Syntheses and Characterization of *N*-(Indolyl)pyridinium Salts and of Their Ylides

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3-Methylindole reacts with pyridines in the presence of NBS to give indol-2-yl-pyridinium salts which were converted into their ylides by an anion exchange resin in its hydroxide form. Indol-3-amine was subjected to a nucleophilic ring transformation with pyrylium salts which resulted in the formation of indol-3-yl-pyridinium salts, the 2,4,6-trimethylpyridinium derivative of which proved to be unstable. The 2,4,6-triphenylpyridinium derivate was deprotonated to the corresponding ylide. The isomeric indol-2-yl and indol-3-yl derivatives are cycloimmonium ylides which are members of the compound class of heterocyclic mesomeric betaines (MB). By contrast, the ylide of indol-2-yl-pyrrolidinium is a cycloammonium ylide. It was prepared by reaction of 3-methylindole with pyrrolidine in the presence of NBS, followed by deprotonation.

Key words: Mesomeric Betaines, Ylides, Mesoions, Immonium Ylides, Ammonium Ylides

Introduction

Wittig introduced the term "ylid" (engl. also "ylide") into organic chemistry as a combination of the syllables "yl" (organic radical such as meth*yl*) which suggests a free valence and the syllable "id" which expresses a negative charge (such as in "acetyl*id*") [1]. In ylides, represented by the general formula **I**, a carbanion is directly attached to a heteroatom bearing a positive charge. According to Zugrăvescu and Petrovanu, distinct classes of *N*-ylides can be distinguished, *i. e.* ammonium-ylides (**II**), cycloammonium-ylides (**III**), immonium-ylides (**IV**), cycloimmonium-ylides (**V**), nitrile-ylides (**VI**), and diazonium-ylides (**VII**) [1] (Fig. 1).

Ollis, Stanforth, and Ramsden regarded cycloimmonium-ylides (**V**) of heteroaromatics as one of four distinct classes of heterocyclic mesomeric betaines [2 – 4]. They are distinguished from conjugated heterocyclic mesomeric betaines in such a way that ylides can satisfactorily be represented by 1,2-dipolar resonance structures. Compound **1** is an example of such an ylide (Fig. 2). Compound **2** is closely related but belongs to the class of conjugated mesomeric betaines (CMB). In either case, the anionic part is shown in form of its simplified isoconjugate equivalent, the odd alternant hydrocarbon anion penta-1,3-dien-1-ide **VIII**. Characteristically, the cationic part of **1** and **2** is joined through a starred position to the anionic equivalent. These are active positions of the highest occupied molecular orbital (HOMO). Resonance forms of ylides and conjugated mesomeric betaines can be drawn which display common atoms for either charge (*vide infra*). By contrast, in cross-conjugated (CCMB) as well as *pseudo*-cross-conjugated mesomeric betaines (PCCMB), for which **3** and **4** are given as examples, respectively, the cationic parts are bound to the negative part through unstarred positions [2 – 6]. The isoconjugate equivalent of the carboxylate group, *i. e.* propen-1-id **IX**, is shown. These unstarred positions are inactive positions of the HOMO, and this architecture causes a charge separation in the ground state of the molecules and determines the chemical properties. Thus, whereas ylides and conjugated heterocyclic mesomeric betaines are versatile 1,3-dipoles in heterocyclic chemistry [1 – 4], cross-conjugated systems undergo predominantly 1,4-dipolar cycloadditions [2 – 4, 7 – 9] and can therefore be applied as switchable devices in

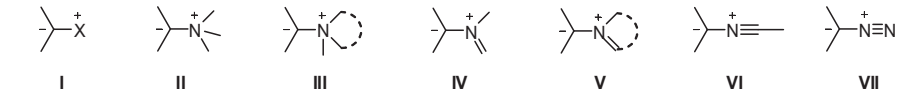


Fig. 1. Classes of ylides.

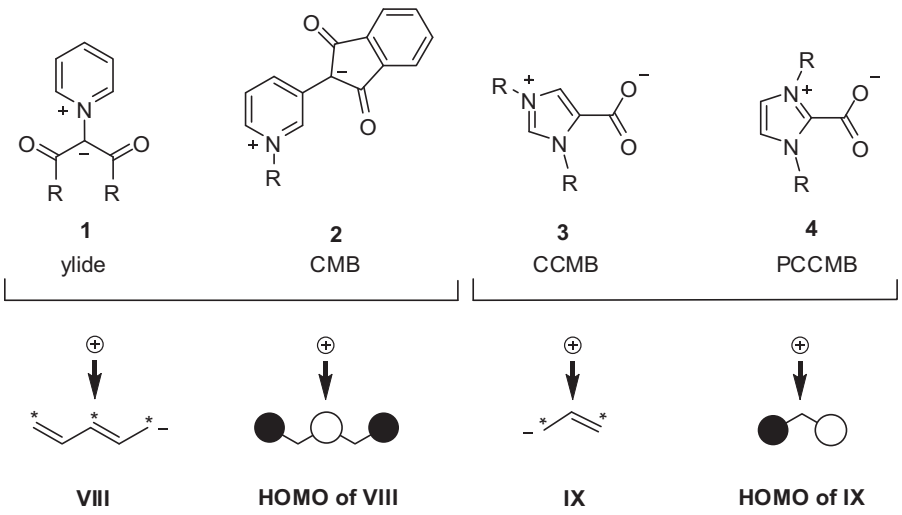


Fig. 2. Four distinct classes of mesomeric betaines.

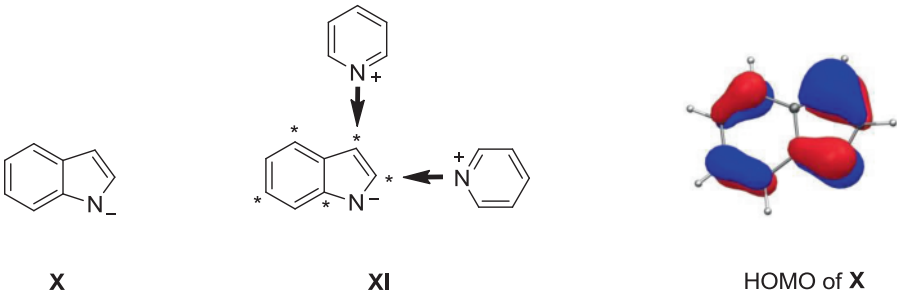
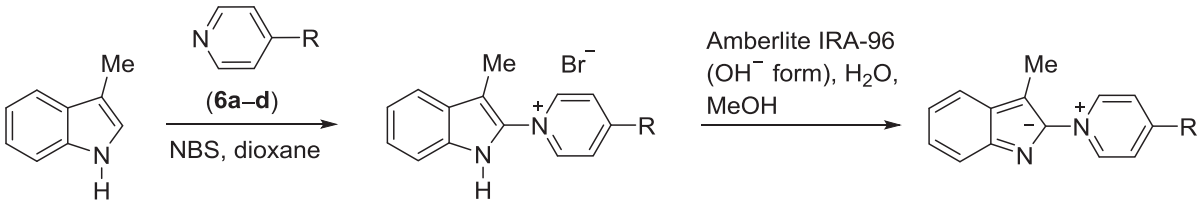


Fig. 3. Architecture of indol-2-yl and indol-3-yl pyridinium betaines.

materials chemistry [10, 11]. Cleavage of the union bond connecting the positive and the negative part of cross-conjugated mesomeric betaines to abnormal *N*-heterocyclic carbenes (aNHC) is rare [12]. By contrast, the generation of normal *N*-heterocyclic carbenes (NHC) by thermal decarboxylations of *pseudo*-cross-conjugated mesomeric betaines, which can be regarded as heterocumulene adducts of NHCs [13], has been widely applied in organometallic chemistry [14 – 17], organocatalysis [18 – 22], and synthesis of heterocycles [23 – 27]. Review articles on betaine-carbene interconversions have appeared recently [28, 29].

The indol-1-ide anion **X** is isoconjugated with an odd, non-alternant hydrocarbon anion (Fig. 3). Therefore, it gives the unique possibility to study two isomeric ylides which are closely related to conjugated heterocyclic mesomeric betaines. They are generated by joining π-conjugated positive partial structures such as pyridinium rings to the 2- or to the 3-position of the indol-1-ide partial structure (*c. f.* **XI**) which are both active positions of the highest occupied molecular orbital (HOMO) according to DFT calculations. To the best of our knowledge, only three examples of the latter type of compound have been published to date (*vide infra*).

In continuation of our work on mesomeric betaines [30] and *N*-heterocyclic carbenes [31] we report here on the synthesis and characterization of new 1-(pyridinium)indol-2-yl-1-ides and of an additional representative of the isomeric 1-(pyridinium)indol-3-yl-1-ides.



Scheme 1. Synthesis of indol-2-yl-pyridinium salts and of their ylides.

Results and Discussion

Reaction of 3-methylindole **5** with pyridine (**6a**), 4-methylpyridine (**6b**), 4-dimethylaminopyridine (**6c**), and 4-(pyrrol-1-yl)pyridine (**6d**) in the presence of *N*-bromosuccinimide resulted in the formation of the pyridinium salts **7a–d** in moderate to excellent yields (Scheme 1). Treatment of solutions of the salts **7a–d** in a mixture of water and methanol with the anion exchange resin Amberlite IRA-96 in its hydroxide form gave the ylides **8a–d** in very good to excellent yields as orange to dark-red compounds. The resonance frequency of the NH group of **7a–d** which is detectable between $\delta = 11.70$ and 12.43 ppm in the ^{1}H NMR spectra measured in [D$_6$]DMSO disappears on deprotonation. Only compound **7a** was mentioned previously in the literature [32]. The ylide formation causes an upfield shift of the indole ^{1}H NMR resonances. As an example, the signal of 4-*H* is shifted from $\delta = 7.63$ (**7c**) to 7.28 ppm (**8c**) in deuterated DMSO.

A selection of mesomeric structures of the ylide **8a** is shown in Fig. 4. As already mentioned, common atoms for positive as well as negative charges exist, and this is a characteristic feature of members of the class of conjugated heterocyclic mesomeric betaines and ylides. The characteristic dipole type which

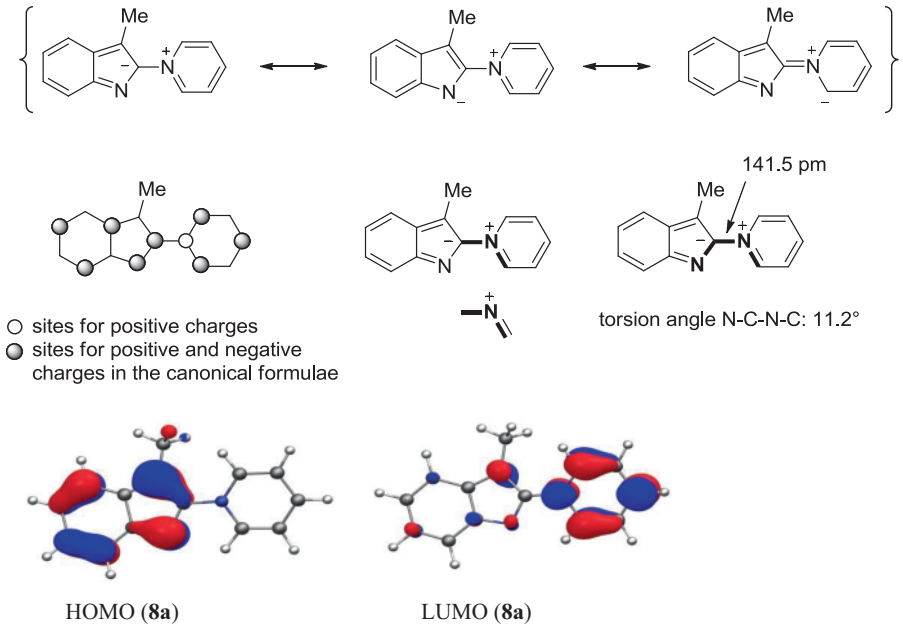
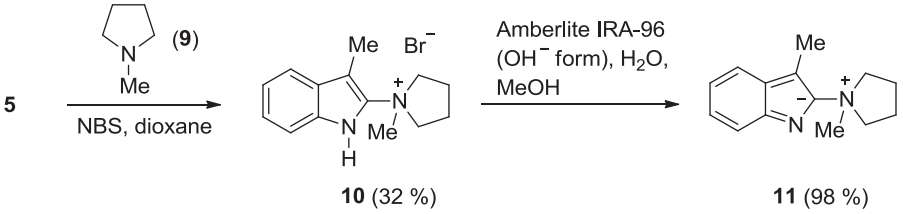


Fig. 4. Architecture of indol-2-yl pyridinium ylides.



Scheme 2. Synthesis of a cycloammonium ylide.

serves for the identification of betaine classes [2] is also shown. The calculated dihedral angle decreases by approximately 28° to 11.2° on ylide formation from the salt in accordance with a higher degree of conjugation between the two parts of the molecule. The bond connecting the two parts was calculated to be approximately 142 pm long. This value is longer than a C_{sp^2}–N bond (138 pm) as found in formamide. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are located essentially in separate parts of the common π-electron system, *i. e.* in the indole ring (HOMO) and the pyridinium ring (LUMO). In accordance with the definition, position 2 of the indole anion partial structure is an active position of the highest occupied molecular orbital (HOMO).

In a similar procedure, 3-methylindole (**5**) and *N*-methylpyrrolidine (**9**) were converted into the 1-(indol-2-yl)-1-methylpyrrolidinium bromide (**10**) which was deprotonated to the ylide 1-methyl-1-(pyrrolidinio)-indolide (**11**) in almost quantitative yield by an anion exchange resin (Scheme 2).

In the ammonium ylide **11** the positive charge is not delocalized. As shown in Fig. 5, in the resonance forms the charges are strictly delocalized in separate parts of the molecule. The characteristic dipole type of cycloammonium ylides (*c. f.* **III** in Fig. 1) is also shown. As expected, the dihedral angle is larger than in the ylide described above, and the bond length connecting

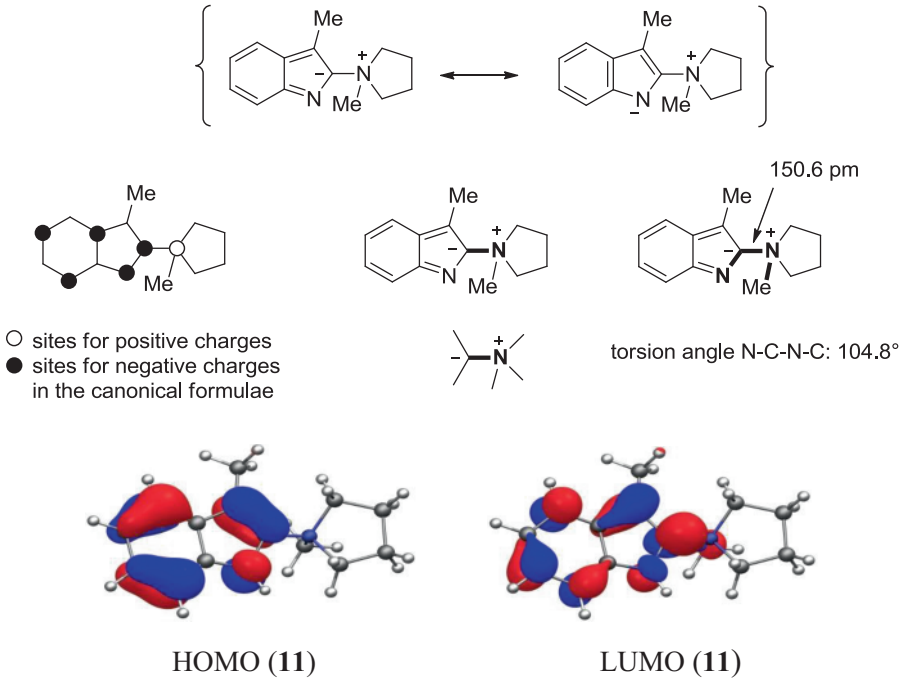
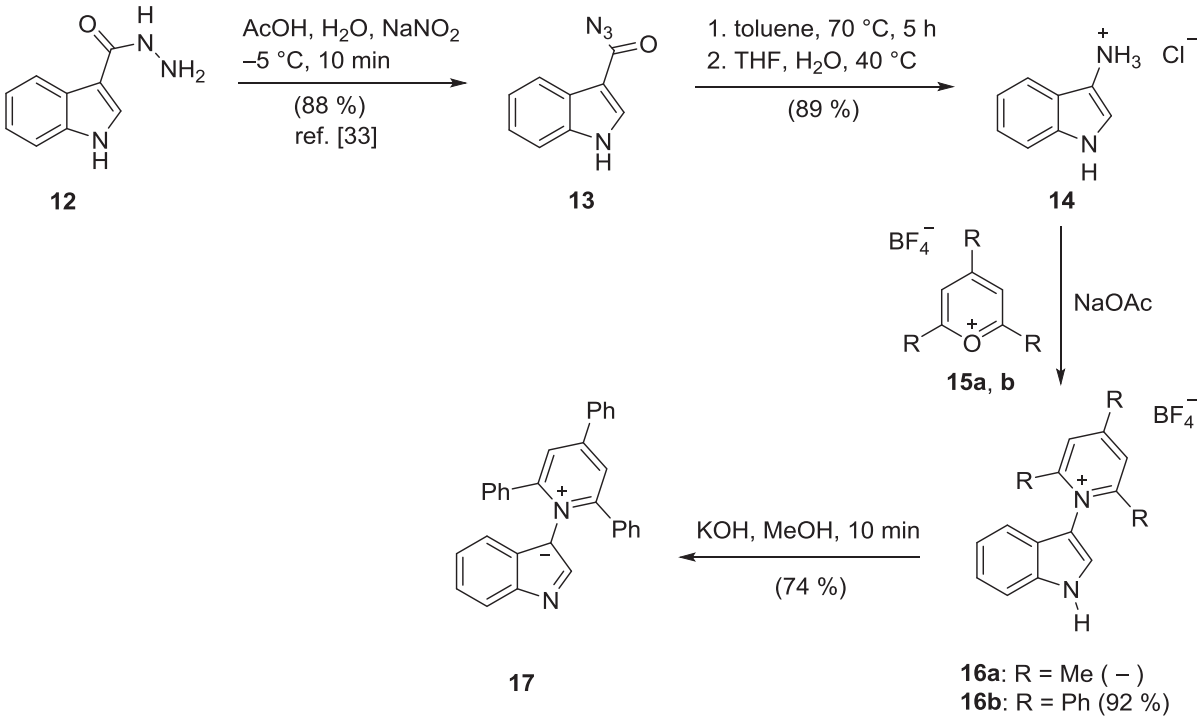


Fig. 5. Architecture of ammonium ylides.

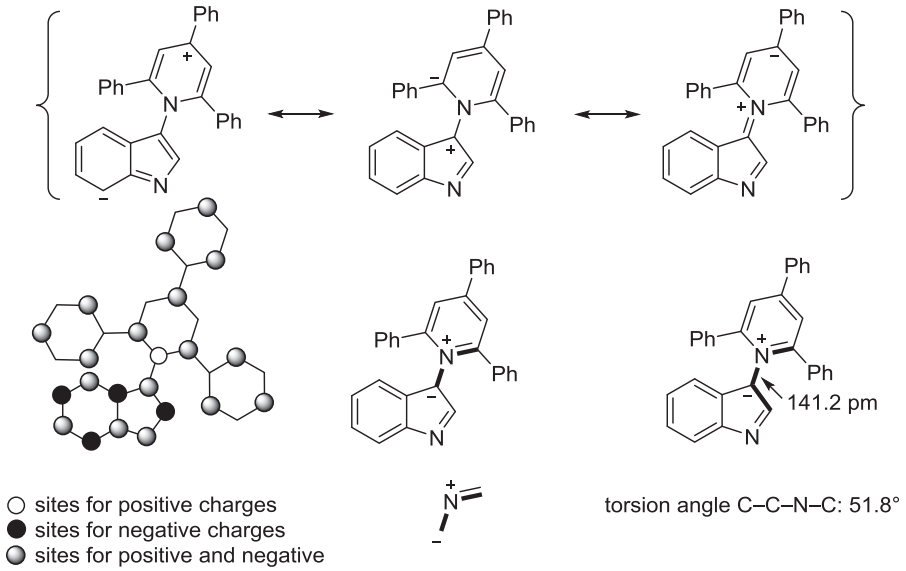


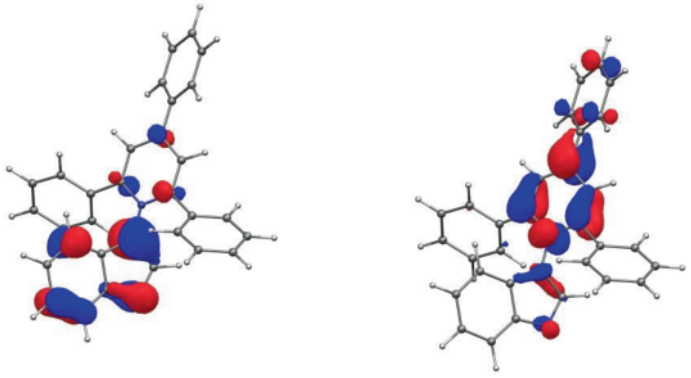
Scheme 3. Synthesis of an indol-3-yl pyridinium ylide.

the two partial structures of the molecule is considerably longer than in conjugated systems. On ylide formation from the salt, the dihedral angle changes from 86.2° to 104.8° according to DFT calculations. Correspondingly, there are marked differences in the frontier orbital profiles in comparison to the ylides described above. The HOMO and LUMO are located in the indole moiety as expected, plus small contributions to the LUMO of the ylide bond (Fig. 5).

We next tried a synthesis of indol-3-yl-pyridinium salts by nucleophilic ring transformation of 1*H*-indol-3-amine with pyrylium salts. 1*H*-Indol-3-yl-pyridinium, -quinolinium and -isoquinolinium salts have been prepared before *via* the highly explosive 3-phenyliodonioindole acetate, prepared by treatment of indole with phenyl iodosoacetate, which was first subjected to an anion exchange and then treated with the corresponding heteroaromatics [32]. We started our synthesis from 1*H*-indole-3-carbohydrazide (**12**) which was transformed into the 1*H*-indole-3-carbonyl azide (**13**) according to modified literature procedures using sodium nitrite in acetic acid [33] (Scheme 3). Rearrangement of **13** to the 3-isocyanato-1*H*-indole, which was not isolated, was accomplished by heating in anhydrous toluene, followed by hydrolysis which resulted in the formation of the hydrochloride of 3-aminoindole (**14**). Nucleophilic ring transformation of the pyrylium salts **15a**, **b** with **14** resulted in the formation of the indol-3-yl-pyridinium salts **16a**, **b**. The trimethyl derivative **16a**, however, could not be isolated in pure form. Attempts to recrystallize the sample met with difficulties, as the product decomposed in a variety of solvents. The salt **16b**, however, proved to be stable and was fully characterized. Its ylide was obtained after treatment with methanolic potassium hydroxide as a dark-green solid in good yield.

The charges in ylide **17b** are delocalized over the entire π-system according to the resonance forms (Fig. 6). The characteristic dipole type is identical with the dipole of conjugated mesomeric betaines as well as with the isomeric indol-2-yl derivative described before. Due to steric hindrance the dihedral angle is much larger than in 2-pyridinio-indolide described above. However, conjugation between the two parts of the molecule induces a considerably decrease of the dihedral angle on conversion of the salt (71.3°) into the





HOMO (**17**) LUMO (**17**)

Fig. 6. Architecture of the indol-3-yl pyridinium ylide **17**.

ylide (51.8°) according to the DFT calculation. As expected the HOMO is essentially located in the indole ring, whereas the LUMO has its largest coefficients is the pyridinium ring. Characteristically, position 3 of the indole partial structure is an active position of the HOMO, so that one of the characteristics of ylides belonging to the class of heterocyclic mesomeric betaines is fulfilled.

In summary, we prepared indol-2-yl and indol-3-yl pyridinium salts and converted them into their ylides which are isomeric members of the class of heterocyclic mesomeric betaines. By contrast, the indol-2-yl pyrrolidinium salt is an ammonium ylide.

Experimental Section

Nuclear magnetic resonance (NMR) spectra were measured with Bruker Avance 400 MHz and Bruker Avance III 600 MHz instruments. ^{1}H NMR spectra were recorded at 400 MHz or 600 MHz, ^{13}C NMR spectra at 100 MHz or 150 MHz, with the solvent peak or tetramethylsilane used as the internal reference. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. The mass spectra were measured with a Varian 320 MS Triple Quad GC/MS/MS with a Varian 450-GC. The electrospray ionization mass spectra (ESIMS) were measured with an Agilent LCMSD series HP 1100 instrument with APIES. Samples for

ESI mass spectrometry were sprayed from methanol at 0 V fragmentor voltage unless otherwise noted. Melting points are uncorrected and were determined in an apparatus according to Dr. Tottoli (Büchi). Yields are not optimized. All density-functional theory (DFT) calculations were carried out by using the JAGUAR 7.7.107 software [34] running on Linux 2.6.18-238.el5 SMP (x86_64) on two AMD Phenom II X6 1090T processor workstations (Beowulf cluster) parallelized with OpenMPI 1.3.4. MM2 optimized structures were used as starting geometries. Complete geometry optimizations were carried out on the implemented LACVP* (Hay-Wadt effective core potential (ECP) basis on heavy atoms, N31G6* for all other atoms) basis set and with the B3LYP density functional. All calculated structures were proven to be true minima by the absence of imaginary frequencies. Plots were obtained using MAESTRO 9.1.207, the graphical interface of JAGUAR. Thermodynamic corrections were estimated from unscaled frequencies, using standard formulae in the ideal gas harmonic oscillator approximation as implemented in JAGUAR, and refer to a standard state of 298.15 K and 1 mol L^{-1} concentration.

*General procedure for the synthesis of the salts **7a–d***

A solution of 3-methylindole (**5**) (2.0 mmol) and the corresponding pyridine (2.0 mmol) in 10 mL of anhydrous benzene was treated at r. t. within 15 min with *N*-bromosuccinimide (1.5 mmol) whereupon a precipitate was formed. The mixtures were stirred for additional 75 min and then heated at reflux temperature for 1 h. The solids were filtered off and washed with hot benzene.

*1-(3-Methylindol-2-yl)pyridinium bromide (**7a**)*

Yield: 0.40 g (98%); m. p. 225 °C. – ^{1}H NMR ([D$_6$]DMSO): $\delta = 2.35$ (s, 3 H, Me), 7.19 – 7.24 (m, 1 H, 5-*H*), 7.32 – 7.38 (m, 1 H, 6-*H*), 7.53 (d, 1 H, 7-*H*, $J = 8.3$ Hz), 7.73 (d, 1 H, 4-*H*, $J = 7.8$ Hz), 8.40 (dd, 2 H, 3′/5′-H, $J = 7.8$ Hz, $J = 6.7$ Hz), 8.81 – 8.89 (m, 1 H, 4′-*H*), 9.38 (dd, 2 H, 2′/6′-*H*, $J = 6.7$ Hz, $J = 1.1$ Hz), 12.40 ppm (s, 1 H, N-*H*). – ^{13}C NMR ([D$_6$]DMSO): $\delta = 7.7$, 105.7, 112.1, 120.0, 120.4, 124.4, 126.8, 128.3, 131.8, 133.9, 145.5, 147.1 ppm. – IR (KBr): $\nu = 3432$, 3001, 1623, 1476, 1449, 1336, 1153, 941, 892, 748, 727, 710, 669, 631, 530, 477 cm^{-1}. – MS ((+)-ESI): m/z (%) = 209.1 (100) [M–Br]$^+$. – HRMS ((+)-ESI): $m/z = 209.1081$ (calcd. 209.1079 for [$C_{14}H_{13}N_2$]$^+$).

*4-Methyl-1-(3-methylindol-2-yl)pyridinium bromide (**7b**)*

Yield: 0.692 g (85%); m. p. 245 °C. – ^{1}H NMR ([D$_6$]DMSO): $\delta = 2.39$ (s, 3H, Me), 2.83 (s, 3H, Me′), 7.22 (ddd, 1H, 5-*H*, $J = 8.1/7.0/1.1$ Hz), 7.35 (ddd, 1H, 6-*H*, $J = 8.1/7.0/1.1$ Hz), 7.48 (d, 1H, 7-*H*, $J = 8.1$ Hz), 7.69 (d, 1H, 4-*H*, $J = 8.1$ Hz), 8.17 (d, 2H, 3′/5′-*H*, $J = 8.1$ Hz), 9.05 (d, 2H, 2′/6′-*H*, $J = 8.1$ Hz), 11.70 (s, 1H, N-*H*) ppm. – ^{13}C NMR ([D$_6$]DMSO): $\delta = 7.9$, 22.6, 107.7, 112.9, 120.9, 122.0, 126.2, 128.7, 130.2, 132.8, 136.2, 145.6, 163.4 ppm. – IR (KBr): $\nu = 758$, 819, 1237, 1337, 1368, 1472, 1633, 2856, 2967 cm^{-1}. – MS ((+)-ESI): m/z (%) = 223 (100) [M–Br]$^+$. – HRMS ((+)-ESI): $m/z = 223.1231$ (calcd. 223.1235 for [$C_{15}H_{15}N_2$]$^+$).

*4-Dimethylamino-1-(3-methylindol-2-yl)pyridinium bromide (**7c**)*

Yield: 0.48 g (95%); m. p. 235 °C. – ^{1}H NMR ([D$_6$]DMSO): $\delta = 2.22$ (s, 3 H, Me), 3.32 (s, 6 H, Me_2N), 7.15 (ddd, 1H, 5-*H*, $J = 8.1/7.2/1.0$ Hz), 7.22 (d, 2H, 3′/5′-*H*, $J = 7.8$ Hz), 7.27 (ddd, 1H, 6-*H*, $J = 8.1/7.2/1.1$ Hz), 7.44 (ddd, 1H, 7-*H*, $J = 8.1/0.9/0.9$ Hz), 7.63 (d, 1H, 4-H, $J = 8.1$ Hz), 8.52 (d, 2H, 2′/6′-H, $J = 7.8$ Hz), 12.02 ppm (s, 1 H, N-*H*). – ^{13}C NMR ([D$_6$]DMSO): $\delta = 7.5$, 66.3, 103.7, 107.7, 111.7, 119.3, 119.9, 123.3, 126.9, 131.6, 133.3, 142.4, 156.0 ppm. – IR (KBr): $\nu = 3419$, 1705, 1645, 1575, 1458, 1340, 1219, 1176, 1011, 812, 753, 528 cm^{-1}. – MS ((+)-ESI): m/z (%) = 252.1 (100) [M–Br]$^+$. – HRMS ((+)-ESI): $m/z = 252.1496$ (calcd. 252.1501 for [$C_{16}H_{18}N_3$]$^+$).

*4-(Pyrrolidin-1-yl)-1-(3-methylindol-2-yl)pyridinium bromide (**7d**)*

Yield: 0.660 g (49%); m. p. 252 °C. – ^{1}H NMR ([D$_6$]DMSO): δ = 2.06 – 2.07 (m, 4H, -C*H*$_2$-), 2.22 (s, 3H, Me), 3.60 – 3.64 (m, 4H, -CH$_2$-), 7.04 (d, 2H, 3′/5′-H, $J = 8.12$ Hz), 7.15 (ddd, 1H, 5-*H*, $J = 8.1/7.1/1.0$ Hz), 7.26 (ddd, 1H, 6-*H*, $J = 8.1/7.1/1.0$ Hz), 7.43 (d, 1H, 7-*H*, $J = 8.1$ Hz), 7.62 (d, 1H, 4-*H*, $J = 8.1$ Hz), 8.45 (d, 2H, 2′/6′-*H*, $J = 7.8$ Hz), 12.00 (s, 1H, N-*H*) ppm. – ^{13}C NMR ([D$_6$]DMSO): δ = 7.5, 24.8, 48.6, 104.0, 108.3, 111.3, 119.7, 120.3, 123.3, 126.9, 131.7, 133.3, 142.4, 153.3 ppm. – IR (KBr): $\nu = 503$, 768, 817, 1008, 1176, 1220, 1346, 1454, 3053 cm^{-1}. – MS ((+)-ESI): m/z (%) = 278 (100) [M–Br]$^+$. – HRMS ((+)-ESI): $m/z = 278.1653$ (calcd. 278.1657 for [$C_{18}H_{20}N_3$]$^+$).

*N-Methyl-1-(3-methylindol-2-yl)pyrrolidinium bromide (**10**)*

Yield: 0.358 g (32%) of a colorless solid; m. p. 163 °C. – ^{1}H NMR ([D$_6$]DMSO): $\delta = 2.12 – 2.33$ (m, 4H, -CH$_2$-), 2.47 (s, 3H, Me), 3.50 (s, 3H, Me), 4.11 – 4.18 (m, 2H, -CH$_2$-), 4.36 – 4.42 (m, 2H, -CH$_2$-), 7.14 (ddd, 1H, 5-*H*, $J = 8.1/7.1/1.0$ Hz), 7.27 (ddd, 1H, 6-*H*, $J = 8.3/7.1/1.0$ Hz), 7.45 (d, 1H, 7-*H*, $J = 8.3$ Hz), 7.64 (d, 1H, 8-*H*, $J = 8.1$ Hz), 12.02 (s, 1H, N-*H*) ppm. – ^{13}C NMR ([D$_6$]DMSO): $\delta = 9.3$, 20.9, 53.4, 66.8, 101.7, 112.0, 119.2, 120.1, 123.8, 127.2, 132.8, 134.7 ppm. – IR (KBr): 761, 800, 924, 1230, 1342, 1460, 1711, 2879, 2980, 3037 cm^{-1}. – MS ((+)-ESI): m/z

(%) = 215 (100) $[M–Br]^+$. – HRMS ((+)-ESI): m/z = 215.1243 (calcd. 215.1548 for $[C_{14}H_{19}N_2]^+$).

*General procedure for the preparation of the ylides **8a–d***

A sample of 60 mL of the anion exchange resin Amberlite® IRA-96 was filled into a column and washed with 3 L of water. Then the resin was treated with 200 mL of an 8 % aqueous NaOH solution over a period of 8 h. Finally, the resin was washed with water until pH = 7 was reached. The salts **7a–d** (0.66 mmol) were dissolved in water-MeOH (1 : 1), given on the resin and eluted with the same solvent mixture. The solvent was finally distilled off *in vacuo* to give the ylides.

*3-Methyl-2-(1-pyridinio)-indol-1-ide (**8a**)*

Yield: 0.148 g (99 %) of a dark-red solid; m. p. 75 °C. – ^{1}H NMR ([D$_6$]DMSO): δ = 2.38 (s, 3H, Me), 7.02 (ddd, 1H, 5-*H*, J = 8.1/7.1/1.0 Hz), 7.14 (ddd, 1H, 6-*H*, J = 8.2 / 7.1 / 1.0 Hz), 7.44 (d, 1H, 7-*H*, J = 8.2 Hz), 7.59 (d, 1H, 4-*H*, J = 8.1 Hz), 8.24 (dd, 2H, 3′/5′-*H*, J = 7.8/5.8 Hz), 8.64 (d, 1H, 4′-*H*, J = 7.8 Hz), 9.36 (d, 2H, 2′/6′-*H*, J = 5.8 Hz) ppm. – ^{13}C NMR ([D$_6$]DMSO): δ = 8.5, 102.1, 114.1, 118.6, 119.3, 122.3, 127.9, 128.4, 135.8, 137.4, 144.2, 145.0 ppm. – IR (KBr): ν = 678, 745, 1071, 1150, 1264, 1335, 1454, 1625, 2859, 3057 cm^{-1}. – MS ((+)-ESI): m/z = 209.1 $[M+H]^+$. – HRMS ((+)-ESI): m/z = 209.1077 (calcd. 209.1079 for $[C_{14}H_{12}N_2]^+$).

*3-Methyl-2-(4-methylpyridinio)-indol-1-ide (**8b**)*

Yield: 0.147 g (98 %) of a brownish oil. – ^{1}H NMR ([D$_6$]DMSO): δ = 2.32 (s, 3H, Me), 2.75 (s, 3H, Me), 7.20 (ddd, 1H, 5-*H*, J = 8.1/7.1/1.1 Hz), 7.33 (ddd, 1H, 6-*H*, J = 8.1/7.1/1.1 Hz), 7.50 (d, 1H, 7-*H*, J = 8.1 Hz), 7.70 (d, 1H, 4-*H*, J = 8.05 Hz), 8.20 (d, 2H, 3′/5′-*H*, J = 6.7 Hz), 9.18 (d, 2H, 2′/6′-*H*, J = 6.7 Hz) ppm. – ^{13}C NMR ([D$_6$]DMSO): δ = 7.6, 21.9, 107.4, 112.1, 119.8, 120.3, 124.2, 128.5, 129.7, 131.3, 138.4, 144.2, 161.3 ppm. – IR (KBr): ν = 749, 1333, 1468, 1635, 2857, 2973, 3057 cm^{-1}. – MS ((+)-ESI): m/z = 223.1 $[M+H]^+$. – HRMS ((+)-ESI): m/z = 223.1238 (calcd. 223.1235 for $[C_{15}H_{14}N_2]^+$).

*3-Methyl-2-(4-dimethylaminopyridinio)-indol-1-ide (**8c**)*

Yield: 0.138 g (83 %) of a yellow solid; m. p. 77 °C. – ^{1}H NMR ([D$_6$]DMSO): δ = 2.30 (s, 3H, Me), 3.23 (s, 6H, Me$_2$N), 6.68 (m, 1H, 5-*H*), 6.74 (m, 1H, 6-*H*), 7.05 (d, 2H, 2′/6′-*H*, J = 7.8 Hz), 7.22 (d, 1H, 7-H, J = 7.9 Hz), 7.28 (d, 1H, 4-*H*, J = 7.3 Hz), 8.57 (d, 2H, 3′/5′-*H*, J = 7.8 Hz) ppm. – ^{13}C NMR ([D$_6$]DMSO): δ = 9.2, 38.6, 94.4, 107.2, 115.5, 116.0, 117.3, 117.9, 130.5, 141.2, 141.6, 141.8, 155.1 ppm. – IR (KBr): 3056, 1644, 1372, 1214, 822, 748 cm^{-1}. – MS ((+)-ESI): m/z = 252.1 $[M+H]^+$. – HRMS ((+)-ESI): m/z = 252.1504 (calcd. 252.1501 for $[C_{16}H_{18}N_3]^+$).

*3-Methyl-2-[4-(pyrrolidin-1-yl)pyridinio]-indol-1-ide (**8d**)*

Yield: 0.147 g (98 %) of a yellow solid; m. p. 105 °C. – ^{1}H NMR ([D$_6$]DMSO): δ = 2.03 – 2.07 (m, 4H, -C*H*$_2$-), 2.23 (s, 3H, Me), 3.22 – 3.26 (m, 4H, -C*H*$_2$-), 7.02 (d, 2H, 3′/5′-*H*, J = 7.70 Hz), 7.07 (dd, 1H, 5-*H*, J = 7.1/7.1 Hz), 7.18 (dd, 1H, 6-*H*, J = 8.0/7.1 Hz), 7.40 (d, 1H, 7-*H*, J = 8.0 Hz), 7.56 (d, 1H, 4-*H*, J = 7.1 Hz), 8.17 (d, 2H, 2′/6′-*H*, J = 7.70 Hz) ppm. – ^{13}C NMR ([D$_6$]DMSO): δ = 7.3, 24.6, 48.7, 103.5, 108.2, 111.7, 119.3, 120.5, 123.4, 127.2, 133.5, 142.0, 148.2 ppm. – IR (KBr): ν = 749, 1180, 1223, 1454, 1566, 1650, 2975, 3057 cm^{-1}. – MS ((+)-ESI): m/z = 278.1 $[M+H]^+$. – HRMS ((+)-ESI): m/z = 278.1661 (calcd. 278.1657 for $[C_{18}H_{19}N_3]^+$).

*3-Methyl-2-(1-methylpyrrolidinio)-indol-1-ide (**11**)*

Yield: 0.108 g (98 %) of a brownish oil. – ^{1}H NMR ([D$_6$]DMSO): δ = 2.13 – 2.28 (m, 4H, -C*H*$_2$-), 2.44 (s, 3H, Me), 3.47 (s, 3H, Me), 4.23 – 4.28 (m, 4H, -C*H*$_2$-), 6.95 (dd, 1H, 5-*H*, J = 8.0/7.7 Hz), 7.04 (dd, 1H, 6-*H*, J = 8.0/7.7 Hz), 7.34 (d, 1H, 7-*H*, J = 7.7 Hz), 7.48 (d, 1H, 4-*H*, J = 8.0 Hz) ppm. – ^{13}C NMR ([D$_6$]DMSO): δ = 9.9, 21.0, 53.1, 66.0, 98.6, 113.8, 117.8, 118.2, 120.8, 128.8, 135.8, 139.4 ppm. – IR (KBr): ν = 752, 1344, 1460, 1710, 2920, 2977, 3015 cm^{-1}.

*Preparation of 1H-indole-3-carbonyl azide (**13**)*

A sample of 1 g (5.71 mmol) of 1*H*-indole-3-carbohydrazide (**12**) was dissolved in 50 mL of 50 % acetic acid. After cooling to –5 °C, a solution of 394 mg (5.71 mmol) of sodium nitrite in water was added dropwise, whereupon the color of the solution changed from orange to brown. After 10 min of stirring the solid was filtered off and washed with water. The crude product was dried *in vacuo*. Yield: 934 mg (88 %). – ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 11.66 (s, 1H, N*H*), 9.81 (s, 1H, NHC*H*), 8.15 (d, 1H, Ar-*H*, J = 9.0 Hz), 7.48 (d, 1H, Ar-H, J = 7.9 Hz), 7.21 – 7.16 (m, 1H, Ar-H), 7.16 – 7.11 (m, 1H, Ar-H) ppm. All spectroscopic data are agreement to those reported in the literature [33].

*1H-Indol-3-amine hydrochloride (**14**)*

Under an inert atmosphere a sample of 8.8 g (47.27 mmol) of 1*H*-indole-3-carbonyl azide (**13**) was suspended in 300 mL of anhydrous toluene. After heating at 70 °C over a period of 5 h the solvent was distilled off *in vacuo*, and the resulting dark residue was treated with 100 mL of THF

and 20 mL of conc hydrochloric acid. After stirring at 40 °C for 1 h, the solvent mixture was distilled off *in vacuo*, the residue was treated with water and extracted three times with diethyl ether. The aqueous solution was finally concentrated *in vacuo*, and the resulting brownish crystals were filtered off and dried. Yield: 7.08 g (89 %). – ^{1}H NMR ([D$_6$]DMSO): δ = 11.45 (br s, 1H, N*H*), 10.40 (s, 3H, N*H*$_3$), 7.69 (d, 1H, CH-C*H*-C, J = 8.1 Hz), 7.51 (d, 1H, NHC*H*, J = 2.7 Hz), 7.45 (d, J = 8.2 Hz, 1H, CH-C*H*-C), 7.19 (ddd, 1H, CHC*H*CH, J = 8.2/7.1/1.1 Hz, 1H), 7.10 (ddd, 1H, CHC*H*CH, J = 8.1/7.1/1.0 Hz) ppm. – ^{13}C NMR ([D$_6$]DMSO): δ = 134.59, 122.25, 121.28, 119.39, 119.09, 117.67, 112.06, 106.84 ppm. All spectroscopic data are in agreement to those reported in the literature [33].

Nucleophilic ring transformation of the pyrylium salts ***15a, b*** *to the pyridinium salts* ***16a, b***

A solution of 0.5 g (2.97 mmol) of 1*H*-indol-3-amine hydrochloride, 1.292 g (3.26 mmol) of 2,4,6-triphenylpyrylium tetrafluoroborate or 0.685 g (3.26 mmol) of 2,4,6-trimethylpyrylium-tetrafluoroborate and 0.468 g (5.93 mmol) of sodium acetate in 40 mL of ethanol was heated at reflux temperature over a period of 24 h and then evaporated to dryness. The resulting residue was then dissolved in ethanol to give a concentrated solution which was poured into diethyl ether at 0 °C. The resulting solid was filtered off and dried.

*1-(1H-Indol-3-yl)-2,4,6-trimethylpyridinium tetrafluoroborate (**16a**)*

The crude product contained impurities. All attempts to recrystallize the salt caused decomposition so that a full characterization failed. – ^{1}H NMR ([D$_6$]DMSO): δ = 12.43 (s, 1H, N*H*), 7.98 (s, 2H, 3′/5′-*H*), 7.84 (s, 1H, NH-C*H*), 7.62 (d, 1H, Ar-*H*, J = 8.4 Hz), 7.29 (m, 2H, Ar-*H*), 7.15 (m, 1H, Ar-*H*), 2.63 (s, 3H, Me), 2.36 (s, 6H, Me) ppm. – MS ((+)-ESI): m/z = 237$[M]^+$.

*1-(1H-Indol-3-yl)-2,4,6-triphenylpyridinium tetrafluoroborate (**16b**)*

Yield: 1.39 g (92 %); m. p. 271 °C. – ^{1}H NMR ([D$_6$]DMSO): δ = 11.87 (s, 1H, N*H*), 8.66 (s, 2H, 3′/5′-*H*), 8.38 (d, 2H, Ar-*H*, J = 7.1 Hz), 7.72 – 7.64 (m, 3H, Ar-*H*), 7.53 (s, 1H, Ar-*H*), 7.49 (d, J = 6.9 Hz, 4H, Ar-*H*), 7.42 (d, 1H, Ar-*H*, J = 7.9 Hz), 7.33 – 7.18 (m, 7H, Ar-*H*), 7.00 (dd, 1H, Ar-*H*, J = 7.4/7.4 Hz), 6.93 (dd, 1H, Ar-*H*, J = 7.4/7.4 Hz) ppm. – ^{13}C NMR ([D$_6$]DMSO): δ = 158.02, 155.31, 133.46, 133.37, 133.30, 132.46, 129.84, 129.65, 128.91, 128.82, 127.72, 126.02, 125.19, 122.81, 122.10, 120.36, 116.99, 115.35, 112.03 ppm. – ATR-IR: ν = 3364, 1619, 1575, 1412, 1241, 1053, 764, 748, 699, 648, 621, 530, 429 cm^{-1}. – MS ((+)-ESI): m/z = 423.1 $[M]^+$. – HRMS ((+)-ESI): m/z = 423.1857 (calcd. 423.1861 for $[C_{31}H_{23}N_2]^+$).

*3-(2,4,6-Triphenylpyridinium-1-yl)-indol-1-ide (**17**)*

A sample of 250 mg (0.59 mmol) of the salt **16b** was dissolved in a solution of 33 mg (0.59 mmol) of KOH in 10 mL of MeOH. After 10 min at r. t. with stirring the solution was treated with 20 mL of water whereupon a dark-green solid formed which was filtered off, washed with small amounts of cold water, and dried *in vacuo*. Yield: 184 mg (74 %); m. p. 249 °C. – ^{1}H NMR ([D$_6$]DMSO): δ = 8.63 (s, 2H, 3′/5′-*H*), 8.37 – 8.32 (m, 2H, Ar-*H*), 7.72 – 7.64 (m, 3H, Ar-*H*), 7.52 – 7.46 (m, 5H, Ar-*H*), 7.41 (d, 1H, Ar-*H*, J = 7.9 Hz), 7.32 – 7.21 (m, 7H, Ar-*H*), 7.04 – 6.98 (m, 1H, Ar-*H*), 6.97 – 6.91 (m, 1H, Ar-*H*) ppm. – ^{13}C NMR ([D$_6$]DMSO): δ = 157.99, 155.39, 133.44, 133.32, 132.49, 129.89, 129.68, 128.89, 128.77, 127.75, 126.05, 125.19, 122.85, 122.24, 120.47, 116.99, 115.44, 112.05 ppm. – ATR-IR: ν = 1619, 1549, 1240, 1055, 888, 764, 748, 699, 530, 430 cm^{-1}. – MS ((+)-ESI): m/z (%) = 423.1 (100) $[M+H]^+$. – HRMS ((+)-ESI): m/z = 423.1864 (calcd. 423.1861 for $[C_{31}H_{23}N_2]^+$).

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