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Excited state dynamics of 4-Pyrrolidino pyridine in different solvents

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Abstract

Photophysical properties of 4-Pyrrolidino Pyridine (PP) have been delineated from the absorption, steady state and time-resolved spectroscopy in different solvents. Preferential hydrogen bonding of PP with water and also protonation with acid at intercyclic (pyrrolidino) nitrogen lone pair site could be observed. The intramolecular exciplex as predicted from semi-empirical calculations controls the photophysics in weakly polar and nonpolar solvents. In water, a ground-state pretwisted pyrrolidino group forms hydrogen-bonded complex that dominates over the intramolecular exciplex and this H-bonded exciplex acts as a quenching channel for the dual fluorescence. Intermolecular exciplexes of PP were found to form in binary and ternary solutions with polar solvent containing N-atom. Fluorescence in β-cyclodextrin cavity resembles intramolecular exciplex in ethanol with high quantum yield.

Keywords: 4-Pyrrolidino pyridine; Photophysical properties; Hydrogen bonding

1. Introduction

Since the first observation of a structureless extra emission band at the red side of the fluorescence emission of the locally excited state due to a complexation between a molecule in the ground state and a molecule in excited state [1], there has been an engaging interest in this field [2]. This new fluorescence band of the molecule containing aromatic donor and acceptor linked by necessary single bond in polar solvent has been attributed to twisted intramolecular charge transfer (TICT) [3]. But the dual fluorescence in nonpolar solvent do not support TICT process [4], which is due to excited state complex formation, but in a different way. Generally, the most favorable geometry for an excited complex formed between an aromatic donor and acceptor is that of a sandwich in which the chromophores are at a distance of 3.3 Å in a plane parallel orientation [5]. Other configurations are also observed, for example, in an intramolecular complex the relative position and orientation of the chromophores are such that the Coulombic interaction [6,7] is maximal.

Originally, intramolecular excited state complex formation was observed only when the chromophores were linked by a propyl chain, which led to the $n=3$ rule [8]. Later, intramolecular exciplex [9] and excimer [10,11] formation were observed for chains of variable length, and the influence of the chain length was investigated systematically in systems containing of an aromatic donor and acceptor or aliphatic donor [12,13].

Again, solvents may drastically affect chemical and physical properties of solutes through specific and non-specific solute–solvent interactions. Since last decade, much attention has been given to the particular question of origin of anomalous large stokes shifts of the fluorescence of certain derivatives of aromatic molecules in polar solvents [14,15].

In addition to this, ground state hydrogen bonding of the TICT molecule has been a challenging issue to show the dual anomalous fluorescence [16,17]. In simplest TICT theory, the molecule either completes its twist in excited state before emitting (which is partially twisted in the ground state) or makes complete twist in excited state. By contrast to these models, which pay attention to only the excited state hydrogen bonding, a 'pretwisting' of the initially planar conformation in the ground state is also necessary for TICT state formation [16]. These hydrogen-bonded complexes occur either with traces of water present as impurities in the solvents (non-hydroxylic) or directly with solvents (hydroxylic solution). Anomalous luminescence behavior correlated with absorption anomalies occurs in these complexes [16,18,19].

The aim of this paper is to study the photophysical behaviors of PP in ground and excited state in different environments and also to confirm the presence of any 'pretwisted' conformer in the ground state.

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2. Experimental

The compound PP (Aldrich Chemical) was sublimated several times under reduced pressure to obtain pure sample and their melting points were checked before use. The beta-cyclodextrin (β-CD) (Aldrich Chemical) was used as supplied. The solvents ethanol (EtOH), acetonitrile (ACN), tetrahydrofuran (THF), diethyl ether (DEE), sulfuric acid and NaOH (E. Merck, spectroscopic grade) were used as supplied, but only after checking the purity fluorimetrically in the wavelength range of interest. The methylcyclohexane (MCH), cyclohexane (CH) and carbon tetrachloride (CCl_4) (E. Merck spectroscopic grade) were used after distillation (dry) and checking of any emission in the required wavelength range. For aqueous solution, we used deionized Milli Pore water.

The absorption spectra at 300 K were recorded with a Shimadzu absorption Spectrophotometer model UV-2101PC, and the fluorescence spectra were obtained with a Hitachi F-4500 Spectrofluorometer. For emission measurement, the sample concentration was maintained at 10^{-5} M, in each case in order to avoid aggregation. The quantum yields were determined by using the secondary standard method with recrystallized naphthalene in cyclohexane ($\varphi_f = 0.23$) described elsewhere [20].

The time-resolved fluorescence decay of PBA in different solvents were observed by employing a CW mode-locked frequency doubled Nd-YAG laser-driven dye (Rhodamine 6G) laser operating at a repetition rate of 800 kHz with pulse width of the order of 4–10 ps [21]. Fluorescence lifetime in different solvents were obtained by using a time-correlated single-photon-counting coupled to a micro channel plate photomultiplier (Model 28090; Hamamatsu). The instrument response function (IRF) was obtained at 295 nm using a dilute colloidal suspension of dried nondairy coffee whitener. The cut-off filter was used to prevent scattering of excitation beam and the emission was monitored at the magic angle (54.7°) to eliminate the contribution from the decay of anisotropy.

3. Results and discussion

3.1. Absorption spectra

At room temperature, 4-Pyrrolidino pyridine (PP) shows two absorption bands (Fig. 1), one strong band around 260 nm wavelength region, and other weak shoulder around 280 nm wavelength region depending on the polarity and hydrogen bonding capability of different organic solvents. The first band (260 nm) exhibits normal solvent dependent character on going from hydrogen bonding environment to non-hydrogen bonding environment. Now, the absorption spectra of PP in which one hydrogen of the 4th carbon atom of pyridine is replaced by pyrrolidino group, is similar to that of the parent compound pyridine, with one extra shoulder at 280 nm region. The shorter wavelength band in PP, although somewhat shifted and intensity is increased, should undoubtedly be assigned to transition similar to those observed in pyridine (PN). So it is quite clear that the appearance of the second band is due to the substitution of H atom by pyrrolidino group in PP. Comparing the absorption coefficient and solvent effect, we are in a position to ascribe the shorter wavelength band of PP as $\pi \rightarrow \pi^*$ transition, i.e., (${}^1B_1 \rightarrow {}^1A_1, {}^1L_b \leftarrow {}^1A$) transition ($\varepsilon_{max} = 25\,000$), and the second lower energy band as $n \rightarrow \pi^*$, i.e., (${}^1B_2 \rightarrow {}^1A_1$) transition ($\varepsilon_{max} = 3000$).

A comparative study of the first absorption band of PP to the absorption band of pyridine (PN) confirms (Table 1) that substituent pyrrolidino group produces both bathochromic and hyperchromic effect. These effects of PP are due to the direct interaction between the π electrons of the chro-

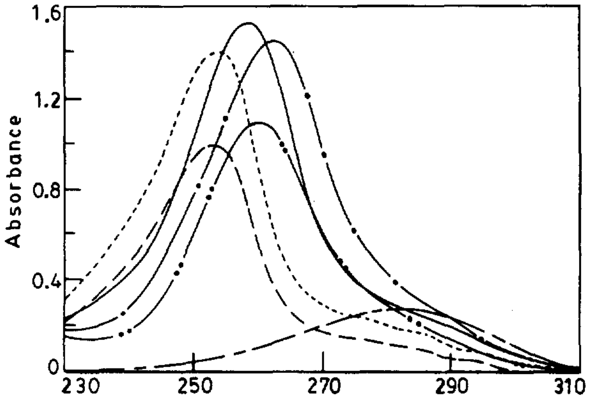


Fig. 1. Absorption spectra of PP in different solvents. (- - -) in MCH, (———) in ACN, (– • –) in $CHCl_3$, (-••-) in ethanol, (– – –) in CH and (— - —) in water (conc. of PP molecule ≈ 6×10^{-5} M).

Table 1
Absorption data of PP and Pyridine (PN) in 298 K

Solvent	4-Pyrrolidino pyridine (PP)		Pyridine (PN)	
	λ_{max}, nm	ε_{max}, M	λ_{max}, nm	ε_{max}, M
n-Heptane	252	25 769		
	276			
	286	2123		
	293			
MCH	254	21 180	252	2090
	276	3944		
	286	2927		
	293			
$CHCl_3$	262	21 277	253	3600
	285	2144		
EtOH	260	20 521		
	286	2531		
ACN	259	24 536		
	285	2514		
N,*N*-DMF	258	25 277		
	284	2328		
Water	280	29 278	253	3600

M = $dm^3\ mol^{-1}\ cm^{-1}$.

mophoric group (PN) and lone pair electrons of pyrrolidino group in their ground state. On going from nonpolar to polar solvent, PP shows bathochromic shift for the first (higher energy) band whereas, the second band (lower energy) remains unaffected (Fig. 1). A careful analysis of these absorption spectra predicts the hydrogen bond formation ability of PP in ground state. In hydrogen-bonding solvent, the intensity of the first band decreases with measurable amount of red shift, whereas, the second band keeps unaltered. But in water solution, only the second band could be observed with large hyperchromic effect keeping the position same. This behavior of absorption spectra can only be explained as due to the hydrogen bonding interaction of PP by sharing lone pair electrons of nitrogen atom with hydrogen atom of water molecule. In PP, a pair of electrons is available for formation of hydrogen bonding in two places, one at pyridine end (intracyclic) and other at the N atom of Pyrrolidino group (intercyclic).

In order to determine the location of hydrogen bonding (pyridine nitrogen or pyrrolidino nitrogen), a comparative study has been made on absorption spectra of PP and PN. In acetonitrile solvent, PP shows a strong $\pi\pi^*$ band and weak $n\pi^*$ band like other solvents, where no question of hydrogen bonding arises. But with addition of little amount of water in acetonitrile solution, a great change of absorption spectra could be observed (Fig. 2). The first band shows both bathochromic and hypochromic shift, and the second band shows only hyperchromic shift with a distinct isosbestic point (266 nm), with increasing concentration of water molecules. This isosbestic point indicates the formation of 1:1 complex between PP and water molecule. An equilibrium may be described as

$$\underset{\text{Planar}}{\mathrm{PP}} + \ldots{}^{-}\mathrm{OH} \leftrightarrow \underset{\text{Perpendicular complex}}{\mathrm{PP}/(\ldots{}^{-}\mathrm{OH})}$$

The equilibrium constant $K_g=[\mathrm{PP}/(\ldots{}^{-}\mathrm{OH})]/[\mathrm{PP}].[\ldots{}^{-}\mathrm{OH}]$ for the ground state reaction was calculated by means of the following equation,

$$(D_\lambda-D_\lambda^0)/C_{\mathrm{OH}}=K_g(D_\lambda^\infty-D_\lambda) \qquad (1)$$

where C_{OH} is the concentration of the water and D_λ, D_λ^{0}, and D_λ^{∞} are optical density at a wavelength of λ at a particular concentration of water C_{OH}, in the absence of H_2O and at infinite concentration of water, i.e., optical density at water solution with same PP concentration. The values of K_g and D^∞ have been calculated from the slope and intersection of the plot $(D_\lambda-D_\lambda^0)/C_{\mathrm{OH}}$ vs. D_λ. K_g is calculated to be $0.089+0.001$ at 300 K. Now using the Eq. (1), D_λ^∞ is calculated for the different λ and a plot of D_λ^∞ against λ could be drawn. This calculated absorption curve follows the real absorption spectra of PP in water solution of equal concentration (i.e., concentration of ACN solution in which the water molecule has been added) with little higher optical density (Fig. 2). So Eq. (1) has a high degree of precision to calculate absorption curve, although the ground state equilibrium constant is small. But the same experiment on PN shows only blue shift and which is indicative of hydrogen bonding of intracyclic nitrogen with water molecule. In order to have a better understanding about the formation of hydrogen bonding both for intracyclic or intercyclic, absorption spectra of PP were taken in ACN as a function of increasing D_2O concentration keeping PP concentration constant. In D_2O, the absorption spectra of PP has the same shape and structure as in MCH with slight red shift of first band and successive addition of D_2O in ACN solution produced no change in absorption spectra of PP. This difference of absorption spectra of PP in ACN with varying concentration of H_2O and D_2O confirms that the hydrogen bonding complex with PP is formed preferentially on the nitrogen atom of the pyrrolidino group. Also, the hypochromic shift of first band with increasing concentration of water molecule indicates the decreased electronic interaction between nonbonding electrons of auxochrome and π electron of parent chromophore due to engagement of lone-pair electrons in hydrogen bond formation, resulting in enhancement of second band. It is important to note that, at higher concentration of water molecule the first band apparently vanishes, i.e., totally submerged under the enhanced second band. The molar absorption coefficient of this submerged band in the higher energy region in water solution is nearly same as that of PN molecule [22]. Hence, it is obvious that in water electronic interaction of auxochrome to the chromophore is nearly nil, and the interaction is totally involved with water molecule, which is possible only through the formation of hydrogen bonding. In the planar configuration of PP, the formation of hydrogen-bonded complex is hardly possible. Hence, the anomalous behavior of absorption spectra may be correlated with 'pretwisting' conformation induced by hydrogen bond-

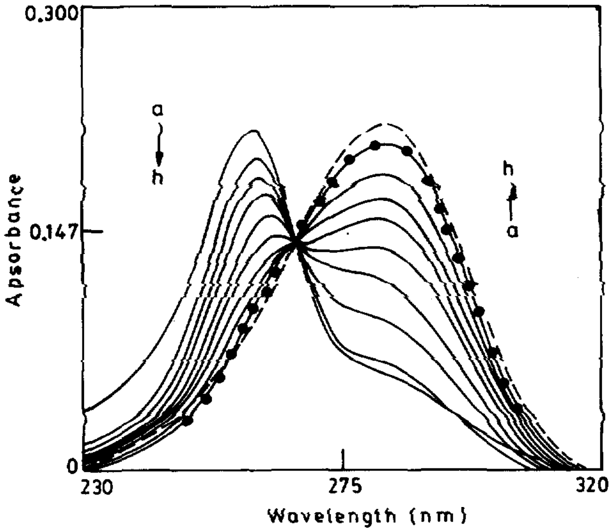


Fig. 2. Absorption spectra of PP in ACN in presence of varying water concentration keeping sample concentration fixed. (sample concentration=8.3×10^{-6} M). The water concentration for (a) 0, (b) 0.7, (c) 2.0, (d) 3.5, (e) 4.5, (f) 5.5, (g) 6.5, (h) 7 M, respectively, (-●-●-) absorption spectra in pure water and (- - -) calculated absorption spectra of PP from equilibrium constant.

ing with water molecule. Similar results were found for DMABN [23].

3.2. Acidity effect on absorption spectra

In general, a molecule having hydrogen bond formation ability is affected by acidic solution. When acid trace is added to acetonitrile solution of PP, a nearly similar type of phenomena is repeated as in ACN and water mixture. For high concentration of acid, the first band corresponding to the $\ell \rightarrow a_\pi$ transition disappears. But no clear isosbestic point is observed. From this behavior of absorption spectra, it is clear that the pyrrolidino nitrogen is protonated, which inhibits hydrogen bonding between the solute and solvent. This result is in agreement with 4-*N*,*N*-dimethylamino pyridine [24] where the protonated form was located on the intracyclic nitrogen.

3.3. Emission spectra

3.3.1. Solvent polarity effect

Fig. 3a shows the emission spectra of PP in different polar and nonpolar solvents. This emission spectrum of PP consists of structured emission band whose features resemble those of emission due to ${}^1B_{2u} \rightarrow {}^1A_{1g}$ transition which is known as normal fluorescence F_N and a structureless emission band at longer wavelengths (F_{ex}) with polarity dependent bathochromic shift. Upon increase of the polarity of the solvent, the longer wavelength band is quite clear and well separated, whereas the shorter wavelength band remains in fixed position. But in N-containing polar solvent, the normal fluorescence band is slightly red-shifted (Fig. 3a), and the second broad structureless band is also largely red shifted with more quantum yield. This difference in spectral response in N-containing solvent of PP could be resolved by assuming solute–solvent exciplex formation in different geometry, which would be discussed latter on. Now this structured band in nonpolar and weakly polar solvent of PP appears for all excitation wavelengths. The excitation spectrum is independent of wavelength and resembles the absorption spectra for concentration of PP (1.5×10^{-5} M) and optical density below 0.5. The concentration quenching in fluorescence spectra is observed beyond 0.5 absorbance. These observations point that the structureless bathochromic emission is due to an intramolecular exciplex.

According to the Lippert–Mataga equation, the energy of the emission maximum of the exciplex depends in a linear way on the solvent parameter $f(\varepsilon_r, n)$

$$\bar{\nu}_{fa} - \bar{\nu}_f = \frac{2\mu_e^2}{4\pi\varepsilon_0 hc\rho^3} f^1(\varepsilon_r - n)$$

where

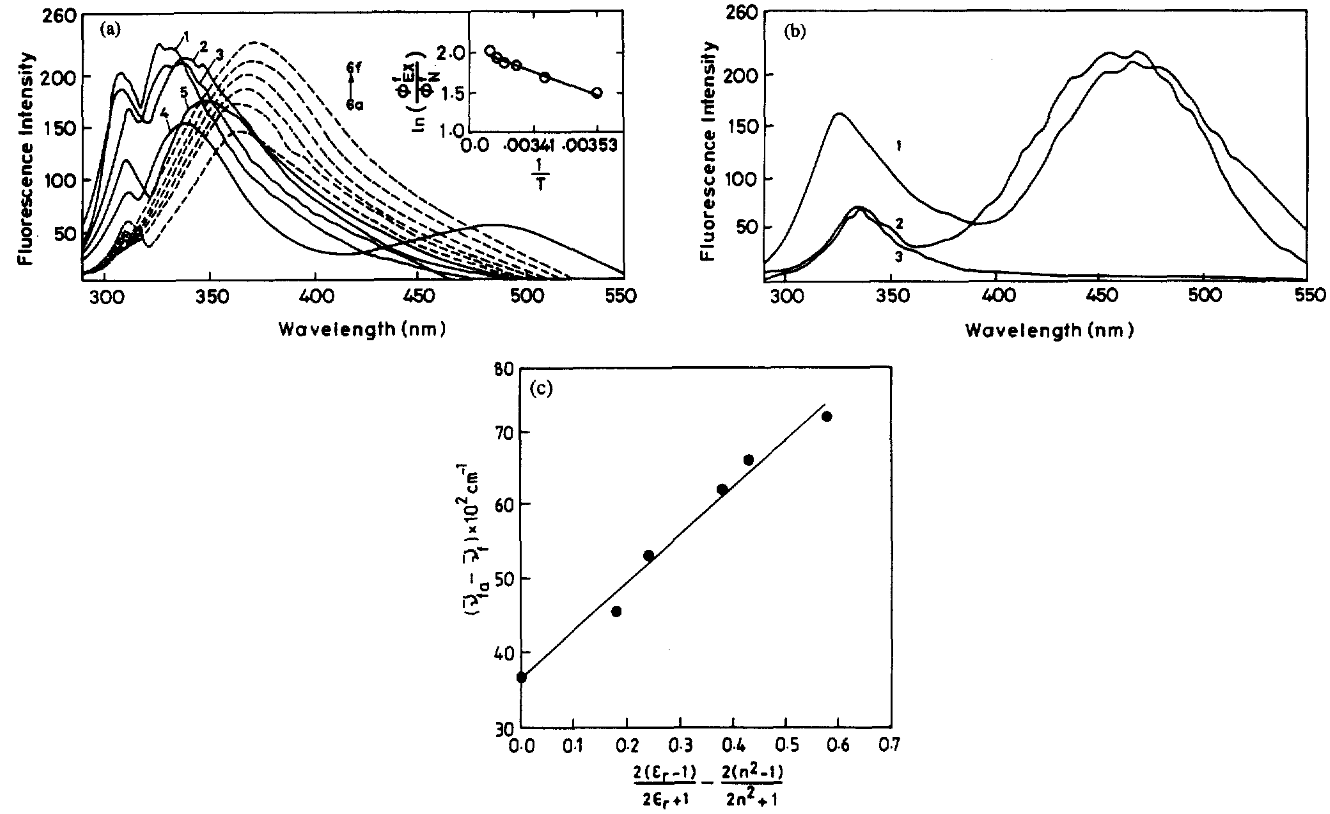


Fig. 3. (a) Fluorescence spectra of PP in different solvents. (1) in MCH (2) in DEE, (3) in *n*-heptane, (4) in EtOH, (5) in THF, and (6) in $CHCl_3$ at different temperatures, where (a) at 283 K, (b) at 290 K, (c) at 300 K, (d) at 313 K, (e) at 323 K, and (f) at 333 K respectively. Inset is the $\ln(\varphi_{EX}{}^f/\varphi_N{}^f)$ vs. $1/T$ plot in $CHCl_3$ solution. (b) Fluorescence spectra in different N atom containing solvents. (1) in *N*,*N*-DMF, (2) in ACN and (3) in ACN + H_2SO_4 respectively. (c) Lippert–Mataga plot of PP.

$$f^1(\varepsilon_r - n) = \left[\frac{\varepsilon_r - 1}{2\varepsilon_r + 1} - \frac{n^2 - 1}{2n^2 + 1} \right]$$

and absorption frequency v_f and v_{fa} corresponds to the emission and absorption frequency in a solvent with dielectric ε_r and refractive index n respectively. ε_0, h, c and ρ correspond to the permittivity of vacuum (8.85×10^{12} V C^{-1} m^{-1}), Planck's constant (6.6×10^{-34} J S), the velocity of light in vacuum (3.0×10^8 m s^{-1}), and radius of the solvent cavity (in meters), respectively. μ_e (C m^{-1}) is the dipole moment in excited state. This relationship is based on the assumption that solvation occurs only on dipole–dipole interaction, and that the dipole moment in ground state is negligible. Quantum semi-empirical calculation done for PP shows that dipole moment in ground state is less than 1 Debye. Assuming a value of 2.9 Å for ρ, the exciplex dipole moment of PP can be obtained from the ratio of the slope and $2\mu_e^2/4\pi\varepsilon_0\rho^3hc$ as 8.5 D (Fig. 3c).

Normally the intramolecular exciplex formation is favorable when the chromophores are separated by alkyl chain [8], but in PP the separator of the interacting groups would hinder the formation of intramolecular exciplex because the short chain prevents a parallel plane configuration. Yet for PP, the formation of exciplex has been concluded from the observed data but it does not have a well defined stoichiometry. Possibly, they derive their stability mainly from dipole–dipole interaction. The two well separated fluorescence bands in ACN and DMF, give some insight about the formation of TICT excited state. But this possibility has been ruled out due to dual fluorescence behavior of PP in nonpolar solvents.

Actually, the above experimental results from steady-state spectroscopy resemble one of the following possibilities. The first one is the intramolecular exciplex which already is assumed, the second one is the twisted intramolecular charge transfer process, and the third one is pretwisted conformation induced by hydrogen bonding by complexation with traces of water present in the solvent. In this case, the first possibility takes the main role revealing the photophysics of PP in different nonpolar or weakly polar environment over the second and third. When the solvents are thoroughly dried, the anomalous fluorescence does not disappear. This evidence completely rules out the possibility of pretwisting conformation induced by hydrogen bonding for anomalous fluorescence band.

In the case of hydrogen bonding solvent the fluorescence behavior has somewhat different character along with the formation of intramolecular exciplex. In ethanol, total fluorescence quantum yield is decreased by half (Table 2) than that in protic solvents and an extra third band appears at 467 nm which is too weak to detect but in water all the fluorescence bands vanish. The appearance of extra third band in ethanol and the decrease of total quantum yield may be due to combined action of intramolecular exciplex and hydrogen-bonded complex. Water, being strong hydrogen bonding agent normally it causes to form hydrogen bonded complex which finally suppresses the intramolecular exciplex. As pyrrolidino group is restricted to be coplanar with pyridine, no specific interactions with polar solvents including alcohol and water could be found. Nevertheless, a better flow of electron from the pyrrolidino group will render pyridine more negative. So the conceivable interaction with PP is the hydrogen-bonded complex and that is only possible by pretwisted position of pyrrolidino group in ground state and this has already been observed from absorption spectra (Section 3.1).

Table 2
Fluorescence data of PP in weakly polar and nonpolar solvent

Solvent	λ_N^I, nm	λ_{EX}^I, nm	φ_N^I	φ_{EX}^I	τ_N^I, ns	τ_{ex}^I, ns
MCH	313	328	0.09	0.15	11	10.6
CH	313	328	0.1	0.16	12	11
EtOH	313	340	0.05	0.06	–	–
$CHCl_3$	313	361	0.03	0.12	–	–
DEE	313	345	0.07	0.10	–	–
CCl_4	313	348	0.05	0.09	–	–
THF	313	350	0.05	0.13	13.1	13
Water	–	–	–	–	–	–
β-CD + water	313	343	0.02	0.08	20	20

3.3.2. Temperature effect in nonpolar and weakly polar solvent

In nonpolar MCH solvent, the relative emission of the locally excited state of PP decreases in favor of the emission of the exciplex when temperature is increased from 278 K to 338 K. Due to the small relative quantum yield of the emission of locally excited states and also due to the overlap of emission of locally excited states and the exciplex, it is no longer possible to determine $\ln(\varphi_{INA}^f/\varphi_N^f)$ accurately at this temperature range.

In chloroform, the relative emission spectra of the locally excited state of PP decreases in favour of intramolecular exciplex, when the temperature is increased from 283 K to 333 K (Fig. 3a). A further increase of the temperature induces an increase of the relative intensity of the emission of locally excited state. At temperature between 283 K to 333 K $\ln(\varphi_{ex}^f/\varphi_N^f)$ depends linear way upon $1/T$ (Fig. 3). Also, PP in tetrahydrofuran shows an increase of the ratio $(\varphi_{ex}^f/\varphi_N^f)$ between 283 K to 333 K, followed by a decrease at higher temperature. In diethyl ether, the relative emission of the locally excited state of PP decreases in favour of the emission of the exciplex when temperature is increased.

3.3.3. Fluorescence decay in MCH

The fluorescence of PP at 300 K measured at different wavelengths of exciplex emission band may be analysed as a single exponential with a decay time of 11 ns while the fluorescence monitored at 313 nm, i.e., locally excited band could be found as a linear combination of two exponentials with decay time of 157 ps and 11 ns, respectively. According to the dynamics of intramolecular exciplex formation described by Van der Auweraer et al. [25], the first decay component of the locally excited state is the formation time, i.e., the growth time of exciplex state. The equality of fluorescence decay in both bands is also explained by Van der Auweraer et al. [25]. Since the growth rate is very high than the fluorescence decay rate, a secular equilibrium is established between the locally excited state and exciplex state.

4. Formation of intermolecular exciplex through solute–solvent interaction

4.1. Type 1

PP in ACN and N,N DMF shows (Fig. 3b) a fluorescence band in the same wavelength region where the intramolecular exciplex fluorescence F_{ex} in MCH appears. To distinguish this band from F_{ex} band in MCH or other weakly polar solvents, we denote higher energy band (335 nm–340 nm) in ACN and *N,N*-DMF as F_l and longer wavelength band as F_A. In ACN or *N,N*-DMF solution F_l decays with linear combination of two exponentials with decay times 2.61 ns and 52 ps (Fig. 4) and other long wavelength band (F_A) (Table 3) decays monoexponentially (Fig. 5) with decay time 2.61 ns. The lifetime of intramolecular exciplex state obtained from the decay of the fluorescence F_{ex} of the solution in MCH is 10.1 ns. So the fluorescence F_l of ACN solution must have arisen from a state other than intramolecular exciplex state. We surmise that the fluorescence F_l is emitted by solute–solvent exciplex as $^1E_1$ in which the pyrrolidino group of the solute is coplanar with the pyridine ring and that F_A is emitted by exciplex $^1E_2$ with the pyrrolidino group perpendicular to the ring. Evidence for the formation of emissive solute–solvent exciplexes of type $^1E_1$ has been provided previously for 1-methyl-6-cyano-1,2,3,4 tetrahydroquinoline in 1,4 dioxane [26]. In order to explain the equality $\iota_f(F_1) = \iota_f(F_A)$, we propose that after excitation the state S_1 (normal) is converted to $^1E_1$ and a thermal equilibrium exists between $^1E_1$ and E_2 in a time ι_{eq} which is the fast component of decay, i.e., 52 ps. We also put forward that $^1E_1$ decays much faster than $^1E_2$ which means that the lifetime of the equilibrium is determined by the decay of $^1E_1$ (Scheme 1).

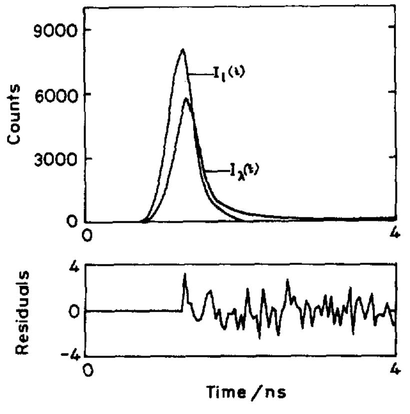


Fig. 4. Fluorescence decay profile of $I_\lambda(t)$ of PP in ACN, excited at 295 nm and monitored at 313 nm. $I_l(t)$ is lamp function. $\tau_1 = 0.052$ ns (90%) and $\tau_2 = 2.62$ ns (10%) and $\chi^2 = 1.1$.

Table 3
Fluorescence data of PP in N atom containing polar solvents

Solvent	$\lambda_{1E1}{}^f$, nm	$\lambda_{1E2}{}^f$, nm	$\varphi_{1E1}{}^f$	$\varphi_{1E2}{}^f$	$\tau_{1E1}{}^f$, ns	$\tau_{1E2}{}^f$, ns
ACN	338	460	0.05	0.2	2.62	2.61
N,N-DMF	340	465	0.06	0.2	2.59	2.57

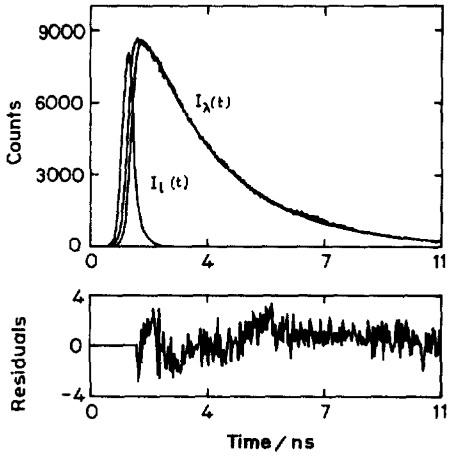


Fig. 5. Fluorescence decay profile of $I_\lambda(t)$ of PP in ACN, excited at 295 nm and monitored at 460 nm. $I_l(t)$ is lamp function. The fluorescence decay time $\tau = 0.052$ ns and $\chi^2 = 1.1$.

All the decay rate constants for the solutions in ACN and *N,N* DMF could not be determined. From the rise time (growth time of $^1E_2$ state from $^1E_1$) we can estimate the forward rate constant k_+ ($19 \times 10^9\ s^{-1}$) but we could not estimate k_- enough because accurate measurement of φ_T yield (Triplet state yield), the sum of the contribution to triplet state population from both $^1E_1$ and $^1E_2$ states could not be possible in this study. The equilibrium constant $K \equiv k_+/k_-$ may be obtained from the ratio of quantum yield of fluorescence $\varphi_F(1)$ $\varphi_F(2)$ from $^1E_1$ and $^1E_2$ states respectively (Table 3). According to the Scheme 2, the ratio given by [27] Scheme 2.

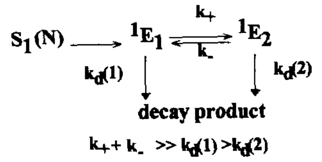
$$\frac{\varphi_F(2)}{\varphi_F(1)} = \frac{k_F(2)}{k_F(1)} \frac{k_+}{k_- + k_F(2) + k_{ic}(2) + k_{isc}(2)} \tag{2}$$

$$\text{Assuming } k_- \gg k_F(2) + k_{ic}(2) + k_{isc}(2) \tag{3}$$

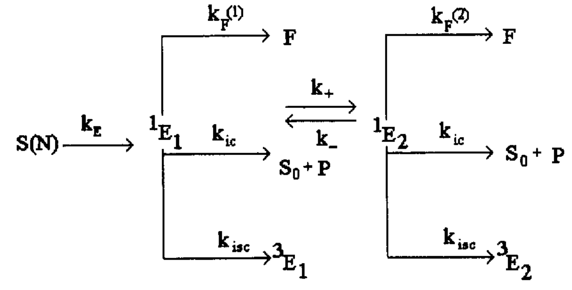
$$\frac{\varphi_F(2)}{\varphi_F(1)} = \frac{k_F(2) k_+}{k_F(1) k_-} \tag{4}$$

Since $k_F(1) > k_F(2)$ we get from Eq. (3)

$$\frac{\varphi_F(2)}{\varphi_F(1)} < K \tag{5}$$



Scheme 1.



Scheme 2.

Eq. (5) confirms that, a forward reaction is dominated, i.e., generation of $^1E_2$ exciplex from $^1E_1$ exciplex is well favorable.

In order to confirm it we observed the effect of dual fluorescence spectra of PP in acetonitrile (ACN) solution with varying concentration of water molecule in that solution (Fig. 6). As percentage of the water in the solution is increased continuously, the relative intensity of the long wavelength band (anomalous) goes to minimal and finally for a certain concentration of water it vanishes, whereas, the normal fluorescence decreases initially, and finally it could be seen as a weak intensity band. Fig. 6 shows the variation of intensity ratio I_{FI}/I_{FA} for various concentration of added water in ACN solution. From this experimental result, we suspect that the formation of intramolecular exciplex of PP in ACN is destroyed by successive addition of water in the solution and hydrogen bonded complex is formed. This hydrogen bonded complex acts as fluorescence quenching channel [28]. Beside this, in the presence of a trace of H_2SO_4 in ACN solution the anomalous long wavelength fluorescence band disappears as the PP molecule gets protonated. Similarly, when water molecule is added to ACN solution, a hydrogen bond is formed by sharing the lone pair electron of pyrrolidino group nitrogen atom and the of anomalous fluorescence band disappears.

4.2. Temperature effect on fluorescence spectra in ACN solution

In ACN the emission spectra of PP changes with temperature. Fig. 7 shows the variation of emission spectra with temperature. Upon increasing the temperature, the relative intensity of exciplexes is increased with little hypsochromic effect. At temperature less than 288 K the relative intensity decreases more rapidly. The ratio ($\varphi_{1E2}/\varphi_{1E1}$) increases from 288 K to 338 K. The variation of $\ln(\varphi_{1E2}/\varphi_{1E1})$ vs. $1/T$, which is linear (Fig. 7) in the lower temperature range (288 K to 338 K) and it sharply increases in the higher temperature range. At higher temperature, the fluorescence quantum yield due to solute–solvent exciplex with flat geometry decreases and the fluorescence quantum yield due to exciplex with perpendicular geometry increases on account of increase in dipole–dipole interaction through vibrational motion of two moieties on rising temperatures. On decreasing temperature to 77 K, all types of interactions decrease along with vibrational motion which stops to fluoresce the exciplex emissions and increases the normal fluorescence to a reasonable amount along with high phosphorescence.

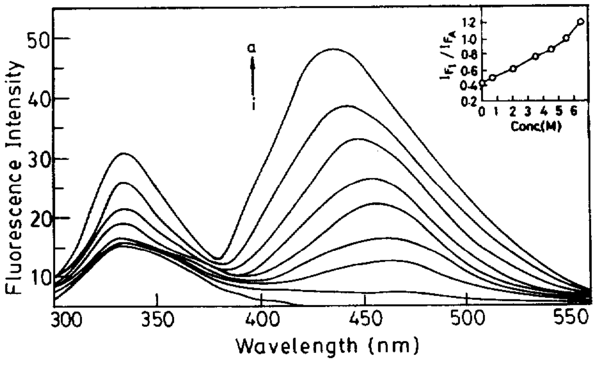


Fig. 6. Fluorescence spectra of PP as function of water concentration in ACN solution. The water concentration for (a) 0, (b) 0.7, (c) 2.0, (d) 3.5, (e) 4.5, (f) 5.5 (g) 6.5 (h) 7 (i) 7.5 M, respectively and inset shows the concentration of water molecule vs. I_{FI}/I_{FA} plot.

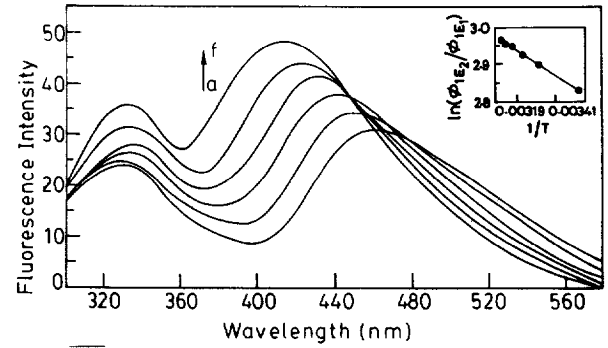


Fig. 7. Fluorescence spectra in ACN as function of temperature. (a) at 288 K, (b) at 298 K, (c) at 308 K, (d) at 318 K, (e) at 328 K and (f) at 338 K respectively and inset straight line is the ln ($\varphi_{1E2}^f/\varphi_{1E1}^f$) vs. $1/T$ plot.

4.3. Formation of intermolecular exciplex by specific solute–solvent interactions: (Type 2)

The appearance of new fluorescence band of PP have been studied in mixture on nonpolar and polar solvents. Variation of the concentration of the polar component in the nonpolar solvent (Fig. 8.) enables a distinction to be made between the effects of specific solute–solvent interactions and of dielectric polarization on the fluorescence spectrum. The addition of small amount of polar solvent P to a dilute solution of PP in methylcyclohexane (MCH) causes a quenching of the normal (F_N) as well as intramolecular exciplex fluorescence (F_{INA}) with simultaneous appearance of a new emission F_A (intermolecular exciplex fluorescence). The ratio $R=I(F_A)/I(F_{N+INA})$ where $I(F_A)$ and $I(F_{N+INA})$ are the intensities of the third band and intensity of the of normal and intramolecular exciplex emission respectively. $F_{(N+INA)}$ and F_A depends linearly on the concentration of P in a manner given by $R=K[P]$. This implies that the third emitting species is either formed from a reaction of a single acetonitrile molecule P with a molecule of PP in first excited singlet state or has arisen from an already existing ground state complex between solute and solvents up to a certain concentration of

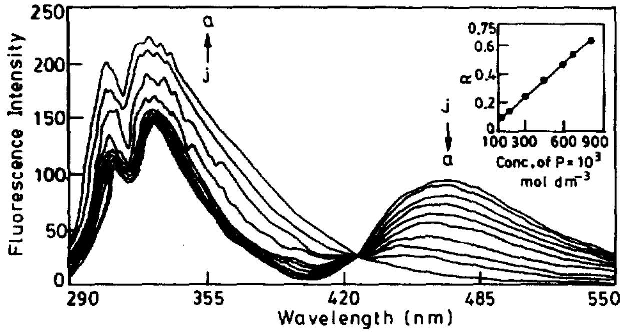


Fig. 8. Fluorescence spectra of PP in MCH as a function of polar solvent concentration P (acetonitrile). The concentration of P (a) 0, (b) 116.45, (c) 180.1, (d) 310.13, (e) 448.1, (f) 595, (g) 673.42, (h) 810, (i) 915 (j) 1000 m M. In plot shows the $I(F_A)/I(F_{N+INA})$ vs. concentration of P.

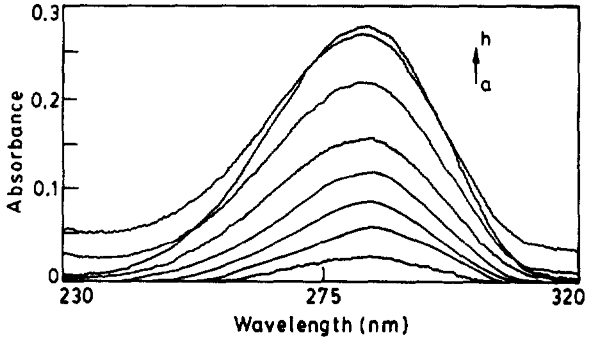


Fig. 9. Absorption spectra of PP in aqueous solution as a function of β-CD concentration. The concentration of β-CD in (a) 3.2×10^{-2}, (b) 1.6×10^{-2}, (c) 8×10^{-3}, (d) 4×10^{-3} (e) 2×10^{-3}, (f) 1×10^{-3}, (g) 5×10^{-4} M, respectively (h) absorption spectra of PP in pure water.

acetonitrile in solution. Since no change in absorption spectra of PP in MCH solvent with addition of polar solvent could be observed, the ground state complex cannot be considered as the major source of the new fluorescence band. The relation $R=K[P]$ has been verified in two polar solvents and K values have been calculated to be 0.79 and 0.62 with acetonitrile and *N,N*-dimethylformamide, respectively. Fig. 8 represents the R vs. $[P]$ plot which is linear up to a certain concentration. These K values display higher reactivity in exciplex formation of PP relative to DMABN [29].

The binding between the constituents in the exciplex appears to involve a σ type bond between lone pair electrons of the pyrrolidino group nitrogen atom the one hand and the lone pair electron of P on the other hand i.e. a bond between localized electrons. In the excited state of the compound PP the pyrrolidino group appears to sacrifice the conjugation with π electron system in favor of a σ bond by rotating towards the plane perpendicular to the pyridine ring. The binding between the constituents of an exciplex of PP and a polar solvent molecule P may be explained with the help of simple model of Visser and Varma [30] in terms of localized interaction between lone pair electrons of polar solvent and that of pyrrolidino nitrogen in the excited state.

5. β-CD cavity effect of PP in water solution

5.1. Absorption spectra

As already mentioned PP shows only one band at 280 nm in water solution. Now, in aqueous β-CD solution a new feature in absorption spectra of PP could be observed (Fig. 9). At highest concentration of β-CD, the absorbance of the sample at λ_{max} decreases 12 times than that of water solution and it increases with decrease of β-CD concentration. In other words with the decrement of β-CD concentration the absorption peak touches the absorption spectra of PP in water solution crossing at two points (273 and 293 nm).

It has been observed form acetonitrile and water mixture, the enhancement of 280 nm band is due to hydrogen-bonded complex. Now, when a molecule has formed inclusion complex in β-CD cavity, it gets estranged from surrounding water molecule and the probability of formation of hydrogen bonded complex [31] is decreased, and hence the decrease of absorption λ_{max} in β-CD solution. If we turn our attention to Fig. 2, we find that PP shows 260 nm band in all organic solvents. But in Fig. 9, the highest β-CD concentration does not yield the 260 nm band. The reason for this probably is PP. β-CD complex does not absorb at all at 260 nm.

5.2. Fluorescence spectra

PP in water solution is non-emissive at room temperature, but in β-CD solution it produces moderately high intense fluorescence band system. Fig. 10 shows the fluorescence spectra of PP in water solution as a function of β-CD concentration. At higher concentration of β-CD, nearly all the guest molecules enter into the β-CD cavity, which forbids the hydrogen bond formation and emission goes up in absence of non-emissive hydrogen bonded complex. In β-CD cavity, the molecule shows fluorescence emission spectra consisting of two bands, one short wavelength normal band and other long wavelength intramolecular exciplex band. The position of exciplex band of PP in β-CD cavity nearly overlaps the

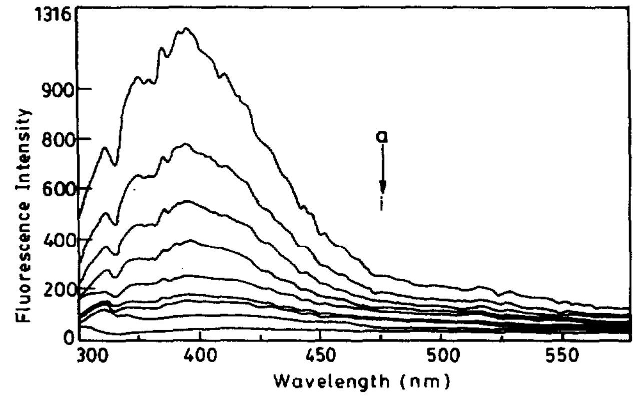


Fig. 10. Fluorescence spectra of PP in aqueous solution as a function of β-CD concentration. The concentration of β-CD in (a) 3.2×10^{-2}, (b) 1.6×10^{-2}, (c) 8×10^{-3}, (d) 4×10^{-3}, (e) 2×10^{-3}, (f) 1×10^{-3}, (g) 5×10^{-4}, (h) 2.5×10^{-4} M, respectively and (i) fluorescence spectra of PP in pure water.

exciplex band of PP in ethanol, and the quantum yield of fluorescence emission of first band is 5 times greater than the latter. Higher fluorescence quantum yield confirms that the hydrogen bonded complex formation with PP molecule in β-CD cavity is totally stopped. Now, comparing the positions of the exciplex band in β-CD cavity and in ethanol, we get an idea about the polarity of the cavity. Again, the appearance of second band in β-CD cavity indicates that the band arises only from intramolecular exciplex. Because in our case, cavity effect is limited to 1:1 complex due to the size of PP and the volume of β-CD. Hence, the cavity effect with this molecule is confined to deal with intramolecular phenomena as we see in earlier paper to TICT properties of the other molecules [31].

6. Quantum semi-empirical approach

In order to get ground and excited state optimized geometry along with dipole moments in ground and excited states of this molecule, the help of MOPAC (version 5) package with AM1 Hamiltonian [32–34] was taken. Precise geometry optimization was obtained by MOPAC's NLLSQ gradient optimization criterion. Fig. 11 shows the energy minimized geometry in ground state of PP molecule. In this energy-minimized configuration, the molecule is slightly deviated from the flat configuration, i.e., the pyridine ring and pyrrolidino group lie in different planes where the angle of twist of pyrrolidino group around CN bond is 12°. But in the excited state (Fig. 12), the optimized geometry retains the same twist angle making 40° bending angle between pyridine and pyrrolidino group. It is clear from the figure that the excited-state geometry is conducive to form intramolecular exciplex with a nearly sandwich-like structure, which is also predicted from experiment in case of nonpolar and weakly polar solvent. Also semi-empirical calculation provides the ground and excited state dipole moments to be 0.433 and 10 Debye, respectively.

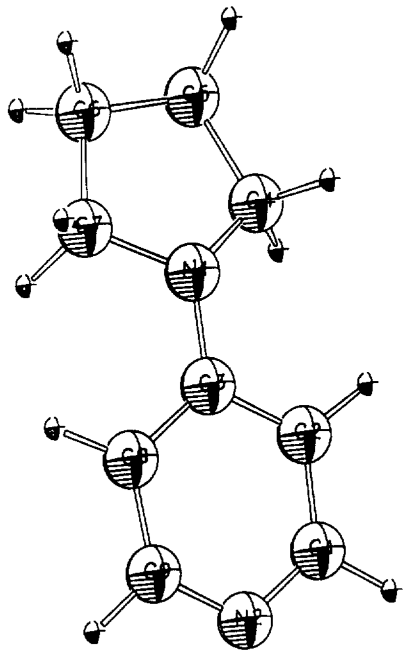


Fig. 11. Optimized ground state geometry of PP.

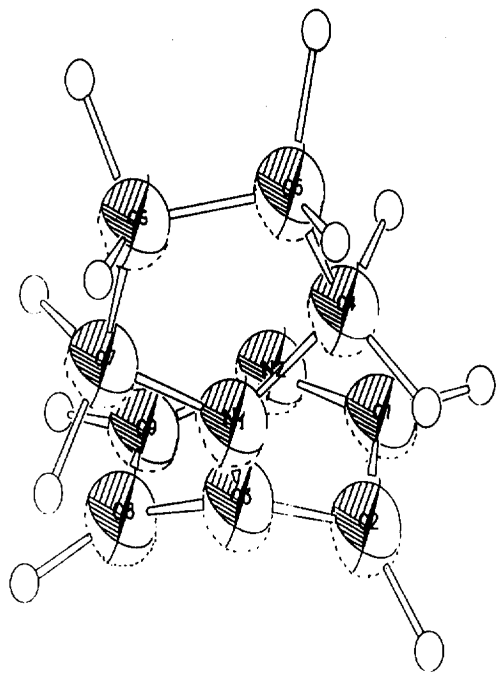


Fig. 12. Optimized excited state geometry of PP.

7. Conclusions

From the investigation of absorption, time-resolved and steady-state emission spectra of PP we find different photophysics in different solvents on excitation. First, in ground state, PP produces hydrogen bonding, yielding a 'pretwisting' of the initially planar conformation in hydroxylic solvent which reduces the emissive fluorescence, and in extreme case stops the radiative transition (water). Second, a nearly sandwich type intramolecular exciplex upon excitation of PP in nonpolar, weakly polar solvent and in β-CD cavity could be observed. Third, in N atom containing solvents such as ACN and *N,N*-dimethylformamide, PP emits fluorescence by solute–solvent exciplexes $^1E_1$ in which pyrrolidino group of the solute is coplanar with the pyridine ring and also exciplex $^1E_2$ emission with the pyrrolidino group perpendicular to the pyridine ring could be observed. Finally, the anomalous fluorescence of PP originates from a complex between excited-state solute and polar solvent molecule in mixture of MCH and a small amount of polar liquid. In this case, the binding between the constituents is σ type bond between lone-pair electrons of pyrrolidino nitrogen and lone-pair electron of P.

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