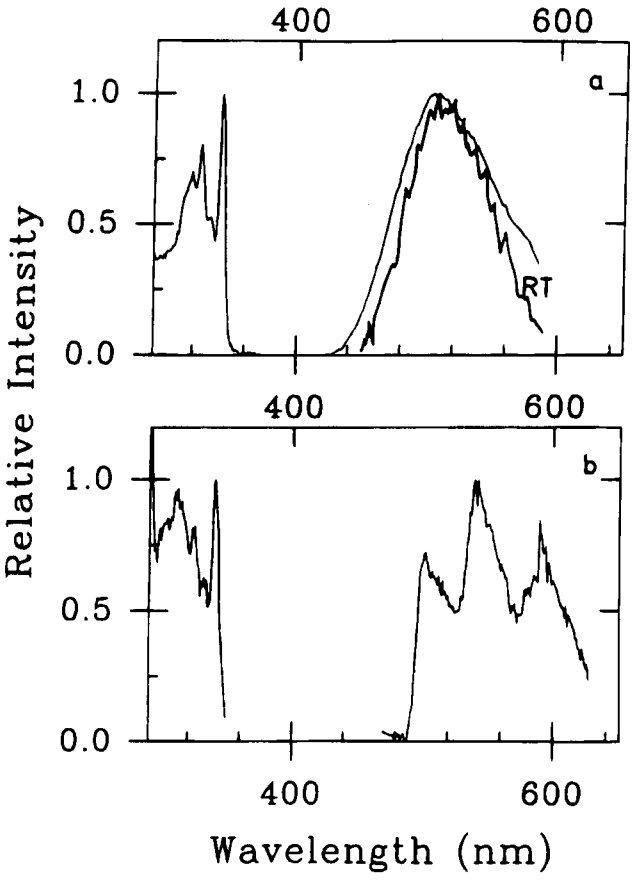


Figure 5. Luminescence of **2a** in CyH and luminescence excitation spectra: (a) at 77K and at room temperature (rt); (b) phosphorescence at 77K recorded with a delay of 3 ms.

In EtOH, ACN, and DMSO, the decay is monoexponential for compounds **6a** and **7a**, biexponential for **3a** and **5a**, and even triexponential for **5a** in DMSO, proving the complexity of such emissions.

The emissions at 350 nm of 3(5)-(1′-hydroxy-2′-naphthyl)pyrazole (**2a**) and 1-methyl-3-(1′-hydroxy-2′-naphthyl)pyrazole (**4a**) are 200 times weaker than that of **3a**, **5a**, **6a**, and **7a**, in CyH, which was unexpected in light of the results obtained in the 3(5)-(2′-hydroxyphenyl)-pyrazoles **I** and **II**, in which no emission could be detected.[2]

According to theoretical calculations, compounds **2a** and **4a** possess the features to follow an excited-state intramolecular proton transfer (ESIPT) process to dissipate energy.[23] In Figures 5 and 6 are presented the emission spectra which correspond to the proton transfer in CyH (10^{-4} M) at room temperature and 77 K, the excitation and absorption spectra of these two derivatives being in agreement. At room temperature the estimated relative strengths between the nontransferred and the transferred emissions are in a ratio of around 10:1 for both compounds, **2a** and **4a**.

Compared to the case of the 1′-hydroxy-2′-acetonaphtone where the ESIPT process does not occur,[9] the behavior of the 3(5)-(1′-hydroxy-2′-naphthyl)pyrazole (**2a**) and 1-methyl-3-(1′-hydroxy-2′-naphthyl)pyrazole (**4a**) prove

(23) The theoretical proton transfer curves obtained for 3-(1′-hydroxy-2′-naphthyl)pyrazole (**2a**) according to ref 3 confirm that, while the energy minima of the ground and the excited $1(\pi,\pi^*)^3$ states appear at an O–H distance of 1.09 Å, in the excited state $1(\pi,\pi^*)^1$ that minimum corresponds to 1.32 Å. The intramolecular proton transfer can only take place in the first singlet electronic excited state.

Table 5. Fluorescence Quantum Yields and Lifetimes[a] (ns) of the UV Emission for the a Series Derivatives

compd		CyH	ACN	EtOH	DMSO
2a	Φ_f	0.0003 ± 0.00005	0.0026 ± 0.0002	0.0036 ± 0.0003	0.004 ± 0.001
	τ_f			3.75; 0.02; 1.85	0.12; 8.46
				(45); (40); (15)	(76); (24)
4a	Φ_f	0.0003 ± 0.00005	0.0006 ± 0.0001	0.0023 ± 0.0003	
	τ_f	0.26	0.60	0.28; 4.82	0.12; 5.48
				(69); (31)	(96); (4)
5a	Φ_f	0.047 ± 0.003	0.10 ± 0.01	0.054 ± 0.003	0.013 ± 0.002
	τ_f	0.80	2.71; 4.18	1.19; 3.78	0.33; 8.98; 2.54
			(90); (10)	(73); (27)	(65); (19); (16)
3a	Φ_f	0.078 ± 0.007	0.069 ± 0.003	0.083 ± 0.001	0.11 ± 0.01
	τ_f	16.16; 0.80	12.70; 6.28	16.99; 1.23	19.98; 7.90
		(96); (4)	(66); (34)	(94); (6)	(56); (44)
6a	Φ_f	0.079 ± 0.004	0.067 ± 0.01	0.101 ± 0.004	0.15 ± 0.01
	τ_f	13.46	10.37	12.86	17.19
7a	Φ_f	0.026 ± 0.001	0.015 ± 0.001	0.021 ± 0.001	0.014 ± 0.001
	τ_f	3.88	1.64	2.15	1.28

[a] In parentheses are given the fractional contributions expressed in percent.

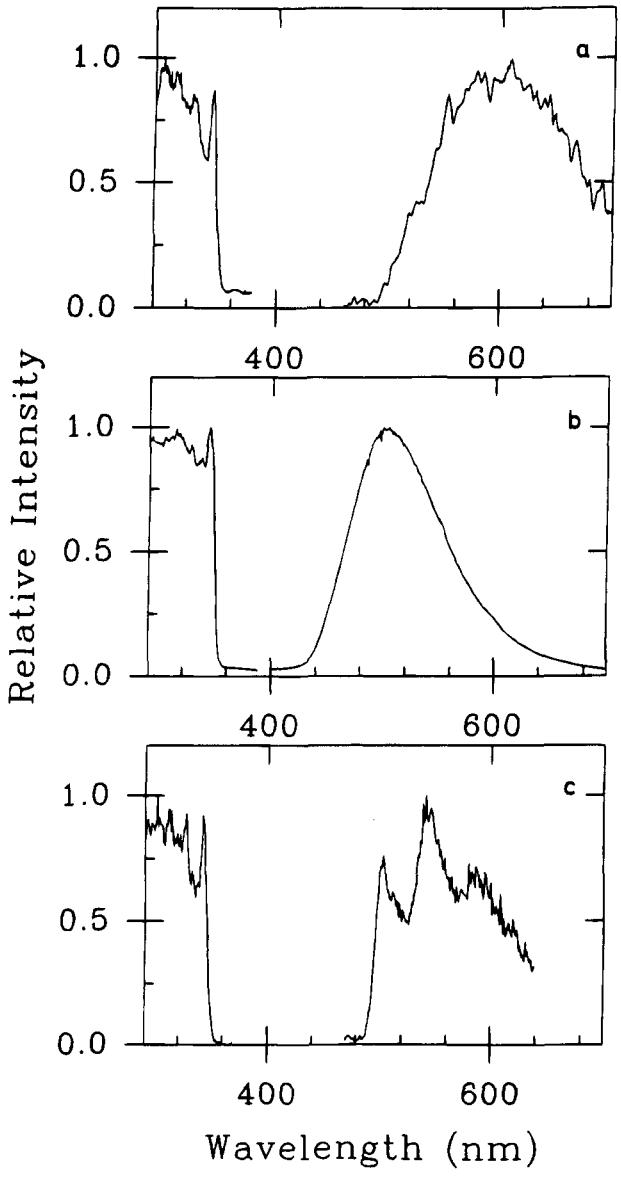


Figure 6. Luminescence of **4a** in CyH and luminescence excitation spectra: (a) at room temperature; (b) at 77K; (c) phosphorescence at 77K recorded with a delay of 3 ms.

that the increasing basicity of the substituent in the 2′-position of the naphthalene ring is responsible for such an ESIPT process. The intrinsic basicity of acetophenone is 825.9 kJ/mol[24] and of 3-phenylpyrazole and 1-methyl-3-phenylpyrazole 880.3 and 898.3 kJ/mol, respectively.[25]

The phosphorescence spectra of **2a** and **4a** do not clearly appear in the red zone of the fluorescence emissions and present vibrational structure; the detected triplets should correspond to the nontransferred form.[23]

In EtOH, ACN, and DMSO, emissions at 450−600 nm were observed for **2a** and **4a** that could be due either to proton transfer or to emitting naphtholate anionic forms.[26]

3- and 5-(2′-Hydroxy-1′-naphthyl)pyrazoles (b series). The 2′-hydroxy derivatives **2b** and **4b** show superimposable UV spectra in CyH with maxima at 346 nm, denoting that in the ground state both compounds have similar structures (Figure 7), with some degree of conjugation between the pyrazole and naphthyl rings due to an intramolecular hydrogen bond between the naphthol group and the nitrogen atom in the 2-position. In Figure 8 we observe that the positions of the maxima of the first absorption bands are insensitive to the basicity of the solvent, but the relative intensity decreases as basicity increases. In the nonplanar **5b** the maximum is shifted to 332 nm (CyH, Figure 7).

The spectra of the 2′-methoxy compounds **3b**, **6b**, and **7b**, are very similar with maxima at 337 nm (Figure 7b), reflecting that all exist as nonplanar structures.

The fluorescence spectra of 5(3)-(2′-methoxy-1′-naphthyl)pyrazole (**3b**), 1-methyl-5-(2′-hydroxy-1′-naphthyl)-pyrazole (**5b**), 1-methyl-3-(2′-methoxy-1′-naphthyl)pyrazole (**6b**) and 1-methyl-5-(2′-methoxy-1′-naphthyl)pyrazole (**7b**) measured in CyH are presented in Figures 9 a,b. Compounds with bulky substituents such as **5b** and **7b** show maxima around 356 nm and the less sterically hindered **3b** and **6b** around 376 nm; such behavior is attributable to the loss of coplanarity between the pyrazole and the naphthalene rings in **5b** and **7b** (see Scheme 2). In EtOH, ACN, and DMSO a similar behavior was observed, and in all solvents the Stokes shifts are systematically smaller by about 900 cm^{-1} for derivatives **5b** and **7b**. The excitation spectra correspond quite well with the absorption ones.

3-(2′-Hydroxy-1′-naphthyl)pyrazole (**2b**) and 1-methyl-3-(2′-hydroxy-1′-naphthyl)pyrazole (**4b**) give emission

(24) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

(25) Abboud, J.-L. M.; Cabildo, P.; Cañada, T.; Catalán, J.; Claramunt, R. M.; de Paz, J. L. G.; Elguero, J.; Homan, H.; Notario, R.; Toiron, C.; Yranzo, G. I. *J. Org. Chem.* **1992**, *57*, 3938.

(26) Toribio, F.; Catalán, J.; Amat, F.; Acuña, A. U. *J. Phys. Chem.* **1983**, *87*, 817.

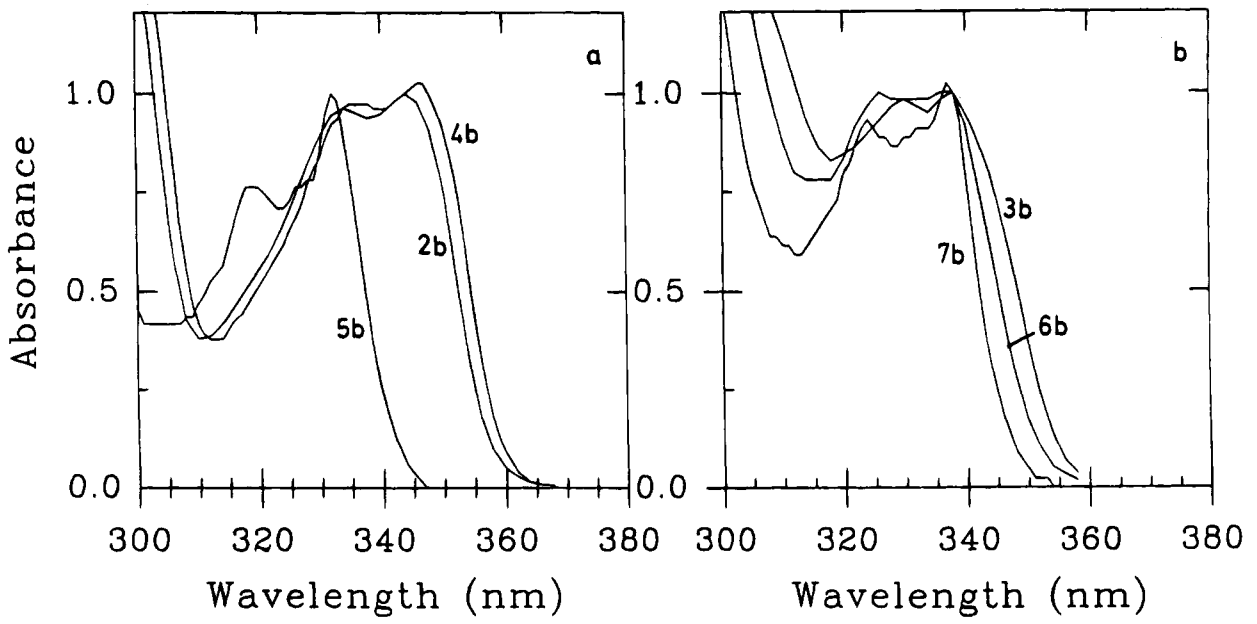


Figure 7. UV absorption spectra in CyH normalized with respect to the first maximum wavelength: (a) 2′-hydroxy-1′-naphthyl derivatives **2b**, **4b**, and **5b**; (b) 2′-methoxy-1′-naphthyl derivatives **3b**, **6b**, and **7b**.

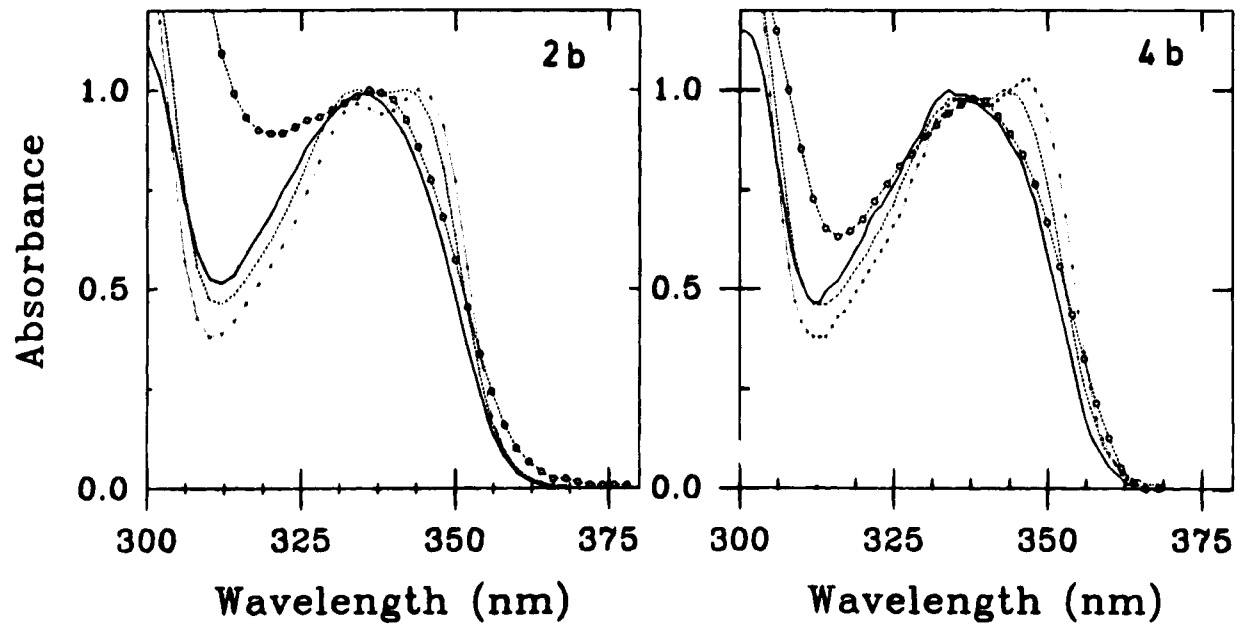


Figure 8. UV absorption spectra of **2b** and **4b** normalized with respect to the first maximum wavelength in CyH (···), ACN (- - -), EtOH (—), and DMSO (— ○ —).

around 369 nm (Figure 9b). By comparing the fluorescence spectra in ACN or CyH and EtOH or DMSO, it appears that the emitting forms in such compounds should be the ones in which intramolecular hydrogen bonds are disrupted. The corresponding excitation spectra in CyH and ACN do not show the peak more shifted to the red in the absorption spectra, but in EtOH and DMSO the excitation and the absorption spectra are closer (Figure 10).

In Table 6 are given the fluorescence quantum yields and the lifetimes for compounds of the **b** series. The quantum yields are significantly higher than the ones of the **a** series isomers, and the fluorescence decays are mainly monoexponentials. Derivatives **5b** and **7b** have quantum yield and lifetime values independent of the nature of the solvent.

In compound **4b** we have found that in CyH there is a weak emission in the visible region at 630 nm, most probably due to an ESIPT process, with an excitation spectrum identical to the absorption one. At room temperature the strengths ratio between the nontransferred and the transferred emissions is about 10:1.

However we have been unsuccessful in evidencing such fluorescence in the parent compound **2b,** neither increasing the concentration (1×10^{-5}, 5×10^{-5}, and 6×10^{-4} M) nor lowering the temperature to 77 K. Again, an explanation can be provided considering that the 1*H*-3-pyrazolyl substituent is less basic than the 1-methyl-3-pyrazolyl one;[25] consequently the intramolecular hydrogen bond in 3-(2′-hydroxy-1′-naphthyl)pyrazole (**2b**) is not strong enough to overcome the H-8′ *peri* interaction and the proton transfer *via* ESIPT is not permitted.

Table 6. Fluorescence Quantum Yields and Lifetimes[a] (ns) of the UV Emission for the b Series Derivatives

compd		CyH	ACN	EtOH	DMSO
2b	Φ_f	0.0019 ± 0.0007	0.021 ± 0.002	0.093 ± 0.004	0.20 ± 0.01
	τ_f	0.13; 1.84 (71); (29)	3.39	3.65; 1.06 (92); (8)	6.12
4b	Φ_f	0.0004 ± 0.00005	0.008 ± 0.002	0.05 ± 0.01	0.12 ± 0.02
	τ_f	0.21	4.13; 0.14 (82); (18)	4.09	6.36
5b	Φ_f	0.30 ± 0.03	0.35 ± 0.03	0.33 ± 0.03	0.42 ± 0.03
	τ_f	4.43	5.10	4.94	6.03
3b	Φ_f	0.24 ± 0.01	0.22 ± 0.01	0.234 ± 0.006	0.53 ± 0.02
	τ_f	2.04	2.98; 1.09 (77); (23)	2.42	5.71; 2.64 (77); (23)
6b	Φ_f	0.30 ± 0.02	0.45 ± 0.02	0.25 ± 0.02	0.65 ± 0.02
	τ_f	2.60	3.88	2.88	5.51
7b	Φ_f	0.50 ± 0.01	0.37 ± 0.02	0.42 ± 0.02	0.52 ± 0.04
	τ_f	4.82	5.21	5.52	6.26

[a] In parentheses are given the fractional contributions expressed in percent.

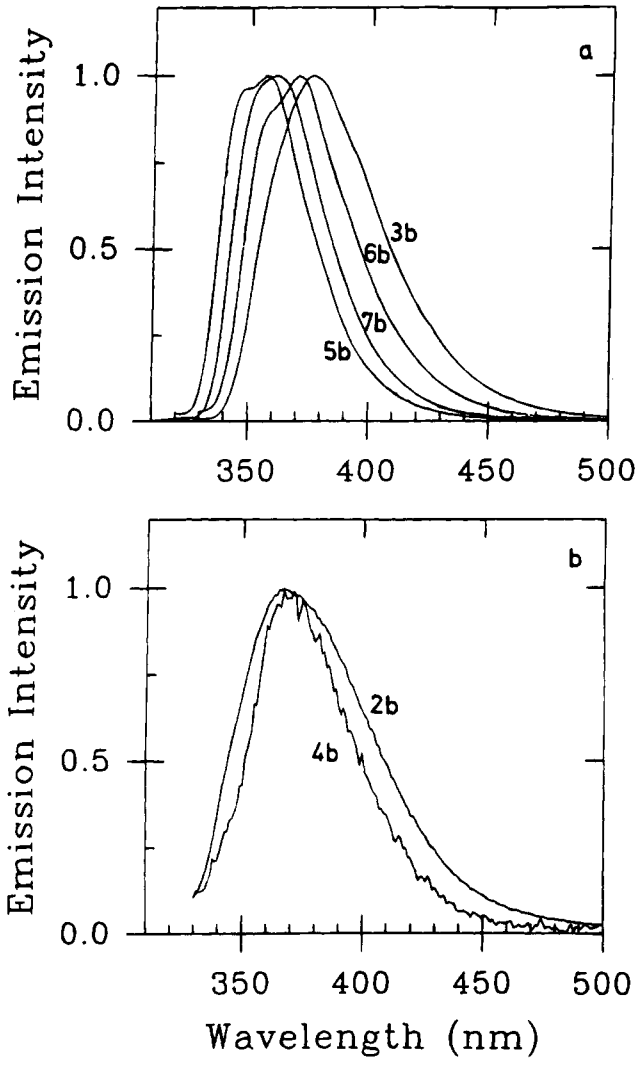


Figure 9. Fluorescence emission spectra in CyH at room temperature: (a) **3b**, **5b**, **6b**, and **7b**; (b) **2b** and **4b**.

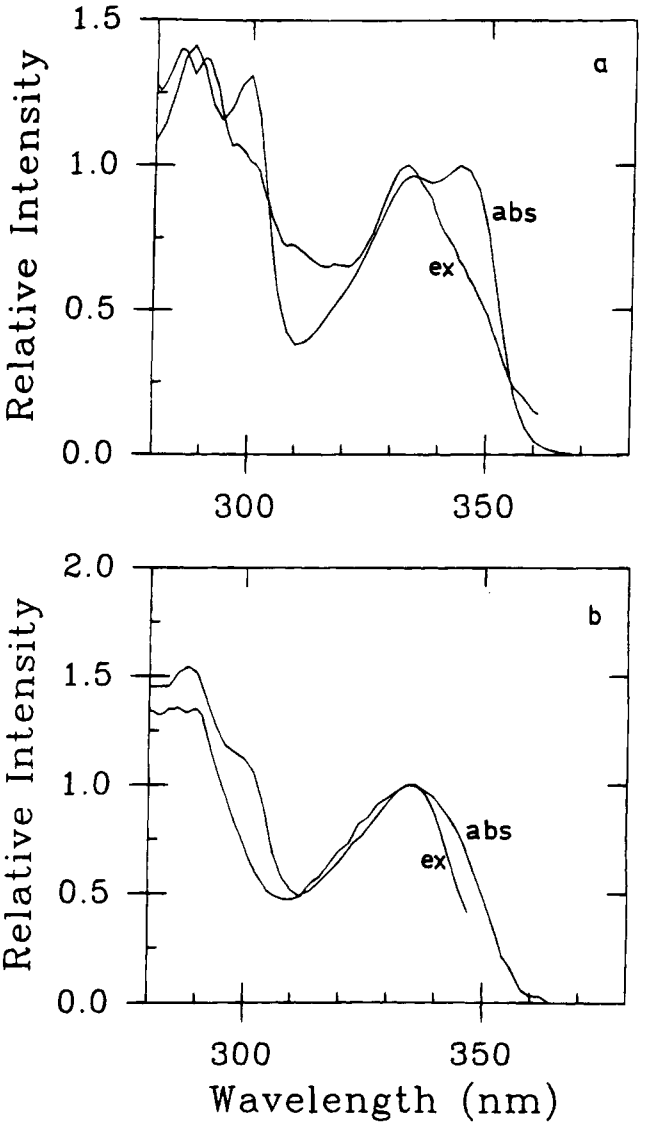


Figure 10. UV absorption and fluorescence excitation spectra of **2b** in (a) CyH and (b) EtOH.

Photostability Studies. In Table 7 are assembled the results for a representative set of the foregoing studied compounds. For comparison purposes 1-methyl-3-(2′-hydroxyphenyl)pyrazole (**I**, R = CH_3)[2] and Tinuvin P as standards have also been included.

In CyH the photostability of all derivatives is quite remarkable, with the order of photostability **4b** > **I** (R = CH_3) > **2a** > **2b** > **4a** > **7b** > **7a** > **3b** related to the possibility of forming an intramolecular O−H···N hydrogen bond in compounds **4b**, **2a**, **2b**, and **4a** and N−H···OCH_3 in **3b**. However, the results obtained for 1-methyl-5-(2′-methoxy-1′-naphthyl)pyrazole (**7b**) and 1-methyl-5-(1′-methoxy-2′-naphthyl)pyrazole (**7a**) indicate that the photostability of all the compounds series is an intrinsic property of their molecular structure.

At this point we want to remark that our work

Table 7. Photostabilities

compd	λ_{ex}[a]	photodegradation velocity,[b] (mol L^{-1} h^{-1}) × 10^6
CyH		
4b	345	0.3
1-methyl-3-(2′-hydroxyphenyl)pyrazole		0.46[c]
2a	327	1.2
2b	340	1.4
4a	327	1.6
7b	333	3.1
7a	290	4.2
3b	333	6.7
DMSO		
Tinuvin P	310	4.1
3b	333	8.7
3a	300	20.0
4a	327	21.6
4b	337	23.3
2a	327	30.0
1-methyl-3-(2′-hydroxyphenyl)pyrazole	300	30.8
2b	337	35.0

[a] ±12 nm. [b] Expressed in molarity diminution with irradiation time. Calculated from the slope of the relationship of absorbance versus irradiation time and conversion to concentration units. [c] See ref 2.

concerns mainly photostable compounds able to absorb the UV light and dissipate it by nonradiative processes, therefore with very low quantum yields ϕ_f.

In DMSO solution where the intramolecular hydrogen bonds are partially disrupted, the most photostable derivative is the 5(3)-(2′-methoxy-1′-naphthyl)pyrazole (**3b**), similar to Tinuvin P. The photostability shown by compounds of the **b** series in this solvent is due to the high fluorescence quantum yield ϕ_f which in some cases exceeds 50%.

In spite of the high photostability presented by all compounds, their possible use as UV stabilizers needs further consideration. In the **a** series only 3(5)-(1′-hydroxy-2′-naphthyl)pyrazole (**2a**) and 1-methyl-3-(1′-hydroxy-2′-naphthyl)pyrazole (**4a**) and in the **b** series all derivatives except 1-methyl-5-(2′-methoxy-1′-naphthyl)-pyrazole (**5b**) will properly cover the zone up to 350 nm. However, due to the fact that they emit in the UV region, *only compounds with low quantum yields ϕ_f such as **2a** and **4a** in all solvents or **2b** and **4b** in solvents of low basicity will be useful.*

Conclusions

The photostability of 3(5)-(1′-hydroxy-2′-naphthyl)-pyrazoles (**a** series) and 3(5)-(2′-hydroxy-1′-naphthyl)-pyrazoles (**b** series) is an intrinsic property of their molecular structure, and the existence of an intramolecular hydrogen bond is not an essential condition for providing UV stability.

From our ^1H and ^{13}C NMR (chemical shifts and coupling constants criteria) and photophysical studies (absorption and emission spectra), we can conclude that 3(5)-(1′-hydroxy-2′-naphthyl)pyrazole (**2a**) and 1-methyl-3-(1′-hydroxy-2′-naphthyl)pyrazole (**4a**) show the presence of an IMHB linking the hydroxyl proton with the pyrazole N_2 lone pair, follow the ESIPT mechanism, and cover the spectral zone below 350 nm.

3-(2′-Hydroxy-1′-naphthyl)pyrazole (**2b**) and 1-methyl-3-(2′-hydroxy-1′-naphthyl)pyrazole (**4b**) despite the H-8′ *peri* steric effect possess an IMHB, cover the range of 240−340 nm, and are photostable in weak basic solvents.

The observed phosphorescence in such compounds is produced by the nontransferred form. Proton transfer does not occur in the first triplet state.

Acknowledgment. We are greatly indebted to DGICYT of Spain for financial support (Project Number PB90-0226-C02). Two of us (V.B. and R.M.) thank the Ministry of Education of Spain for grants. Thanks are also given to the Comunidad de Madrid (Acción Especial no. AE00315/94) for a post-doctoral fellowship to (M.D.S.M.).

Supplementary Material Available: ^{13}C NMR spectra of **1a−7a** and **1b−7b** (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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