Pyridoneimines and Pyridonemethides: Substituent- and Solvent-Tunable Intramolecular Charge Transfer and Geometric Isomerism

Alessandro Abbotto, Silvia Bradamante, and Giorgio A. Pagani*

Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Via Cozzi 53, I-20125, Milano, Italy, and Centro CNR Speciali Sistemi Organici, Via Golgi 19, I-20133, Milano, Italy

giorgio.pagani@mater.unimib.it

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We have prepared and fully characterized by means of multinuclear NMR and UV−vis spectroscopy a series of pyridoneimines and pyridonemethides in order to show how it is possible to finely tune π-electron structure properties by properly exploiting substituent and solvent effects. Substituents with different electron-withdrawing capacities were introduced in pyridoneimines **2**−**4**, pyridonemethides **5** and **6**, and pyridine sulfonamido derivatives **7**−**9**. The anisochrony of the carbon position of the azinium ring (geometric isomerism) and the exploitation of previously reported ^{13}C and ^{15}N shift/π-electron density relationships allowed the investigation of the extent of intramolecular charge transfer from the donor group to the acceptor pyridinium moiety. By combining different substitutions with the polarity of the surrounding media, we were able to access a whole range of push−pull electron structures in solution, from fully aromatic-zwitterionic to quinoid-neutral, through many possible intermediate situations along the path. Due to the strict correlation between the π-electron structure of push−pull derivatives and many photonic properties such as nonlinear optical activity, we believe that the achieved results should be valuable for the development of new efficient, tailor-made, heteroaromatic systems with optimized features as advanced organic materials.

Introduction

Investigation of the properties of push−pull derivatives, where a conjugated π-system is end-capped by a donor and an acceptor group, has been the focus of many recent works, including the design of new efficient organic materials.[1] Such systems can be approximately described in terms of the contribution of two limit forms, with an intramolecular charge-transfer taking place from the donor to the acceptor moiety. The importance and relative stability of the two resonance forms define the π-electron structure and, ultimately, many properties of the push−pull molecules. In the past several years, a number of studies have focused the attention on the relationship between the electronic nature of the constituting parts of the push−pull molecule and the value of nonlinear optical figures of merit.[2] Within this research field, Marder and co-workers have correlated the value of the nonlinear second-order polarizability β with a geometrical parameter, the bond-length alternation (BLA), defined as the average difference between the length of adjacent carbon−carbon formal single and double bonds in the polyconjugated molecule.[3] It has been shown that optimization of β requires a specific combination of geometric and electronic parameters, strictly dictated by the nature and position of terminal groups as well as surrounding media properties,[4,5] which leads to an optimal electronic pattern of the ground state of the chromophore.

We here report an investigation on a class of pyridine-based push−pull derivatives, having the general formula

* To whom correspondence should be addressed. Fax: (+39) 026 448 5403.

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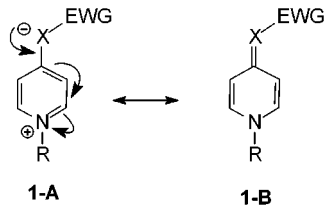
1, which can be described in terms of the contribution of two-limit forms, **1-A** and **1-B** (zwitterionic and neutral, respectively). We show how it is possible to finely tune the intramolecular charge transfer and π-electron distribution by varying the nature of the electron-withdrawing groups (EWG), the bridging site (X), and the solvent polarity. Properly adjusting the relative contribution of these three factors makes it possible to access a whole range of π-electron structures, which should ultimately lead to a finely tuned spectrum of electronic structure dependent properties.



1-A **1-B**

We chose to design pyridine-based push−pull chromophores because this ring has widely been shown to represent a key factor in the design of efficient organic materials.[1,6−8] However, it should be noted that, with few exceptions, the ring is reported exclusively in its more common aromatic form.

Within our multiyear investigation on the π-electron properties of π-deficient and π-excessive heteroaromatic rings,[9] we have already established the strong electron-withdrawing nature of the pyridinyl substituent:[10] this group is highly ranked among primary electron-withdrawing organic functionalities and π-deficient heteroaromatics. Its electron-withdrawing power is comparable to that of carbonyl and carboxyl functionalities and is much higher than that of common acceptor moieties such as cyano,[11] sulfones, and sulfoxide.[12] In particular, we investigated the geometric isomerism exhibited by a series of 4-picolyl carbanions, where the 4-pyridyl (4-Py) moiety was used as a probe to quantitatively rank the electron-withdrawing properties of primary organic functionalities.[12] The anisochrony of C(3) and C(5) carbon atoms of the pyridine ring in the series 4-Py-CH^--Y was used to probe the double-bond character between C(4) and the carbanionic carbon, and thus the charge partitioning between the 4-pyridyl and Y groups. Consequently, when Y is a stronger acceptor than pyridine, the negative charge is preferably delocalized onto Y, with the heteroaromatic ring being in the aromatic form (low double-bond character between C(4) and C^- and isochrony of C(3) and C(5)). Conversely, when Y is weaker than pyridine, charge transfer takes place from the negative center to the ring, leading to a negatively charged quinoid form of the heterocycle.

Our investigation of charge distribution in aza-heterocyclic species is based on the exploitation of ^{13}C and ^{15}N NMR spectroscopy and application of shift/π-electron density relationships.[9] Relationships 1[13] and 2[11,12,14] allow empirical access to the relative π-electron densities (Δq^{π}, electrons), once the difference between their chemical shifts is measured ($\Delta\delta$, ppm), for each pair of carbon or nitrogen atoms belonging to two compounds of the same series, where corresponding sites have the same hybridization character but different substitution patterns. In this manner, it is possible to quantitatively compare the π-electron distribution in a homogeneous series of compounds with respect to a reference system, the proper figures of merit of which are clearly established.

$$\Delta\delta^{13}\mathrm{C} = -160\Delta q^{\pi}_{\mathrm{C}} \quad (1)$$

$$\Delta\delta^{15}\mathrm{N} = -366\Delta q^{\pi}_{\mathrm{N}} \quad (2)$$

With these premises, we chose to consider for the present work the pyridine-based push−pull derivatives **2**−**9**. In the series **2**−**4**, we consider *N*-aryl substituted 1-methyl-4-pyridoneimines, therefore setting the bridging unit X equal to N. Going from **2** to **4**, one finds that the aryl substituent is increasingly more electron-withdrawing. Compounds **5** and **6** are the *CH*-analogues of pyridoneimines **3** and **4**, with X = CH. Finally, in compounds **7** and **8**, we replaced the electron-poor aryl moiety of **3** and **4** with the SO_2 group, giving rise to the deprotonated form of sulfonamides. In compound **9** of the sulfonamide series, the electron-withdrawing capacity of the pyridyl ring is increased by derivatizing the pyridic nitrogen atom with the strong acceptor 2,4-dinitrophenyl substituent. The compounds were investigated by means of multinuclear NMR and electronic spectroscopy. Geometric isomerism and π-charge distribution have been used in order to determine their π-electron structure and the contribution of the two limit forms **1-A** and **1-B** to describe their ground state. Finally, we have taken into account the role of the surrounding media by investigating all of the systems in two solvents of different polarity, $CHCl_3$ and DMSO. According to the well-known $E_T(30)$ Reichardt's polarity scale,[15] $CHCl_3$ (E_T = 39.10) is middle ranked, whereas DMSO (E_T = 45.10) is a highly polar solvent, ranked lower than only alcohols and water.

Results

Synthesis. To the best of our knowledge, the substituted pyridoneimine series **2**−**4** was previously unknown in the literature. The parent compound **2** was prepared

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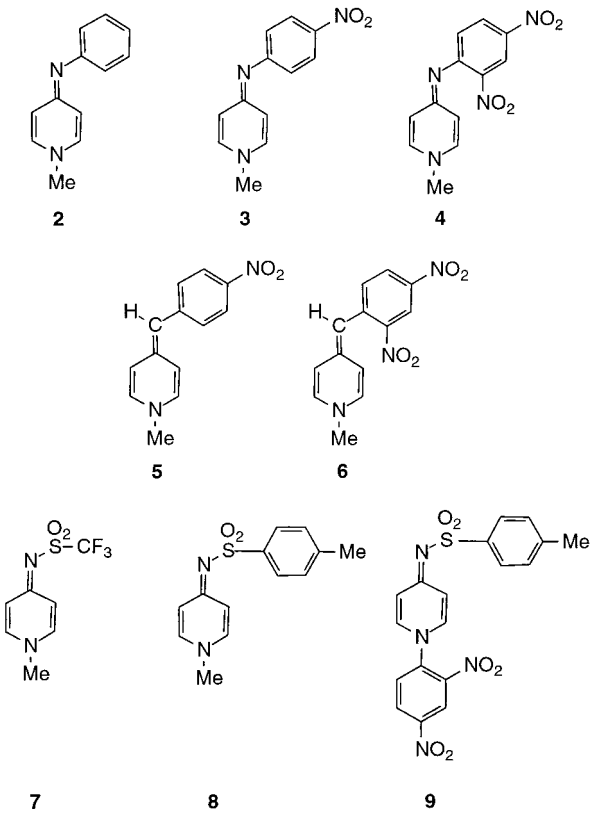


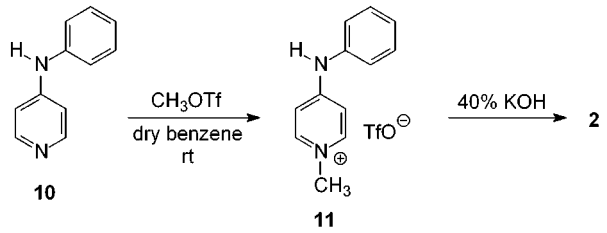
by alkylation of 4-anilinopyridine (**10**),[16] followed by deprotonation with potassium hydroxide of the pyridinium salt **11** (Scheme 1). The latter was previously reported just as iodide in a few patents.[17] The last step afforded a crude oil that, after distillation in a Kugelrohr apparatus at 5×10^{-3} mmHg, gave **2** as a low-melting yellow solid. The corresponding iodide[17] of the pyridinium salt **11** can be prepared from **10** and methyl iodide, but the reaction is sluggish and yields are much lower. Alternatively, the salt **11** may be obtained by nucleophilic substitution of 4-bromo-1-methylpyridinium triflate with aniline and using Et_3N as a base. However, also in this case, yields are not satisfactory and purification from byproducts (triethylammonium salts or excess aniline) is tedious and seldom successful.

Nucleophilic substitution of 4-amino-1-methylpyridinium triflate **12** with 4-nitrofluorobenzene and 2,4-dinitrofluorobenzene led to the mono- and dinitroderivatives **3** and **4**, respectively (Scheme 2). In the latter case, formation of the disubstitution coproduct **13** was observed, in relative amounts depending on temperature and reaction stoichiometry. The two products **4** and **13** could be separated by column chromatography on neutral alumina. In the reaction with dinitrofluorobenzene, potassium carbonate was sufficient as a base, but stronger basic conditions were needed for the substitution with mononitrofluorobenzene.

Corresponding *CH*-analogues **5**[18] and **6**[19] were prepared according to literature methods, with slight modifications.

Sulfonamido derivatives **7**−**9** were previously unknown in the literature, with the exception of the tosylate **8**,

Scheme 1



which was reported in very few cases.[20] The general procedure we have followed for the synthesis of **7** and **8** implied condensation of the amine **12** with the proper sulfonyl chloride. If the reaction is carried out in the presence of a base, the zwitterions **7** and **8** are directly formed, with no isolation of the intermediate sulfonamide salts (Scheme 3). Tosyl derivative **8** may alternatively be obtained, with lower yields, by deprotonation with sodium hydride of the tosylamide **14**[20a] of 4-amino pyridine and subsequent alkylation (Scheme 4). The last step proceeds fully regioselectively on the pyridic nitrogen of the bidentate nucleophilic anion **15** when methyl triflate is used as an alkylating agent. The same intermediate **14** is used for the synthesis in good yields of the dinitrophenyl derivative **9**, via regioselective arylation of the anion **15** with 2,4-dinitrofluorobenzene (Scheme 4).

NMR Characterization: Geometric Isomerism and Bond Order Tuning. The ^{13}C and ^{15}N chemical shifts of compounds **2**−**9** are collected in Table 1. The NMR analysis of pyridoneimines **2**−**4** and pyridonemethides **5** and **6** was carried out in DMSO and $CHCl_3$. In some cases, the low solubility in the less polar solvent prevented the recording of their ^{15}N chemical shifts. Solubility in $CHCl_3$ of sulfonamides **7**−**9** was even lower, so ^{13}C and ^{15}N shifts were recorded only in DMSO. However, to investigate geometric isomerism (vide infra) in two differently polar solvents, ^1H and ^{13}C shifts were obtained in acetone, the E_T value of which (42.20)[15] is middle ranked between those of DMSO and chloroform.

The anisochrony of C(3) and C(5) carbon atoms, as well as H(3) and H(5) hydrogen atoms, of the pyridine ring is the most direct evidence of the predominant contribution of the quinoid limit formula **1-B** with respect to the aromatic form **1-A**. As can be seen from the values of Table 1, the anisochrony of the 3 and 5 positions of the pyridine ring was observed in only two cases, that is, in the unsubstituted pyridoneimine **2** and the nitrophenylpyridonemethide **5**. In all of the other cases, the corresponding positions of the heterocyclic ring have the same chemical shifts.

The aromatic region of the ^{13}C NMR spectrum of compound **2** in $CHCl_3$ at 243 K is shown in Figure 1. The higher-field values of positions 3 and 5 in compounds **2** and **5** were assigned to the position facing (cis) the phenyl ring due to known compression effects[21] operating on similar systems. Indeed, in the anion of 4-benzylpyridine, the phenyl group induces a shielding of ca. 9−10 ppm on the carbon atom of the heterocycle cis to it.[10a] Both

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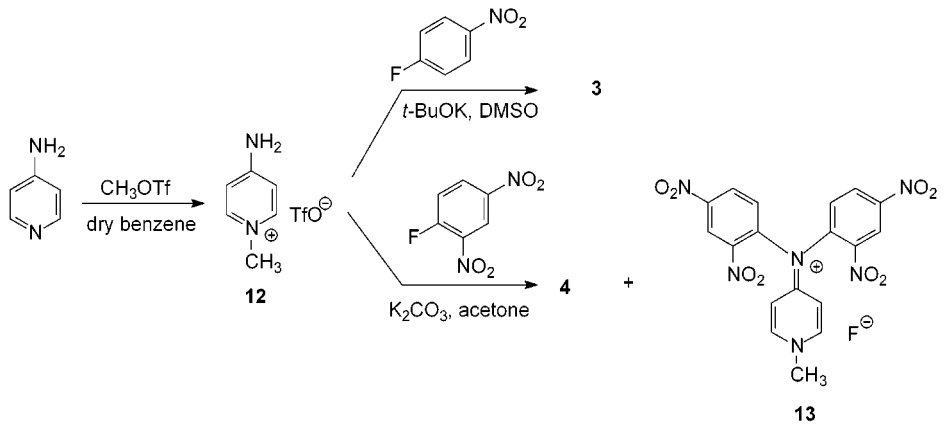
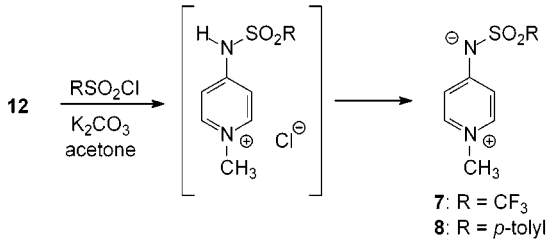
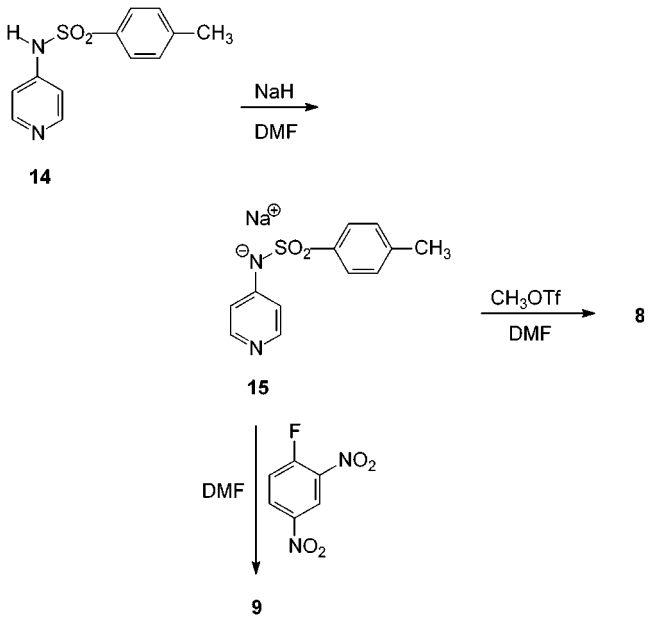
Scheme 2



Scheme 3



Scheme 4



data of Table 1 and the spectrum of Figure 1 clearly prove that in compounds **2** and **5**, a high double-bond character between C(4) of the heterocycle and the bridging atoms is present, leading to hindered rotation around the same bond. In other terms, it is firmly established that for these systems, the ground state is predominantly described by the quinoid form **1-B**. Hindered rotation between C(4) and the bridging unit is also present in compound **6**, as evidenced by the broadening of the C(3) and C(5) signals in $CHCl_3$. However, in this case, only one value has been recorded for both positions, demonstrating that the contribution of the aromatic form **1-A** is slightly predominant, although the quinoid form is important in the description of the ground state. Broadening of signals disappears in the spectrum recorded in DMSO, suggesting that in this solvent the aromatic form is further stabilized with respect to the other one. In the remaining compounds, only one set of sharp signals was recorded and thus the formula **1-A** is the best descriptor for their electron structure.

Variable-Temperature Experiments and Activation Parameters. The fact that the parent compound **2** has a quinoid structure is of significant interest because, by setting this system as a reference, we have been provided with a basis for discriminating neutral-quinoid from aromatic-zwitterionic structures. Consequently, we have decided to perform a detailed NMR investigation of rotameric equilibria in solvents of different polarity (DMSO and $CHCl_3$) and at different temperatures. The most representative set of spectra related to this study is shown in Figure 2. The ^{1}H NMR analysis shows that the pyridine proton shifts are indeed sensitive to temperature and solvent effects. NMR anisochronies of positions 3 and 5 and positions 2 and 6 are observed at 243 K in the less polar solvent $CHCl_3$. Under these conditions, signals are sharp and well resolved. By raising the temperature to room temperature, anisochrony is still present but broadening of signals is now observed. When spectra are recorded in the highly polar solvent DMSO, broadening is further enhanced with the temperature (295 K) being now close to coalescence conditions. In fact, in this solvent, signals ascribed to positions 3 and 5 collapse at 313 K into one single broad pattern (not represented in Figure 2). At higher temperatures (363 K), positions 2 and 6 and positions 3 and 5 are equivalent and each is responsible for a sharp doublet, showing that under these conditions, free rotation along the bond linking C(4) of the heterocycle and the nitranionic bridge is occurring. The pattern assignment of the aromatic systems of **2** has been obtained from COSY NMR experiments. Again, as described above for carbon atoms, we have assigned the most shielded resonances to protons cis to the phenyl ring because of compression effects.

We have performed similar variable-temperature experiments on the representative set of compounds **3**, **5**, **6**, and **9**, focusing once more our attention on the isochrony/anisochrony of protons of the azine ring. We have recorded ^{1}H NMR spectra at 10 K intervals using different solvents depending on the coalescence temperature T_C of the considered compounds. When H(3) and H(5) are nonequivalent at room temperature, which is the case of the unsubstituted pyridoneimine **2** and mononitrophenyl pyridonemethide **5**, investigation was

Table 1. $^{13}C^{a}$ and $^{15}N^{b}$ NMR Shifts (ppm) of Compounds 2−9 at 298 K

		pyridine ring positions							phenyl ring positions[c]						
compd	solvent[d]	N(1)	C(2)	C(3)	C(4)	C(5)	C(6)	N/CH[e]	C(1′)	C(2′)	C(3′)	C(4′)	C(5′)	C(6′)	other
2	DMSO	126.5						240.0							
2	$CHCl_3$[f]		137.5[g]	106.8[g]	156.8	115.6	138.6		151.1	121.89	129.2	121.92	129.2	121.89	CH_3 = 42.7
3	DMSO	137.4	140.7	111.4	155.0	111.4	140.7	236.2	156.9	121.2	125.5	139.6	125.5	121.2	CH_3 = 42.5; NO_2 = 370
3	$CHCl_3$	127.0	138.9	112.2	159.7[h]	112.2	138.9	234.0	157.2[h]	121.7	125.5	141.5	125.5	121.7	CH_3 = 43.0; NO_2 = 369
4	DMSO	147.2	141.6	112.6	158.6	112.6	141.6	226.0	152.8	141.0[i]	121.6	136.8[i]	127.6	122.2	CH_3 = 43.1; NO_2 = 366, 372
4	$CHCl_3$[f]		139.3	112.4	157.5	112.4	139.3		152.9	141.5[j]	122.2	140.1[j]	128.0	125.2	CH_3 = 43.4
5	DMSO	131.6	138.3	108.1	141.4	116.9	135.7	100.3	148.3	123.3	124.3	138.6	124.3	123.3	CH_3 = 41.8; NO_2 = 369
5	$CHCl_3$[f]		136.3[g]	108.1[g]	133.7	116.7	133.7	102.4	148.2	124.6[k]	124.7[k]	136.3	124.7[k]	124.6[k]	CH_3 = 42.2
6	DMSO	153.9	139.9	116.9	148.6	116.9	139.9	97.6	140.2	138.2	123.8	135.0	125.4	123.8	CH_3 = 43.5; NO_2 = 372, 366
6	$CHCl_3$[f]		137.0	114[l]	144.8	114[l]	137.0	98.2	141.8	142.5	123.3	139.4	126.2	125.5	CH_3 = 43.1
7	DMSO	170.0	143.9	117.2	162.1	117.2	143.9	160.3							CH_3 = 44.9; CF_3 = 120.7
7	acetone[f]		144.1	118.3	164.5	118.3	144.1								CH_3 = 45.6; CF_3 = 122.0
8	DMSO[f]		142.1	115.0	161.3	115.0	142.1								CH_3 = 43.7;[m] tolyl positions: 141.2, 140.8, 129.0 (2C), 126.0 (2C), 20.8
9	DMSO	156.9	141.0	114.9	162.1	114.9	141.0	151.2							NO_2 = 361, 363; dinitrophenyl: 147.7, 143.6, 139.4, 131.6, 129.7, 121.6; tolyl: 141.7, 140.5, 129.7 (2C), 126.1 (2C), 20.9
9	acetone[f]		141.6	116.8	165.4	116.8	141.6								dinitrophenyl: 150.6, 146.0, 141.6, 134.1, 131.1, 123.4; tolyl: 143.3, 143.1, 130.6 (2C), 128.0 (2C), 22.0

[a] Relative to Me_4Si (0.0 ppm). [b] Relative to liquid NH_3 (0.0 ppm). [c] Phenyl ring directly bonded to N or CH bridge. [d] Solvents are deuterated. [e] Relative to the imine or the methine bridge. [f] ^{15}N shifts not available due to the low solubility of the compound. [g] Positions cis to the phenyl ring (phenyl compression effect, ref 21). [h] Values can be exchanged. [i] Values can be exchanged. [j] Values can be exchanged. [k] Values can be exchanged. [l] Broad. [m] Methyl bonded to pyridine nitrogen.

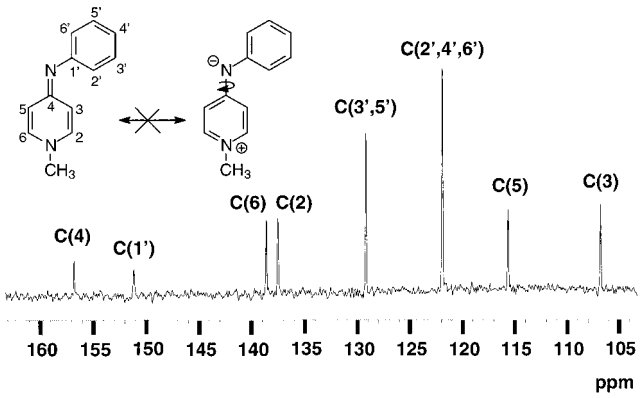


Figure 1. Aromatic region of the ^{13}C NMR spectrum of compound **2** in $CHCl_3$ (T = 243 K).

performed in DMSO by raising the temperature above 298 K. In the remaining systems, since the pyridine protons are equivalent at room temperature, spectra had to be recorded at lower temperatures in different solvents. For the sake of homogeneity with ^{13}C NMR data collected in Table 1, we have used $CHCl_3$ and acetone for compounds **6** and **9**, respectively. The low T_C of the dinitrophenyl pyridoneimine **4** inhibited us from performing this analysis in $CHCl_3$, and a low-melting solvent mixture such as $CH_2Cl_2/CHCl_3$ had to be used. From the experimentally obtained T_C values and peak separations $\Delta\nu$ (in Hertz) of nonequivalent H(3) and H(5) atoms, the activation energies $\Delta G^{\ddagger}$ of the rotational process along the C(4)-bridge bond were obtained by applying eq 3.[22] When possible, peak separation was taken at the highest possible temperature where anisochronous sharp signals

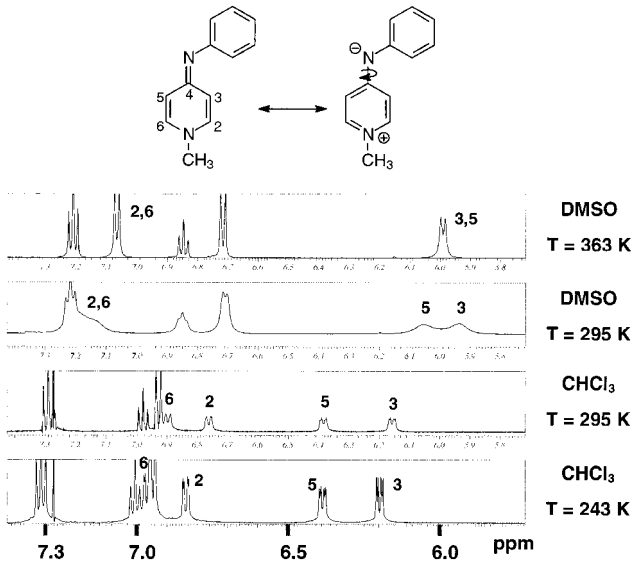


Figure 2. Variable-temperature ^1H NMR spectra of compound **2** in $CHCl_3$ and DMSO (aromatic region).

are observed for H(3) and H(5). For compound **2**, two broad signals at 5.94 and 6.05 ppm for H(3) and H(5), respectively, were recorded in DMSO at 295 K, corresponding to a separation of 55.0 Hz. The high melting point of DMSO prevented lower-temperature NMR studies. All of the relevant data on variable-temperature experiments and activation parameters are collected in Table 2.

$$\Delta G^{\ddagger}(\text{kcal/mol}) = (4.575 \times 10^{-3}) T_C [9.97 + \log(T_C/\Delta\nu)] \quad (3)$$

Solvatochromic Data: Zwitterionic vs Neutral Structure. Solvatochromism, defined as the solvent

(22) Günther, H. *NMR Spectroscopy. An Introduction*; J. Wiley and Sons: Chichester, 1980; p 247.

Table 2. Variable-Temperature Data and Experimental Activation Parameters for Compounds 2, 3, 5, 6, and 9 Relative to the Rotational Process along the C(4)-Bridge Bond

compd	solvent	T_C (K)[a]	$\Delta\nu$ (Hz)[b]	$\Delta G^{\ddagger}$ (kcal/mol^{-1})
2	DMSO	313	55.0	15.4
3	$CH_2Cl_2/CHCl_3$ 8:1	180	6.6	9.4
5	DMSO	333	7.8	17.7
6	$CHCl_3$	290	29.8	14.5
9	acetone	240	44.4	11.8

[a] Coalescence temperature of H(3) and H(5) NMR shifts of the pyridine ring. [b] Peak separation of anisochronous H(3) and H(5) of the pyridine ring (500 MHz NMR instrument).

Table 3. Solvatochromic Data [λ_{max} (nm)] of Chromophores 3−9 in Selected Solvents

solvent	E_T	**3**	**4**	**5**	**6**	**7**	**8**	**9**
MeOH	55.4	408[a]	427	545	577	284	299	303
CH_3CN	45.6	432	449	554	580	286	304	356
DMSO	45.1	457	466	588	594	287	307	305
DMF	43.2	448	460	569	589	288	307	305−357
acetone	42.2	432	447	549	578	*b*	*b*	356
$CHCl_3$	39.1	412	429	541	580	295	310	305−366

[a] A NaOH pellet was added to the solution in order to prevent protonation of the anionic bridging unit. [b] Covered by solvent absorption band.

dependence of the UV−vis absorption spectrum of a molecule, provides a fast and useful qualitative method for determining the zwitterionic or neutral nature of push−pull systems such as the ones investigated in the present work.[23] Table 3 collects absorption data relative to the charge transfer (CT) band in a selected number of solvents, for which E_T values are reported.[15] Pyridoneimines and pyridonemethides **3**−**6** present a clear CT band in the visible region of the spectrum, whereas energy of the electronic absorption of sulfonamido derivatives **7**−**9** falls in the UV region. Due to the strong polarity of the protic solvent MeOH, which stabilizes the zwitterionic character **1-A** of the chromophores **3**−**6** and, thus, the anionic nature of the bridging unit X, the absorption spectrum was recorded in this solvent with addition of a NaOH pellet, to prevent back-protonation to the precursor salt.

Within the common interpretation of solvatochromic interactions,[23] a shorter wavelength shift of the CT band with increasing the solvent polarity indicates a larger value of the molecular dipole moment in the ground state with respect to that of the excited state. In our case, this is in agreement with a zwitterionic nature of the former: in fact, the transition to the excited state, corresponding to an intramolecular CT phenomenon, would lead to a quinoid structure, associated with a smaller dipole moment. Besides other factors that can affect the values of solvatochromism (e.g., aggregation),[23] one source of uncertainty of this type of analysis concerns whether the sign of the shift of the absorption spectrum has to do with the zwitterionic or neutral character of the dye. Indeed, this is true only when the various solvents considered do not dramatically affect the electronic nature of the ground state. In other terms, conclusions of the solvatochromic study are, in principle, valid only when the predominant zwitterionic, or neutral, character is maintained for each couple of solvents considered. Since this is not always the case for the systems of the present work, solvatochromic results are to be cautiously treated and always in conjunction with the NMR results, where the effects of solvents with different polarity are separated.

Discussion

Pertinent conclusions of our investigation on intramolecular charge transfer, geometric isomerism, and therefore bond order, can be reached from both qualitative and quantitative perspectives. From the qualitative point of view, the target is to establish the relative importance of the two limit forms **1-A** and **1-B** in the description of the ground state of chromophores **2**−**9**. The most direct evidence is the presence of geometric isomerism due to a double-bond character between the bridging atom and C(4) of the pyridine ring, which leads to anisochrony of the corresponding positions of the heterocycle. Data of Table 1 indicate that compounds **2** and **5**, for which C(3) and C(5) are anisochronous, are better described by the quinoid structure **1-B**. The dinitrophenyl analogue of **5**, compound **6**, is borderline located between an aromatic and quinoid-like structure. In this case, the solvent plays a key role in the description of the electronic nature of the ground state: whereas in the more polar DMSO the zwitterionic form is stabilized, leading to a single resonance for the 3 and 5 positions, decreasing the polarity of the media increases the importance of the quinoid form, as evidenced by the broadening of the corresponding NMR signals. These results are consistent with the solvatochromic study, for which a shorter wavelength shift from DMSO to $CHCl_3$ is observed for **5** and **6**, thus suggesting that the quinoid character is predominant.

In light of the above comments, conclusions reached thus far are almost qualitative. Although the value of solvatochromism can be used in principle as a quantitative probe, the borderline nature of some systems or the solvent polarity dependence of their electronic structure does not allow clear-cut conclusions to be reached in most of the cases. Table 3 clearly shows that a definite trend of the value of λ_{max} within the E_T polarity scale cannot be extrapolated, leading to uncertainty in most of the cases. For these reasons, our quantitative method of choice relies on the analysis of ^{13}C and ^{15}N chemical shift and their translation into π-electron densities by means of eqs 1 and 2.

The amount of π-electron density residing on the pyridine nitrogen atom is undoubtedly the most evident quantitative probe for determining the extent of the intramolecular charge transfer. However, in the perspective of the aim of our study, it is not important its absolute value but rather the relative differences within the investigated series and the comparison with proper pyridine-based systems for which the π-electron structure is known or intrinsically evident. We have decided to introduce the parent pyridinium salt **16**[24] and the pyridoneimine derivative **17**[25] as limit-representative systems

(23) (a) Reichardt, C. *Solvent Effects in Organic Chemistry*; Verlag: New York, 1979; Chapter 6. (b) Suppan, P.; Ghoneim, N. *Solvatochromism*; The Royal Society of Chemistry: Cambridge, 1997. (c) Liptay, W. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 177−188.

(24) ^{15}N chemical shift of *N*-methylpyridinium iodide (**16**) (DMSO, 1 M) = 200 ppm: Witanowski, M.; Stefaniak, L.; Webb, G. A. In *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: London, 1986; Vol. 18, p 504.

(25) ^{14}N chemical shift (pyridine nitrogen atom) of 1-methyl-1*H*-pyrid-4-one-imine (**17**) (acetone) = 120 ppm: Stefaniak, L. *Org. Magn. Reson.* **1979**, *12*, 379.

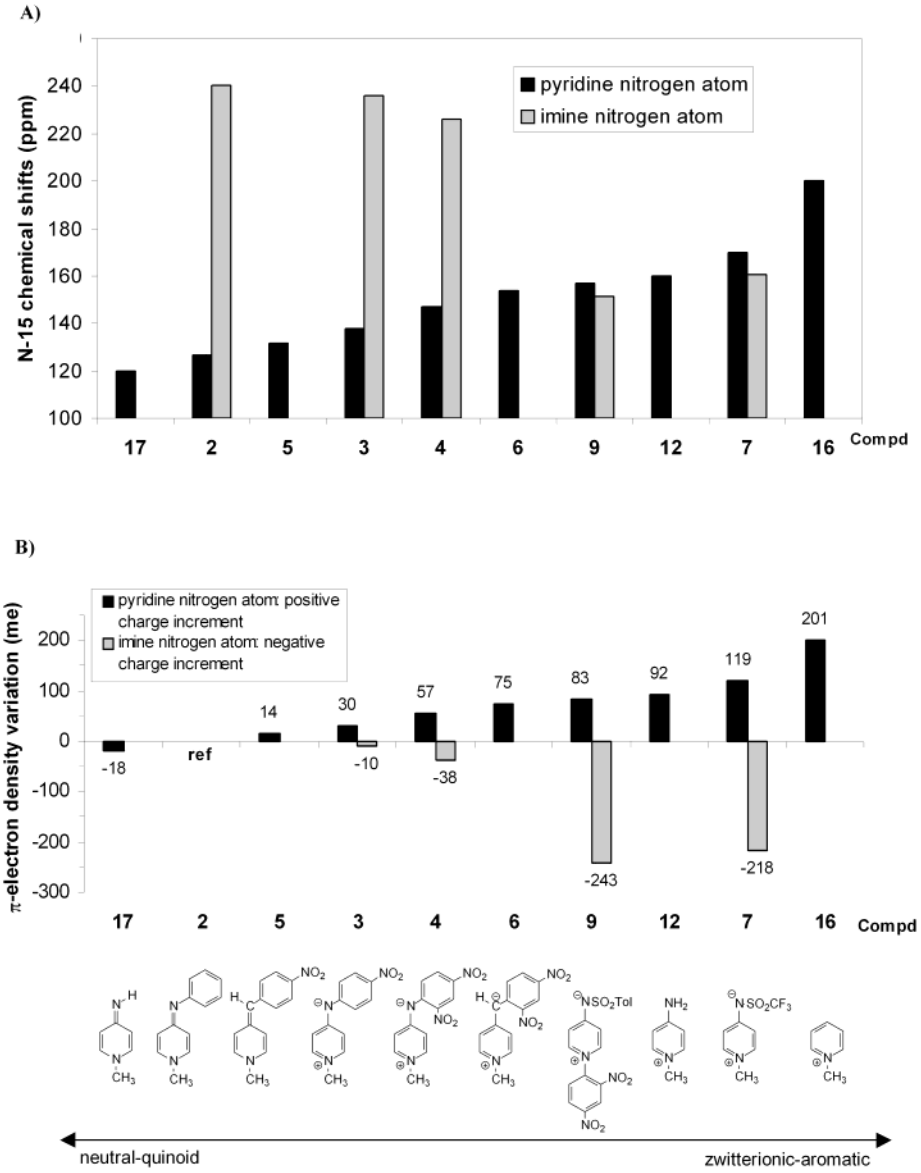


Figure 3. Bar graphs of ^{15}N NMR chemical shifts (A) and π-electron densities data (B) for pyridine (black) and imine (gray) nitrogen atoms, respectively, of compounds **2**−**7**, **9**, **12**, **16**, and **17**. Molecules are ordered from neutral-quinoid to zwitterionic-aromatic character. Each compound is drawn according to the most relevant limit formula descriptor. Shown figures of π-positive and π-negative charge increments (increasing charge separation; values in millielectrons) are calculated with respect to quinoid compound **2** as a reference (ref). Chemical shift values are taken from Table 1 (DMSO) and converted to π-electron density variations through eq 2.

of the structures **1-A** and **1-B**, respectively. We have also included, for comparison, compound **12** as an example of a pyridinium salt bearing a strong, but not anionic, donating group in the para position. ^{15}N NMR data and relative π-electron densities of pyridine and, when applicable, imine nitrogen atoms are shown in Figures 3A and 3B, respectively. Compounds are drawn in their aromatic or quinoid preferred form depending on the recorded isochrony or anisochrony of the carbon atoms of the pyridine ring (see Table 1). It is gratifying for the eye to observe in Figure 3 that the azinium nitrogen site experencies a low-field shift on going from the pyridoneimines **17** and **2** to the pyridinium cation **16**, showing a monotonic increase of positive π-charge and, therefore, an increasingly larger importance of the pyridinium character **1-A**. In other terms, the trend in the ^{15}N chemical shift is able to quantitatively probe the π-donation from the cyclic nitrogen atom to the bridging unit. On the other hand, a high-field shift of the nitrogen bridge is observed from **2** to **7**, consistent with a simultaneous increase of π-negative charge and, therefore, charge separation. Within the series of molecules here investigated, we can conclude that the strongest neutral-quinoid character is associated with imine **2**, whereas sulfonamido derivative **7** owns the largest zwitterionic nature.

^{15}N NMR analysis of pyridine N(1) and, where possible, of the imine nitrogen atom revealed that the qualitative conclusions, as derived from the presence of geometric isomerism and solvatochromic data, are fully consistent with the quantitative trend of intramolecular charge transfer. Unfortunately, the analysis of the π-electron density of the bridging unit cannot be extended to the carbanions **5** and **6**, due to the fact that eq 1, in the present form, can only be applied for comparing two carbon atoms having the same substitution pattern.[13]

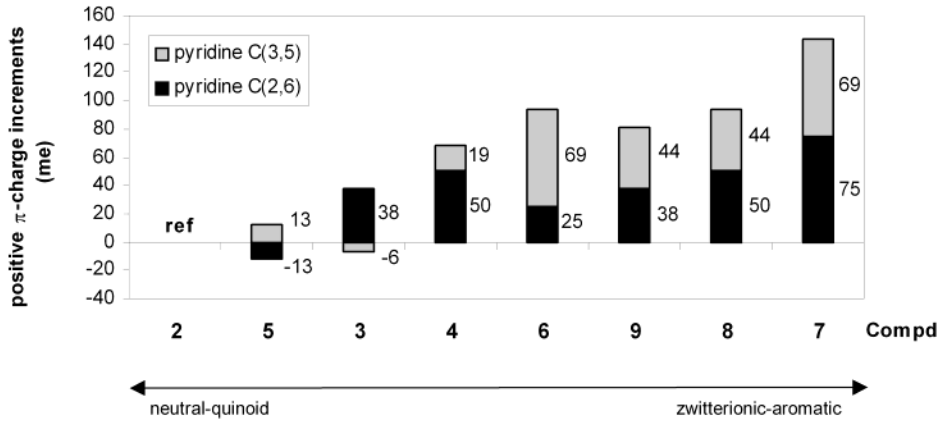


Figure 4. Bar graphs of π-electron density variation for pyridine *C*H carbon atoms of compounds **2**−**9**. Systems are sorted as in Figure 3. Shown figures of π-positive charge increments (millielectrons) are calculated with respect to corresponding positions of quinoid system **2** as a reference (ref). Values are obtained from eq 1 using ^{13}C chemical shifts reported in Table 1 (DMSO, when available).

^{13}C NMR analysis, and their translations into relative π-electron densities, of the *C*H pyridine carbon atoms reveal that a significant portion of the positive π-charge increment (increase of charge separation) on going from the quinoid compound **2** to the zwitterionic compound **7** involves the carbon framework of the heterocyclic ring (Figure 4). The quantitative trend of the increase in charge separation is once again in full agreement with the whole situation so far depicted.

It is evident how the presence of the function SO_2R stabilizes the negative charge on the nitranionic center, with respect to the pyridoneimines **2**−**4**, increasing the weight of the zwitterionic character in the description of the ground state. These results therefore suggest that the SO_2R is able to stabilize a negative charge in the α position with limited delocalization onto itself, as we have previously reported for a number of anionic derivatives bearing this group directly linked to the negative center.[11,13b,26] As far as pyridoneimines **2**−**4** are concerned, the extent of intramolecular charge transfer increases by decreasing the electron-withdrawing power of the aryl moiety substituting the exocyclic nitrogen atom. When the strong dinitrophenyl group is present, the negative charge on the imine center is stabilized, likely also for resonance effects, and is not available for donation to the heterocyclic ring. In compound **2**, the nitranionic center does not have any stabilizing factors other than delocalizing a significant part of the charge to the azine (and most of it to the N(1) atom), leading to a stable quinoid form. It is rewarding to find that in this series of compounds the increasing electron-withdrawing character of the aryl group on going from **2** to **4** does not diminish the negative charge in its α positions. In other terms, the imine nitrogen experiences a high-field shift on going from **2** to **4**, consistent with a larger π-electron density. These findings lead us to conclude that the main intramolecular charge-transfer mechanism involve the anionic central group and the pyridine ring, with cooperative effects of the other substituents.

The role of the polar solvent DMSO is that to stabilize, as expected, the charge separated structure **1-A** with respect to the less polar $CHCl_3$. The most striking effect was found for compound **2**, for which ^{1}H NMR spectra are shown in Figure 2. Comparing the spectra at 295 K in the two solvents reveals how the anisochrony of the pyridine protons in $CHCl_3$ is still present in DMSO but signals move from rather defined doublets to broad patterns, as a consequence of the increased contribution of the zwitterionic form and thus of the decrease of the rotational barrier along the C(4)−N bond. However, in this case, as in all of the others, the solvent effect alone is not able to swap over the relative contribution of the two structures. To achieve this result, solvent and substituent control must be operating simultaneously. A similar behavior is observed for pyridine carbon shift of **6**. For this compound, isochronous C(3) and C(5) signals shift from broad to resolved patterns on going from $CHCl_3$ to DMSO, in agreement with an improved contribution of form **1-A** to the description of the ground state in the latter solvent.

Conclusion

On the basis of multinuclear NMR analysis and exploitation of shift/π-electron density relationships, accompanied by solvatochromic data, we have provided evidence of how it is possible to finely tune the extent of intramolecular charge transfer, and thus electron structure, in a series of pyridine-based push−pull chromophores by properly playing with substituent and solvent effects.

Results relative to compounds **2**−**9** can be schematically summarized as follows. (1) Sulfonamido derivatives **7**−**9** are better described by the charge-separated structure **1-A**, thanks to the ability of the $-SO_2-$ functionality to stabilize a negative charge α to itself. (2) If the other substituent effects are taken as constant, the nitranionic bridge stabilizes the form **1-A** with respect to a carbanionic moiety. This result is evidently associated with the higher ability of the nitrogen atom to accept negative charge with respect to a carbon atom, because of its higher electronegativity; so, pyridoneimine **3** exists prevalently as aromatic-zwitterionic form, but the corresponding pyridonemethide **5** has a clear quinoid character. (3) Electron-withdrawing aryl substituents on the bridging atom favor the presence of a higher π-electron density on this site but do not significantly decrease it by delocalization; as a consequence, charge-separated structures are favored. As an example, dinitrophenyl-

(26) Barchiesi, E.; Bradamante, S.; Ferraccioli, R.; Pagani, G. A. *J. Chem. Soc., Perkin Trans. 2* **1990**, 375−383.

pyridoneimine **4** exists predominantly in the zwitterionic form, whereas phenylpyridoneimine **2** is neutral-quinoid. (4) The polarity of the media is able to significantly affect the relative importance of the two limit forms **1-A** and **1-B**.

In conclusion, we have accessed a whole range of push−pull electron structures, from fully aromatic-zwitterionic to quinoid-neutral forms, going through all the intermediate situations along the path. Most importantly, this result was achieved in a relatively small homogeneous series of compounds, by careful use of substituent and media effects. We believe that the results we have shown should be valuable in the search and investigation of new efficient organic push−pull systems having optimized π-electron structure dependent advanced properties.

Experimental Section

^{13}C and ^{15}N NMR spectra were recorded using a Bruker AMX-500 spectrometer operating at 125.70 and 50.75 MHz, respectively. The spectral parameters and calibrations have been previously reported.[14a] ^{15}N chemical shifts are relative to liquid NH_3 (380.23 from nitromethane). Coupling constants are presented in Hertz. Anhydrous *N*,*N*-dimethylformamide (DMF) was supplied by Fluka and stored over molecular sieves. Benzene and acetone were dried over Na_2SO_4 or Drierite for a few days. Melting points are uncorrected.

4-Anilino-1-methylpyridinium Triflate (11). A solution of methyl triflate (1.496 g, 9.12 mmol) in dry benzene (3 mL) was added to a stirred suspension of 4-anilinopyridine[16] (1.505 g, 8.84 mmol) in the same solvent (15 mL) at room temperature. The mixture was stirred overnight and the precipitate collected to give the practically pure product as a whitish solid (2.896 g, 8.66 mmol, 98%): mp 97−98 °C; ^1H NMR (DMSO-d_6) δ 10.5 (broad, 1H), 8.25 (d, 2H, J = 7.5), 7.50 (t, 2H, J = 7.9), 7.34−7.29 (m, 3H), 7.11 (d, 2H, J = 7.5), 3.95 (s, 3H). Anal. Calcd for $C_{13}H_{13}F_3N_2O_3S\cdot 1/2H_2O$: C, 45.48; H, 4.11; N, 8.16. Found: C, 45.36; H, 3.91; N, 7.86.

***N*-(1-Methyl-1*H*-pyridin-4-ylidene)aniline (2).** 4-Anilino-1-methylpyridinium triflate (**11**) (1.004 g, 2.17 mmol) was treated with 40% aqueous KOH (10 mL) leading to the separation of a dark yellow oil, which was extracted with diethyl ether (70 mL). The organic layer was dried and evaporated to dryness to leave the crude product as a yellow oil (0.384 g, 1.89 mmol, 87%). A sample was purified by distillation in a Kugelrohr apparatus (60 °C/0.005 mmHg) to give a yellow solid: mp 70−72 °C; ^1H NMR (DMSO-d_6) δ 7.3−7.1 (m, 4H), 6.86 (t, 1 H, J = 6.2), 6.71 (d, 2H, J = 7.0), 6.05 (broad, 1H), 5.94 (broad, 1H), 3.48 (s, 1H); ^1H NMR ($CDCl_3$) δ 7.30 (t, 2H, J = 7.7), 6.97 (t, 1H, J = 7.3), 6.94−6.89 (m, 3H), 6.76 (d, 2H, J = 7.4), 6.38 (d, 1H, J = 8.0), 6.16 (d, 1H, J = 7.4), 3.5 (s, 3H). Anal. Calcd for $C_{12}H_{12}N_2$: C, 78.23; H, 6.56; N, 15.20. Found: C, 77.72; H, 6.50; N, 14.83.

1-Methyl-4-aminopyridinium Triflate (12). A solution of methyl triflate (0.90 g, 5.3 mmol) in dry benzene (4 mL) was added dropwise to a suspension of 4-aminopyridine (0.50 g, 5.3 mmol) in the same solvent (13 mL) at room temperature. After the mixture was stirred for 15 h, the resulting solid was separated by filtration and washed with dry benzene to give the practically pure product as a white solid (1.23 g, 4.8 mmol, 90%), which was used without further purification in the next step: mp 109−113 °C; ^1H NMR (DMSO-d_6) δ 8.08 (d, 2H, J = 7.5), 8.15−7.80 (broad, 2H), 6.78 (d, 2H, J = 7.5), 3.82 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 158.5, 143.7 (2C), 109.3 (2C), 44.4; ^{15}N NMR (DMSO-d_6) δ 160 (pyridinium nitrogen).

***N*-(1-Methyl-1*H*-pyridin-4-ylidene)-4-nitroaniline (3).** A solution of fluoro-4-nitrobenzene (0.28 g, 2.0 mmol) in DMSO (7 mL) was added dropwise to a solution of 1-methyl-4-aminopyridinium triflate (**12**) (0.52 g, 2.0 mmol) and potassium *tert*-butoxide (0.27 g, 2.2 mmol) in the same solvent (13 mL). After being stirred for 24 h at room temperature, the reddish mixture was poured onto ice, and the resulting precipitate was collected by filtration to give the crude product as a yellow-orange solid, which was purified by sublimation (130 °C, 0.008 mmHg) (0.15 g, 0.7 mmol, 33%): mp 164−167 °C; ^1H NMR (DMSO-d_6) δ 8.07 (d, 2H, J = 9.0), 7.48 (d, 2H, J = 7.5), 6.83 (d, 2H, J = 9.0), 6.34 (d, 2H, J = 7.4), 3.57 (s, 3H); ^1H NMR ($CDCl_3$) δ 8.08 (d, 2H, J = 9.0), 6.96 (d, 2H, J = 7.0), 6.94 (d, 2H, J = 9.0), 6.29 (d, 2H, J = 7.0), 3.50 (s, 3H). Anal. Calcd. for $C_{12}H_{11}N_3O_2$: C, 62.86; H, 4.85; N, 18.33. Found: C, 63.13; H, 4.70; N, 18.30.

***N*-(1-Methyl-1*H*-pyridin-4-ylidene)-2,4-dinitroaniline (4).** Powdery potassium carbonate (0.552 g, 4.0 mmol) was added to a stirred solution of 1-methyl-4-aminopyridinium triflate (**12**) (0.775 g, 3.0 mmol) in dry acetone (40 mL). After the mixture was stirred for 30 min, a solution of fluoro-2,4-dinitrobenzene (0.558 g, 3.0 mmol) in dry acetone (10 mL) was added dropwise to the above solution, and the mixture was stirred for 72 h at room temperature. The solvent was removed under reduced pressure from the filtered brown reaction mixture to leave a residue, which was washed wih water (few mL) and subsequently submitted to chromatography (acetone) on neutral alumina. Compound **4** was obtained[27] as a bright red solid, which was purified by sublimation (180 °C, 0.005 mmHg) (0.180 g, 0.7 mmol, 23%): mp 208−209 °C; ^1H NMR (DMSO-d_6) δ 8.58 (d, 1H, J = 2.7), 8.15 (dd, 1H, J = 9.2, 2.7), 7.72 (d, 2H, J = 7.5), 7.16 (d, 1H, J = 9.2), 6.51 (d, 2H, J = 7.5), 3.64 (s, 3H); ^1H NMR ($CDCl_3$) δ 8.81 (d, 1H, J = 2.6), 8.26 (dd, 1H, J = 9.0, 2.6), 7.18 (d, 1H, J = 9.0), 7.14 (d, 2H, J = 7.6), 6.37 (d, 2H, J = 7.5), 3.65 (s, 3H); MS (EI) *m*/*e* 274 ($M^{+\bullet}$, 100), 182 (27), 93 (43). Anal. Calcd for $C_{12}H_{10}N_4O_4$: C, 52.56; H, 3.68; N, 20.43. Found: C, 52.37; H, 3.70; N, 20.18.

Trifluoro-*N*-(1-methyl-1*H*-pyridin-4-ylidene)methanesulfonamide (7). Powdery potassium carbonate (1.20 g, 8.7 mmol) was added to a solution of 1-methyl-4-aminopyridinium triflate (**12**) (0.900 g, 3.5 mmol) in dry acetone (20 mL). After the mixture was stirred for 30 min, a solution of trifluoromethanesulfonyl chloride (0.59 g, 3.5 mmol) in dry acetone (12 mL) was added dropwise, and the reaction mixture was stirred for 5 days at room temperature. The solid was filtered off from the brown mixture while being protected from light, and the solvent was removed at reduced pressure to leave a residue, which was taken up with water (5 mL). The resulting solid was collected by filtration to afford the crude product as a pink solid (0.27 g, 1.1 mmol, 31%): mp 168−170 °C (EtOH, pink-yellow solid);^1H NMR (DMSO-d_6) δ 8.27 (d, 2H, J = 7.3), 7.27 (d, 2H, J = 7.3), 4.00 (s, 3H); ^1H NMR (acetone-d_6) δ 8.22 (d, 2H, J = 7.3), 7.31 (d, 2H, J = 7.3), 4.15 (s, 3H). Anal. Calcd for $C_7H_7F_3N_2O_2S$: C, 35.00; H, 2.94; N, 11.66. Found: C, 35.18; H, 2.83; N, 11.64.

***N*-(1-Methyl-1*H*-pyridin-4-ylidene)-*p*-toluenesulfonamide (8). Method A.** A solution of *N*-pyrid-4-yl-*p*-toluenesulfonamide (**14**) (0.500 g, 2.0 mmol) in anhydrous DMF (8 mL) was added dropwise to a supension of sodium hydride (0.10 g, 60% oily, 2.5 mmol) in the same solvent (5 mL), under a nitrogen atmosphere and at a temperature maintained below 25 °C. The reaction mixture was stirred for 30 min at 25 °C, turning from whitish to pale yellow. A solution of methyl triflate 0.33 g, 2.0 mmol) in anydrous DMF (2 mL) was then added dropwise to the ice-cooled mixture. After the mixture was stirred for 48 h at room temperature, the milky precipitate was collected, washed with water, and dried over $CaCl_2$ at reduced pressure to give the practically pure product as a white solid (0.20 g 0.8 mmol, 40%): mp 238−242 °C (lit.[20a] 238−239 °C); ^1H NMR (DMSO-d_6) δ 7.87 (d, 2H, J = 7.4), 7.64 (d, 2H, J = 8.2), 7.25 (d, 2H, J = 8.1), 6.84 (d, 2H, J = 7.4), 3.74 (s, 3H), 2.35 (s, 3H).

Method B. Powdery potassium carbonate (0.622 g, 4.5 mmol) was added to a solution of 1-methyl-4-aminopyridinium

(27) A byproduct was separated by column chromatography and identified as the disubstitution product **13** as a brown solid by ^1H NMR: ^1H NMR (DMSO-d_6) δ 9.06 (d, 2H, J = 2.6), 8.74 (dd, 2H, J = 8.9, 2.6), 8.63 (d, 2H, J = 7.3), 7.96 (d, 2H, J = 8.9), 7.47 (d, 2H, J = 7.4), 4.12 (s, 3H). No attempts were made to obtain an analytically purified sample.

triflate (**12**) (0.387 g, 1.5 mmol) in dry acetone (10 mL). After the mixture was stirred for 30 min, a solution of *p*-toluenesulfonyl chloride (0.314 g, 1.6 mmol) in dry acetone (10 mL) was added dropwise, and the reaction mixture was stirred for 72 h at room temperature. The white precipitate was collected by filtration, washed with water (a few milliliters), and dried over $CaCl_2$ at reduced pressure to provide the product (0.240 g, 0.9 mmol, 60%): mp 234−235 °C.

***N*-[1-(2,4-Dinitrophenyl)-1*H*-pyridin-4-ylidene]-*p*-toluenesulfonamide (9).** A solution of *N*-pyrid-4-yl-*p*-toluenesulfonamide (**14**) (0.50 g, 2.0 mmol) in anhydrous DMF (10 mL) was added dropwise to a supension of sodium hydride (0.10 g, 60% oily, 2.5 mmol) in the same solvent (5 mL), under a nitrogen atmosphere and at a temperature maintained below 25 °C. After the mixture was stirred for 30 min, a solution of 2,4-dinitrofluorobenzene (0.38 g, 2.0 mmol) in anydrous DMF (3 mL) was added dropwise. The reaction mixture was stirred for 5 days at room temperature under nitrogen, poured into a saturated aqueous solution of sodium chloride (70 mL), and extracted with ethyl acetate (4 × 70 mL). The combined organic layers were washed with a saturated aqueous sodium chloride solution (15 mL), dried, and evaporated to dryness under reduced pressure to leave a yellowish residue, which was taken up with diethyl ether to afford the product as a yellow solid (0.71 g, 1.7 mmol, 85%): mp 245−246 °C; ^{1}H NMR (acetone-d_6) δ 9.08 (d, 1H, J = 2.6), 8.86 (dd, 1H, J = 8.7, 2.6), 8.33 (d, 1H, J = 8.7), 8.01 (d, 2H, J = 7.8), 7.82 (d, 2H, J = 8.2), 7.34 (d, 2H, J = 7.9), 7.11 (broad, 2H), 2.41 (s, 3H). Anal. Calcd for $C_{18}H_{14}N_4O_6S$: C, 52.17; H, 3.41; N, 13.52. Found: C, 52.03; H, 3.51; N, 13.37.

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