On the solvatochromism, dimerization and tautomerism of indazole

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Dedicated to Prof. Rosa Maria Claramunt on the occasion of her 65th anniversary
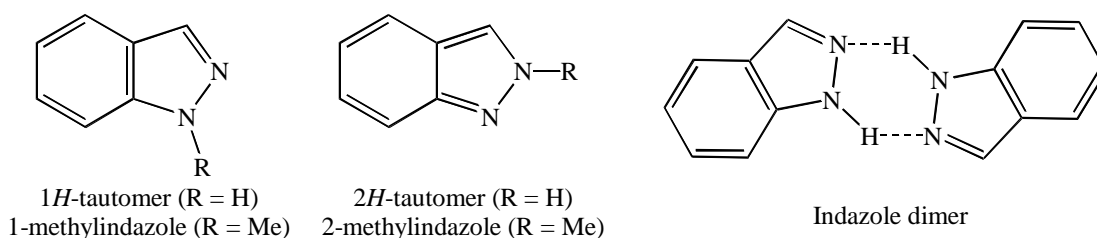
Abstract

A careful study of the solvatochromism of indazole was for the first time conducted in this work. The study revealed that indazole solvatochromism is governed mainly by the polarizability of the medium and, to a lesser extent, by its acidity and basicity. Based on the results of the solvatochromic analysis and their processing with Abe's model, this polar compound undergoes no significant change in dipole moment from its ground electronic state to its first excited state, which contradicts the predictions of other authors. Indazole dimerizes in both 2-methylbutane and 1-chlorobutane. However, neither its monomer nor its dimer undergoes tautomerization to 2*H*-indazole in the ground state in response to an increase in dipolarity of the medium. Also, based on experimental evidence, no tautomerization occurs in the first excited singlet or triplet of the compound.

Keywords: Indazole, solvatochromism, dimerization, tautomerization.

Introduction

Indazole is a polar asymmetric bicyclic diazole heterocycle with a dipole moment in the gas phase of 1.76 D.[1] It contains a basic pyridine nitrogen with an intrinsic basicity in the gas phase of 214.2 kcal/mol and an acidic pyrrole nitrogen with an intrinsic basicity in protonated form of 348.4 kcal/mol.[2] The fact that these two nitrogen sites are located in adjacent positions in the molecular structure (see Scheme 1) allows indazole at low concentrations in mildly acid or basic media to form 1*H* and 2*H* tautomers via acid–base interactions (see Scheme 1),[3-10] as well as symmetrical dimers by hydrogen bonding.[11,12]

1*H*-tautomer (R = H)   2*H*-tautomer (R = H)

1-methylindazole (R = Me)   2-methylindazole (R = Me)   Indazole dimer

Scheme 1

Despite the wide range of potential interactions between dissolved indazole and solvents, few authors have shown interest in investigating its solvatochromism. In fact, a literature search for references to this topic retrieved just a single paper by Saha and Dogra entitled "Solvatochromic effects in the absorption and fluorescence spectra of indazole and its amino derivatives" where they examine the behaviour of the solute in only four solvents, namely: cyclohexane, acetonitrile, methanol and water.[13] These authors concluded that the dipole moment of indazole increases from 1.62 D in the ground electronic state to 2.44–2.96 D in its first excited singlet (i.e. that the dipole moment is nearly doubled upon excitation to the first excited singlet).

Although 1H↔2H tautomerism of indazole in the ground state was previously ruled out,[9-12] according to Hirota *et al.* it occurs in the first triplet state of the indazole – benzoic acid complex,[14] and in the first excited singlet of the indazole – acetic acid complex.[15] They ascribed both instances of tautomerism to a double proton transfer in the complexes. In the present author's opinion, however, there is the scarcely explored possibility that the solvent dipolarity might enable indazole tautomerism since 1-methylindazole possesses a dipole moment of 1.5 D,[16] whereas 2-methylindazole has one of 3.4 D,[16] and is therefore considerably more polar.

The dimerization of indazole by double hydrogen bonding produces a symmetric dimer which, according to Hirota *et al*.,[14,15] might facilitate the formation of the 2H tautomer –at least via its excited electronic state –and that of the dimer tautomer in highly polar media.

In this work, we studied the solvatochromism of indazole in 22 different solvents of variable dipolarity (SdP), polarizability (SP), acidity (SA) and basicity (SB) as measured on the empirical scales previously developed by our research group[17–20] and compared the results with those for 1-methylindazole. Measurements were additionally made in 1-chlorobutane (ClB) at temperatures from 273 to 153 K and in 2-methylbutane (2MB) at 298–248 K in order to assess the sensitivity of indazole to the polarizability and dipolarity of the medium. We also examined the dimerization of indazole and its potential tautomerization. Finally, we used Abe's model[21] to quantify the change in dipole moment upon electronic excitation from S_0 to S_1.

Results and Discussion

We first examined the results of the solvatochromic analysis of indazole in 21 different solvents and the gas phase, and those of its thermochromic analysis in ClB at 283–153 K and 2MB at 298–248 K, and then compared them with those of the solvatochromic analysis of 1-methylindazole in 11 different solvents and the gas phase. Finally, we used Abe's method[21] to assess polarizability and dipole moment changes in indazole from the ground state (S_0) to the first excited state (S_1), and examined the potential dimerization and tautomerization of the compound in dilute solutions in ClB and 2MB.

On the solvatochromism of indazole

Table 1. Wave numbers (in cm^{-1}) of the 0-0 component of the first absorption band of indazole and of 1-methylindazole in the studied solvents[a]

Indazole

Solvent	v (cm^{-1})	Solvent [b]	v (cm^{-1})
gas-phase	34407	2,2,2-trifluoroethanol	33918
Perfluorohexane	34266	acetic acid	33711
n-pentane	33986	2-methylbutane (2MB) 293	34005
n-hexane	33973	2MB283	34000
Decalin	33880	2MB273	33995
diethyl ether	33776	2MB263	33989
di-n-butyl ether	33727	2MB253	33981
1,4-dioxane	33732	2MB243	33968
Tetrahydrofuran	33715	1-chlorobutane (ClB) 293	33881
ethyl acetate	33818	ClB273	33875
Dichloromethane	33808	ClB253	33867
Chloroform	33735	ClB233	33856
Methanol	33732	ClB213	33848
Ethanol	33701	ClB193	33840
1-propanol	33686	ClB173	33827
1-butanol	33650	ClB153	33808
Water	33792	acetonitrile	33864

[a] The derivative function was used while estimating the maximum absorption wavelength for the 0-0 component. [b] Temperature (K) is indicated; room temperature (293 K) can be assumed, otherwise.

1-Methylindazole

Solvent	ν (cm^{-1})	Solvent	ν (cm^{-1})
gas-phase	33369	di-*n*-butyl ether	32848
Perfluorohexane	33202	methanol	32885
n-pentane	32920	ethanol	32870
n-hexane	32897	1-propanol	32829
Decalin	32799	1-butanol	32844
diethyl ether	32891	acetic acid	32828

Table 1 shows the energy, in cm^{-1}, of the 0–0 component of the first absorption band of indazole in the different solvents as the starting point for its solvatochromic study. The results provided by the solvatochromic scales conformed to the following equation (see Figure 1):

$$\nu = -(786 \pm 39)SP - (128 \pm 20)SA - (321 \pm 23)SB + (34\,470 \pm 25) \tag{1}$$
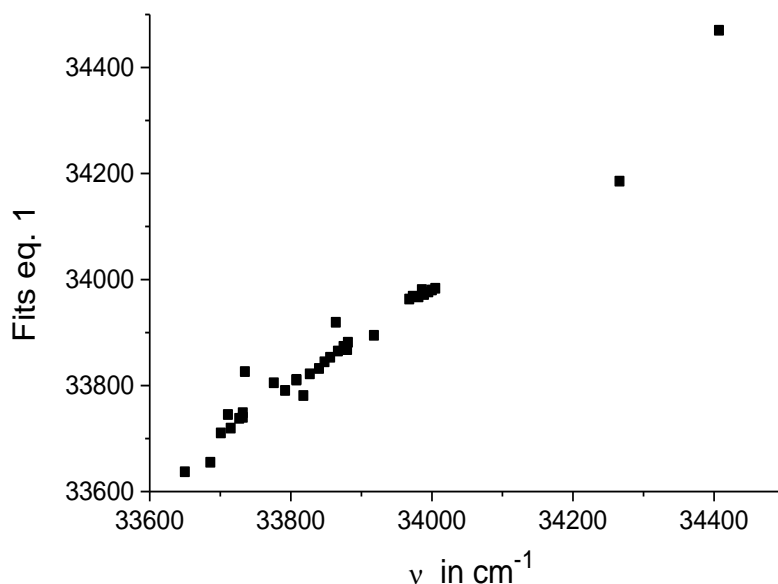
with $n = 34$, $r = 0.982$ and sd $= 31$ cm^{-1}.

Figure1. Fits from Equation 1 (ν = - 786SP – 128SA – 321SB + 34470) *vs* the corresponding experimental ν data values from Table 1.

Rather unexpectedly, the solvatochromism of such a polar molecule as indazole is insensitive to the dipolarity SdP of the medium. As a result, its electronic states S_0 and S_1 should possess an identical dipole moment, which contradicts previous findings of Saha and Dogra.[13] We shall return to this point later. Also, the independent term of the equation, 34 470 $\pm$ 25 cm^{-1}, is quite

consistent with the value 34 471.691 ± 0.006 cm^{-1} obtained by Berden *et al.*[22] using rotationally resolved ultraviolet spectroscopy in a supersonic jet.

Based on Equation 1, the solvatochromism of indazole depends mainly on the polarizability SP of the medium and also, to a lesser extent, on its basicity SB, and even less so on its acidity SA. These specific contributions to the solvatochromism of indazole expose the roles of its pyrrole nitrogen (an acid site) and pyridine nitrogen (a basic site).

One interesting way of confirming the solvatochromic behaviour of indazole would be by suppressing its acid site (i.e. by using its 1-methyl derivative [Scheme 1] instead of the parent compound). The energies of the 0–0 component of the first absorption band for 1-methylindazole in 11 different solvents and in the gas phase are included in Table 1. The results obtained from the solvatochromic scales[17] fitted the following equation:

$$\nu = - (811 \pm 45)SP - (61 \pm 34)SA + (33\ 404 \pm 26) \tag{2}$$

with $n = 12$, $r = 0.988$ and sd $= 29$ cm^{-1}.

As can be seen from Equation 2, the solvatochromism of 1-methylindazole is virtually exclusively dependent on the polarizability (SP) of the medium. Also, it is scarcely dependent on its acidity (SA); in fact, the SA coefficient decreased markedly from indazole to 1-methyl-indazole (–128 ± 20 *vs* –61 ± 34), which suggests that the presence of a methyl group in the derivative may hinder interaction between acid solvents and the neighbouring basic nitrogen site. The assumption that the solvatochromism of 1-methylindazole is virtually exclusively governed by the solvent polarizability (SP) is supported by the small statistical deterioration observed in the fitting of Equation 3, which, unlike Equation 2, excludes the influence of acidity (SA) on 1-methylindazole:

$$\nu = - (835 \pm 47)SP + (33\ 405 \pm 28) \tag{3}$$

with $n = 12$, $r = 0.984$ and sd $= 32$ cm^{-1}.

Dipole moment of indazole in its $1(\pi,\pi^*)^1$ state

Based on the above-discussed solvatochromic analysis, we deduce that the dipole moments of indazole and its 1-methyl derivative do not change from the ground electronic state to the first excited state. In order to confirm this crucial hypothesis, we used Abe's approach as formulated via the following equation (Equation 4) to assess changes in dipole moment and isotropic polarizability in indazole on electronic photoexcitation:

$$[(\mu_i)^2 - (\mu_0)^2] + (\alpha_i) \cdot A = B \tag{4}$$

These parameters, which were calculated from the intercept and slope, respectively, of a *B vs A* plot. μ_i and μ_0 in Equation 4, represent the dipole moment of the chromophore in the excited and ground state, respectively, which are involved in the electronic transition, and α_i is the isotropic polarizability of the excited state. *A* and *B* were evaluated from the molecular mass, density, refraction index and dielectric constant for the solvents, as well as from the ionization potential

and electronic transition energy for indazole as formulated in Abe's expressions, which are given in the Experimental Section.

Applying Abe's method to the energy of the 0–0 component of the first absorption band for indazole in the different solvents provided an excellent fit ($r = 0.9999$, Figure 2), with a slope of $(274.4 \pm 0.3) \times 10^{-25}$ cm^3 – the isotropic polarizability for the $1(\pi,\pi^*)^1$ state – and an intercept of $(-0.11 \pm 0.13) \times 10^{-36}$ erg cm^3 —the corresponding dipole moment is $\mu[1(\pi,\pi^*)^1] = 1.73 \pm 0.13$ D. The dipole moment was calculated from the intercept, which was set equal to $(\mu^*)^2 - (\mu_0)^2$ in order to obtain $\mu_0 = 1.76 \pm 0.02$ D^1 for indazole. A total of 14 solvents were used (the ClB at 293–153 K and 2MB at 293–243 K). Therefore, within experimental error, the two dipole moments can be considered identical, which confirms the previous assumption from the solvatochromic results, i.e. that the solvatochromism of indazole is independent of the dipolarity of the medium (see Equation 1).
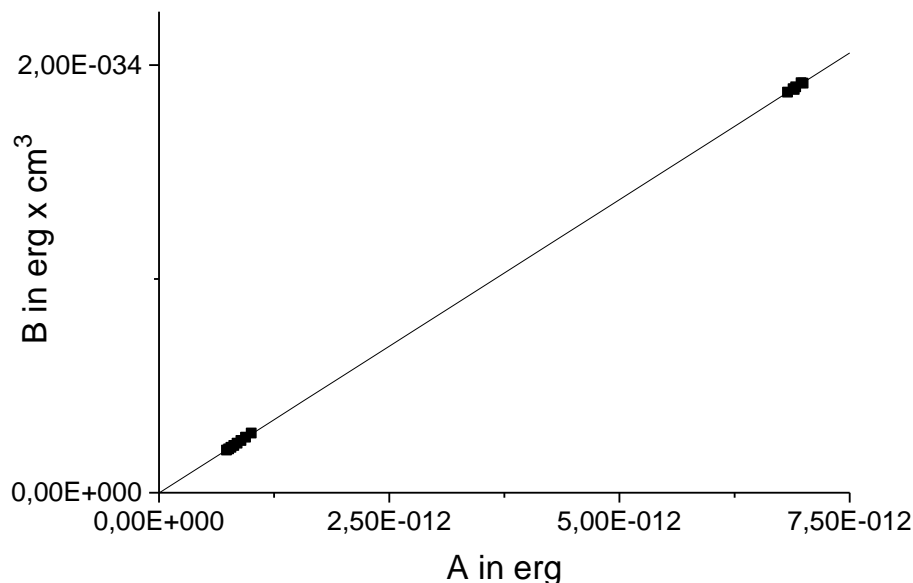

Figure 2. Plot of *B* against *A* following Abe's model for indazole.

The unexpected strong dependence of the $S_0 \rightarrow S_1$ transition of indazole on the solvent polarizability warrants seeking a straightforward explanation, which might be as follows: the transition promotes one of the electrons in the pair contributed by the pyrrole nitrogen to the π cloud and causes its delocalization over the bicyclic system. As a result, the excited compound possesses a substantially increased polarizability that leads to a bathochromic shift in its first transition state by the effect of the polarizability of the medium. This hypothetical increase in polarizability is supported by the fact that, based on mp2 calculations with a 6-31G** basis set, indazole in its ground electronic state possesses an isotropic polarizability of 112.1×10^{-25} cm^3

,[23] and, based on calculations using Abe's method, one of $274.4 \pm 0.3 \times 10^{-25}$ cm^3 (i.e. 2.4 times higher) in its $1(\pi,\pi^*)^1$ state.

No doubt, the proposed mechanism warrants careful investigation, which at the moment is in progress.

On the dimerization of indazole

Because indazole is a polar substance (μ = 1.76 D) containing an acid site (pyrrole nitrogen) and a basic site (pyridine nitrogen) at adjacent positions, it tends to form a non-polar symmetric doubly hydrogen bonded dimer at low concentrations in inert solvents.

Figure 3 illustrates the thermochromic behaviour of a 3.6×10^{-5} M solution of indazole in a highly inert solvent such as 2MB. As can be seen in Figure 4, as the solution temperature was lowered, the chromophore exhibited an unexpected bathochromic shift of *ca.* 268 cm^{-1} in the region from 248 to 223 K clearly indicating a structural change in the compound. Jalviste *et al.* [11] found the shift resulting from the dimerization of indazole at a low temperature in the gas phase to be 321 cm^{-1}.
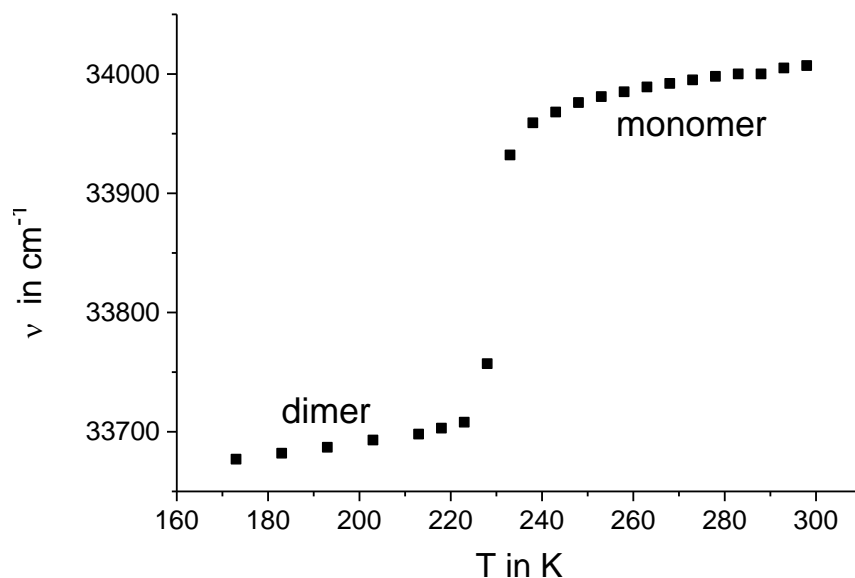

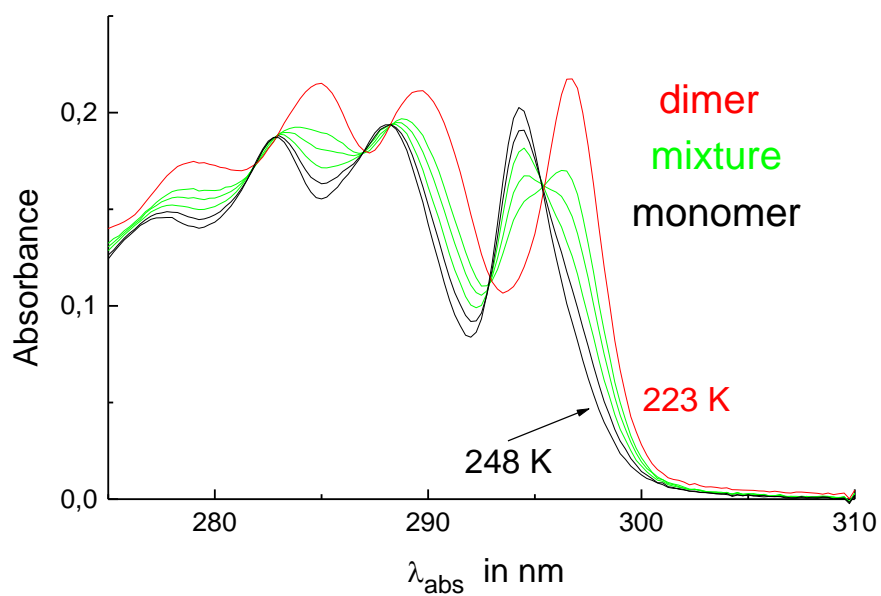**Figure 3**. Thermochromic behaviour of a 3.6×10^{-5} M solution of indazole in 2MB.

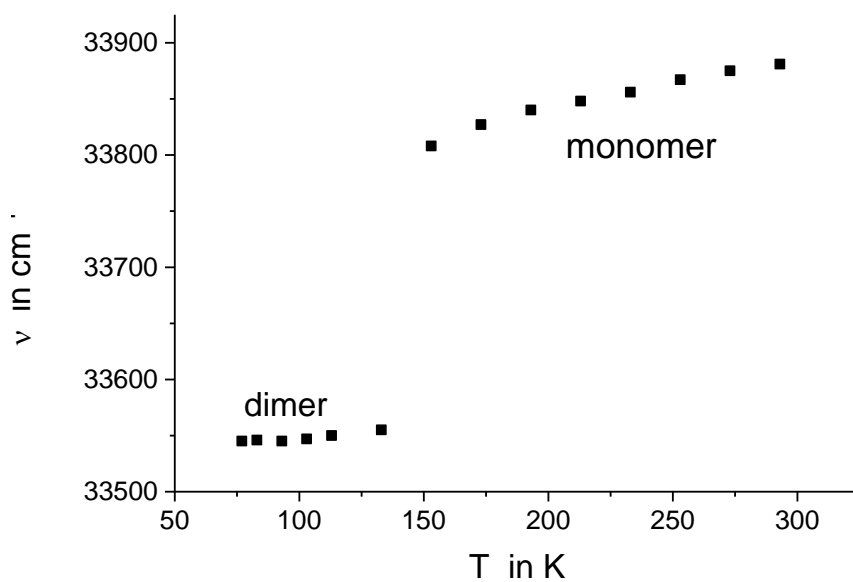**Figure 4**. Absorption spectra of indazole in 2MB at 248, 243, 238, 233, 228 and 223 K.

Figure 5. Thermochromic behaviour of a 3.6×10^{-5} M solution of indazole in ClB.

Figure 5 illustrates the thermochromic behaviour of a 3.6×10^{-5} M solution of indazole in ClB. The figure affords two interesting conclusions, namely:

No change in indazole is apparent from its thermochromic behaviour over the temperature range 293–153 K.

Below 153 K, the compound exhibits a thermochromic change of 253 cm^{-1} indicating dimerization.

On the tautomerization of indazole

In recent work, we showed the dipolarity SdP of ClB to increase markedly from 293 K (0.523) to 77 K (1.294).[24] Taking into account that our SdP dipolarity scale[17] spans the range from 0 for the gas phase to 1 for such a highly polar solvent as DMSO, lowering the temperature of the ClB solution of indazole must obviously have exposed the compound to a strong dipolarity change.

As noted in the Introduction, the tautomerization of indazole from its less polar form (1H, $\mu_{1meindazole} = 1.5$ D[16] to its more polar form (2H, $\mu_{2meindazole} = 3.4$ D[16]) can be facilitated by increasing the polarity of the solvent. As can be seen from Figure 5, neither the segment corresponding to the presence of the monomer (293–153 K) nor that corresponding to the doubly hydrogen bonded dimer suggest that raising the polarity of the medium leads to tautomerization from the 1H form to the 2H form in the ground electronic state.

In 1983, Hirota *et al.*[14] reported that the first excited triplet of the indazole:benzoic acid complex comprises both tautomers (1H and 2H). Also, in 1985 they reported that the first excited singlet of the indazole:acetic acid complex also exhibits tautomerization, via double hydrogen bonding, and hypothesized that such a singlet was very probably the origin of the tautomerism subsequently detected in the triplet state.[15]

Figure 6 shows the emission spectra for the previous ClB solution of indazole over the temperature range 293–113 K. The figure affords some interesting conclusions about the thermochromic behaviour of the compound, namely:

(a) The fluorescence spectra obtained at temperatures from 293 to 173 K exhibit no sign of a thermochromic change in indazole.

(b) Below 173 K, the solution exhibits a thermochromic change indicating dimerization of the compound.

(c) Interestingly, indazole dimerization occurs at a temperature about 20 K higher in the emission spectrum than in the absorption spectrum (i.e. the process is more favourable in the excited singlet state than in the ground state).

(d) The spectra do not preclude a potential tautomerization of indazole monomer or dimer as the dipolarity SdP of the medium is increased.
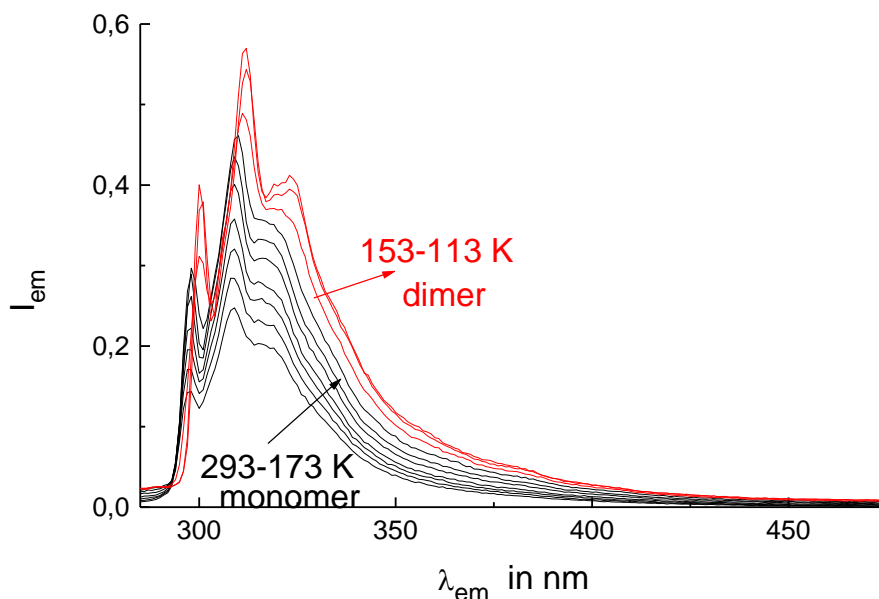
Figure 6. Emission spectra for 3.6×10^{-5} M solution of indazole in ClB at 293-113 K. $\lambda_{exc} = 277$ nm.

Figure 7 shows the emission spectrum for the previous solution at 93 K. The spectrum clearly exhibits the phosphorescence of indazole dimer but its fluorescence has the same envelope as at 113 K (see Figure 6).
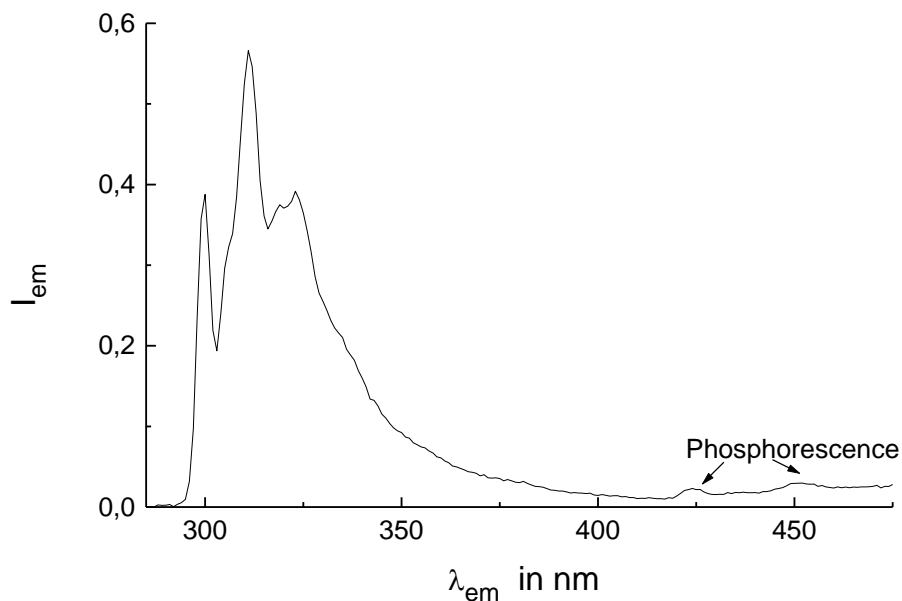

Figure 7.- Emission spectra of a 3.6×10^{-5} M solution of indazole in ClB at 93 K. $\lambda_{exc} = 277$ nm.

Figure 8 shows the phosphorescence spectra for indazole, 1-methylindazole and 2-methylindazole in ClB at 77 K as obtained by using an excitation wavelength of 290 nm and a detection delay of 280 μs. Clearly, the phosphorescence of indazole contains no emission band due to the 2*H* tautomer.
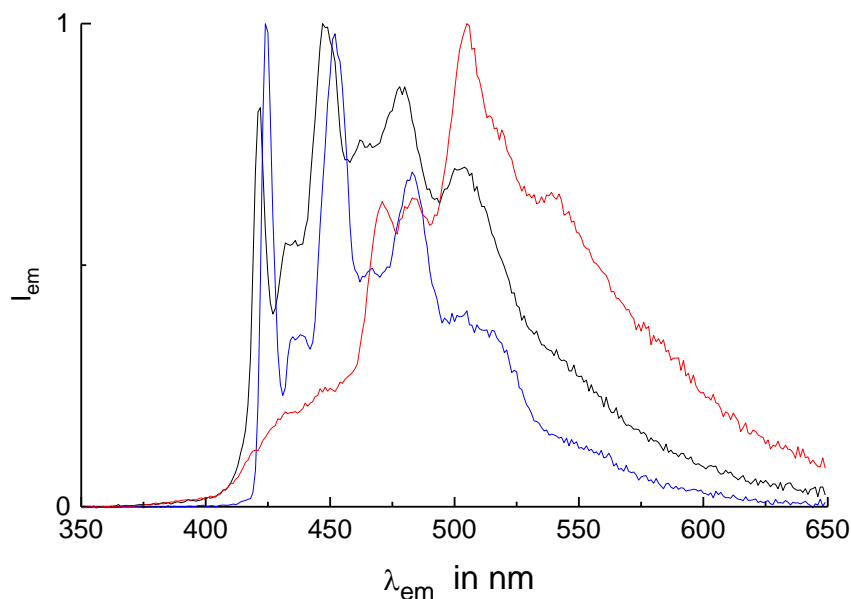

Figure 8. Normalized Phosphorescence spectra of indazole (black), 1-methylindazole (blue), and 2-methylindazole (red).

Conclusions

Examining the solvatochromism of the $S_0 \to S_1$ transition in indazole allowed us to identify the singular effect of the delocalization of the π electron pair contributed by the pyrrole nitrogen, which considerably increases the polarizability of its $1(\pi,\pi^*)^1$ state.

That indazole undergoes dimerization is quite apparent from its thermochromism in a dilute solution in a polar (ClB) or non-polar solvent (2MB). By contrast, no signs of tautomerization in the ground, $1(\pi,\pi^*)^1$ or $1(\pi,\pi^*)^3$ states exist for this compound in its monomeric or dimeric forms.

Experimental Section

General. The 1-chlorobutane (ClB) used was Chromasolv-grade (purity 99.8 %; b.p. 77−78 °C) and contained 0.001 % or less moisture; 2-methylbutane (2MB) was Merck Uvasol-grade (purity ≥ 99.5 %; b.p. 30 °C), 1,4-dioxane, 1-propanol and 1-butanol were Aldrich spectrophotometric-grade (purity 99%+); perfluorohexane, decalin, and 2,2,2-trifluoroethanol were from Aldrich

(purity 99%); dibutyl ether was Aldrich reagent-grade (purity +99%); acetic acid was Sigma ACS Reagent Plus grade (purity 99.7%); and acetonitrile, tetrahydrofuran, ethyl acetate, dichloromethane, chloroform, tetrachloromethane, *n*-hexane, *n*-heptane, methanol, ethanol and diethyl ether were Merck Uvasol-grade (purity ≥ 99 %;). Bi-distilled water was used throughout. The preparations of indazole, 1-methylindazole, and 2-methyl-indazole are previously described.[9]

Temperatures in the range 77–293 K were controlled with an Oxford DN1704 cryostat equipped with an ITC4 controller interfaced to the spectrometers. Solutions were purged with dried nitrogen 99.99 % pure.

All UV/Vis absorption spectra were recorded on a Cary-5 spectrophotometer at variable temperatures from 77 to 293 K, using Suprasil quartz cells of 1 cm path length that were fixed to the cryostat.

Corrected fluorescence spectra were obtained with a calibrated Aminco–Bowman AB2 spectrofluorimeter. The sensitivity factors for the emission channel, which included not only those depending on the detector, but also those related to the emission monochromator and optical arrangement (channel emission included), were obtained by using the FP-123 correction kit from SLM Instruments. This required mounting a standard lamp in a channel at right angles to the emission channel in an OL 254 M spectra irradiance lamp from Optronic Laboratories. The lamp was operated at a constant voltage supplied by an SP-270 power source the light output of which was driven into an integrating sphere with a pinhole leading to the fluorimeter emission channel. The conversion factors thus obtained allowed the measured spectra to be transformed into absolute spectra, which are instrument-independent.

In this work it is not used neither metal ion niether filter paper for facilitating inter system crossing to enhance phosphorescence. Alone we have used to detect the phosphorescence a detection delay of 280 μs.

The terms **A** and **B** of Abe's equation comes given by the expressions:

$\mathbf{A} = 3 \times [(2(\varepsilon^s - (n^s)^2)(\varepsilon^s + (n^s)^2)) / \varepsilon^s ((n^s)^2 + 2)^2 + ((n^s)^2 - 1)/((n^s)^2 + 2)]^{-1} \times [kt \times$
$((\varepsilon^s - (n^s)^2)(2\varepsilon^s + (n^s)^2) / \varepsilon^s ((n^s)^2 + 2)^2 + 0.5((n^s)^2 - 1)/((n^s)^2 + 2))) (I^s(I - hc\nu))/(I^s + I - hc\nu)]$

and

$\mathbf{B} = 3 \times [(2(\varepsilon^s - (n^s)^2)(\varepsilon^s + (n^s)^2)) / \varepsilon^s ((n^s)^2 + 2)^2 + ((n^s)^2 - 1)/((n^s)^2 + 2)]^{-1} \times [kt \times$
$((\varepsilon^s - (n^s)^2)(2\varepsilon^s + (n^s)^2) / \varepsilon^s ((n^s)^2 + 2)^2 + 0.5((n^s)^2 - 1)/((n^s)^2 + 2))) \times (I^s \times I / I^s +)) (\alpha_0) - 8.351$
$\times 10^{-42} \times (\rho^s/M^s)^{1/3} \times \Delta\nu \times (((M/\rho)^{1/3} + (M^s/\rho^s)^{1/3})^{-4} + ((M/\rho)^{1/3} + 3(M^s/\rho^s)^{1/3})^{-4} + ((M/\rho)^{1/3} + 5(M^s/\rho^s)^{1/3})^{-4})^{-1}]$

where the notations s will refer to solvent.

The values of **A** and **B** can be calculated from observed values of : molecular weight (M), densities (ρ), refraction index (n), dielectric constant(ε), ionization potential(I) and electronic transition energies(ν).

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