Synthesis of Substituted Diazoniapentaphene Salts by an Unexpected Rearrangement-Cyclodehydration Sequence

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Dedicated to Professor Werner Mormann on the occasion of his 60th birthday

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The cyclodehydration of bis(pyridiniummethyl)methylbenzenes **3a**–**b** in polyphosphoric acid leads to methyl-substituted diazoniapentaphene salts **4a**–**b** instead of linear diazoniapentacene derivatives, while the 1,3-bis(pyridiniummethyl)bromobenzene **3d** forms a semi-betaine 4a,12a-diazoniapentaphen-14-olate **4d** under these conditions. The mechanistic details of this rearrangement–cyclodehydration sequence may be explained by an intramolecular *ipso*-addition to the substituted benzene moiety, followed by an [1,2]-methyl shift in case of **4a**–**b** or HBr elimination in case of **4d**. The proposed mechanism was confirmed by the isolation of the intermediate hydroxy derivative **10b** from the cyclization of **3a** in refluxing HBr and conversion of **10b** to the final product **4a** by dehydration in polyphosphoric acid. Electronic absorption and fluorescence properties of the previously unknown diazoniapentaphene salts have been studied. Photophysical properties of **4a**–**b** resemble the ones of the parent diazoniapentaphene salts, while semi-betaine **4d** possesses a red-shifted absorption and fluorescence maxima, along with significant solvatochromism with respect to the absorption properties.

Introduction

The synthesis of heterocyclic polyaromatic compounds is still an important goal in organic chemistry, since such aromatic heterocycles represent useful lead structures in bioorganic chemistry and materials science.[1] Along with azinium and azolium salts, quinolizinium ions and their annelated derivatives represent an interesting, but relatively unexplored class of heteroaromatic compounds with a quaternary bridgehead nitrogen atom.[2] The quinolizinium moiety represents a key structural feature in natural products,[3] antitumor compounds,[4] and also constitutes a promising lead structure for DNA intercalators.[5] Recently, these heterocycles have been proposed for use in optical information storage materials and photochromic switches.[6] Although many standard protocols are known for the synthesis of azoniaaromatics such as quinolizinium derivatives,[7] even simple variations in the structure of the starting material may lead to the formation of unexpected main products.

Our initial intention was to synthesize diazoniapentacene derivatives **1a**–**b** in order to study their DNA-binding and DNA-photodamaging properties and compare them with the ones of annelated quinolizinium derivatives.[5] Recently, we have shown that dicationic 12a,14a-diazoniapentaphene **2** binds to the double-stranded DNA with a binding constant almost an order of magnitude higher than singly charged benzoquinolizinium salts and exhibits DNA-photodamaging activity.[8]

According to the well-established cyclodehydration method of Bradsher,[7] we proposed that the bis(pyridinium) derivatives **3a**–**b** may be appropriate precursors for the synthesis of **1a** and **1b** (Scheme 1). It has been observed already in 1964[9] and confirmed recently[10] that the cyclization of the salt **3c** with an unsubstituted benzene moiety leads to formation of the angular 4a,12a-diazoniapentaphene **4c** instead of the desired diazoniapentacene. Therefore, we have introduced methyl substituents as protecting groups in the benzene moiety to avoid the formation of angular derivatives. In a similar approach, these positions have been blocked by methoxy or acetoxy substituents; however, in these cases, due to hydrolytic cleavage of the ether or ester bonds, followed by subsequent aerobic oxidation, the corresponding diazoniapentacene-6,13-diones have been obtained, which could not be reduced to the target diazoniapentacenes.[11] Surprisingly, we have found that the substituted diazoniapentaphene derivatives **4a**–**b** are formed by a twofold acid-catalyzed cyclodehydration of **3a**–**b** via an

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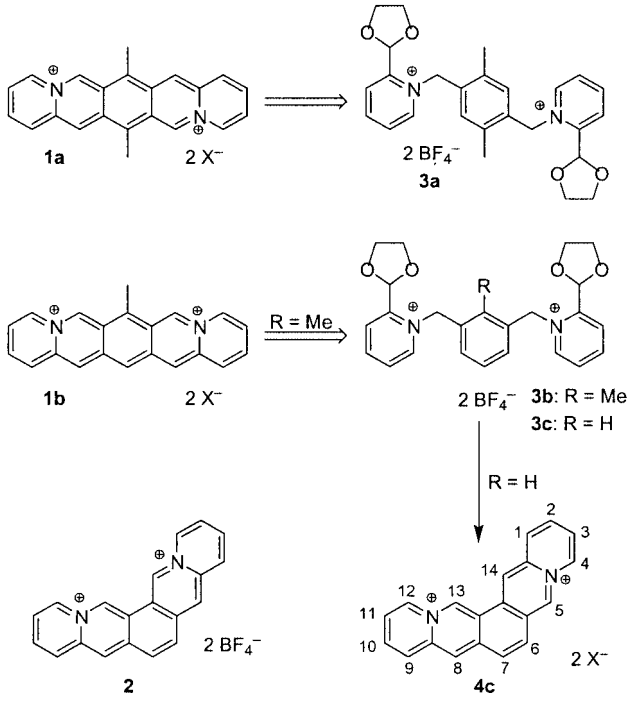
intramolecular aromatic *ipso*-substitution followed by a Wagner–Meerwein migration of a methyl group. In this paper we describe our investigations, which include some mechanistic details on this rearrangement-mediated cyclodehydration as well as UV/Vis and fluorescence spectroscopic data of the new diazoniapentaphenes.



Scheme 1.

Results and Discussion

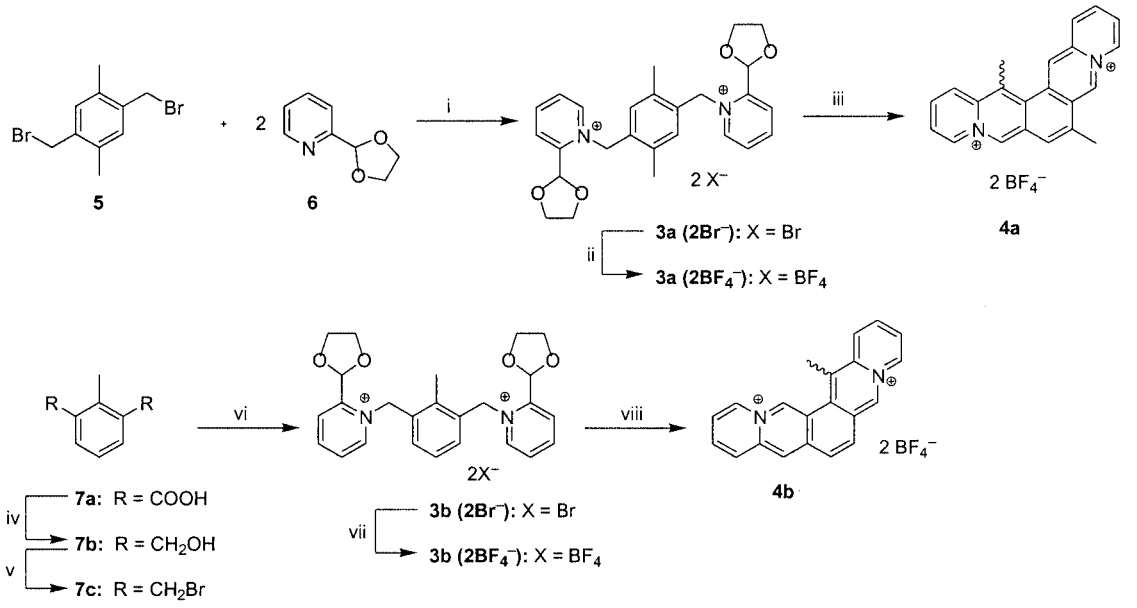
Synthesis

The bis(pyridiniummethyl)benzene derivatives **3a**–**b** were obtained according to Scheme 2. The bis(bromomethyl)arenes **5** and **7c** were treated with excess of 2-(1′,3′-dioxolan-2′-yl)pyridine (**6**). *N*-Methyl-2-pyrrolidone (NMP) is a superior solvent for this twofold quaternization, giving nearly quantitative yields in all cases. The bromide ion in **3a**–**b** was exchanged with tetrafluoroborate to avoid a competing nucleophilic substitution reaction during the second cyclodehydration step.[10,12] Nevertheless, cyclodehydration of **3a (2BF$_4^-$)** in polyphosphoric acid (PPA) at 150 °C gave a single product in 30% yield whose NMR spectra were not consistent with the structure of the diazoniapentacene **1a**. Thus, 12 non-equivalent low-field shifted aromatic ^{1}H NMR signals and 20 non-equivalent ^{13}C NMR signals, as well as two independent signals for the methyl groups, were detected. In addition, ESI mass spectrometry and elemental analysis revealed that the product is a constitutional isomer of **1a**. The lack of symmetry already indicated a pentaphene structure rather than a pentacene skeleton. In fact, X-ray-diffraction analysis showed that the 6,13-dimethyl-4a,8a-diazoniapentaphene **4a** was formed as reaction product. Notably, due to steric repulsion with the neighboring hydrogen atoms the methyl substituent in position 13 points towards one of the enantiotopic faces of the aromatic plane with a deviation angle of about 13°. Thus, **4a** is a chiral compound and is formed as a racemate that crystallizes in the space group $P\bar{1}$, with one single crystal containing both enantiomers in a 1:1 ratio (see part A in Figure 1). It is noteworthy that the distance between the ring planes of the neighboring enantiomeric cations is close to 3.7 Å, presumably due to π stacking (Figure 1, B). The cations overlap with more than half of the area of their aromatic core. Since the methyl groups at C13 point into opposite directions within such a pair, the distances between the C8 and C13′ atoms are somewhat larger (3.9 Å).

Similarly to the reaction of **3a**, the cyclodehydration of **3b (2BF$_4^-$)** under the same conditions (PPA, 150 °C, 24 h) gave the 14-methyl-4a,12a-diazoniapentaphene **4b** in 51% yield (Scheme 2). Its structure was elucidated on the basis of NOE effects between the methyl group and 13-H, the ^{1}H NMR signal of which is strongly downfield-shifted (δ = 10.52 ppm), since C13 is directly bound to the positively charged nitrogen (N12a) atom (Figure 2). NOE interactions between 6-H and 7-H, the signals of which are shifted to relatively high field (δ = 8.25 and 8.19 ppm), and the neighboring 5-H and 8-H atoms, respectively, also confirmed the assignment of the structure of **4b**.

To investigate the versatility of this rearrangement, we have prepared compound **3d** in which the methyl group was replaced by a bromine substituent (Scheme 3). After the cyclization step at the conditions previously employed, a purple product was isolated in 56% yield which, at first glance, was different from the weakly yellow salts **4a**–**b**. However, NMR spectra of the product showed 13 non-equivalent low-field ^{1}H signals and 20 distinct ^{13}C signals, which were consistent with an unsymmetric monosubstituted diazoniapentaphene structure. While NMR spectroscopy did not give unambiguous information about the nature of the substituent, in ESI mass spectra only a single peak with an *m*/*z* value of 297 was observed.[13] This ion mass as well as the isotopic pattern was not consistent with a bromo-substituted derivative. On the basis of mass spectra and elemental analysis, we have assigned the structure of semi-betaine **4d** to the product. This structure is further supported by a ^{13}C NMR signal at δ = 164.3 ppm at C14, which is characteristic for pyridinium-3-olates[14] and by an IR band at $\tilde{\nu}_{max}$ = 1552 cm^{-1}, which is typical of a phenolate C–O$^-$ bond. This structure assignment is in accordance with the observations that under neutral or alkaline conditions 11-hydroxybenzo[*b*]quinolizinium forms a betaine, the electronic spectra of which resemble those of compound **4d**.[15]

In contrast, an attempt to cyclize the bis-pyridinium salt **3e** derived from 2,6-bis(bromomethyl)trifluoromethylbenzene **9** under the similar conditions (PPA, 160 °C, 48 h) gave only an non-separable mixture of unidentified products. The cyclization of **3e** in methanesulfonic acid under slightly milder conditions (120 °C, 3 h) gave presumably a product of mono-cyclization which, however, could not be obtained in pure form. Apparently, the strong electron-acceptor



Scheme 2. Reagents and conditions: (i) NMP, room temp., 7 days (95%); (ii) aq. $NaBF_4$ (92%); (iii) PPA, 150 °C, 24 h (30%); (iv) BF_3·THF, THF, 0 °C → room temp., 18 h (92%); (v) aq. HBr (48%), 50 °C, 1 h (85%); (vi) **6**, NMP, room temp., 2 days (96%); (vii) aq. $NaBF_4$ (93%); (viii) PPA, 150 °C, 24 h (51%).

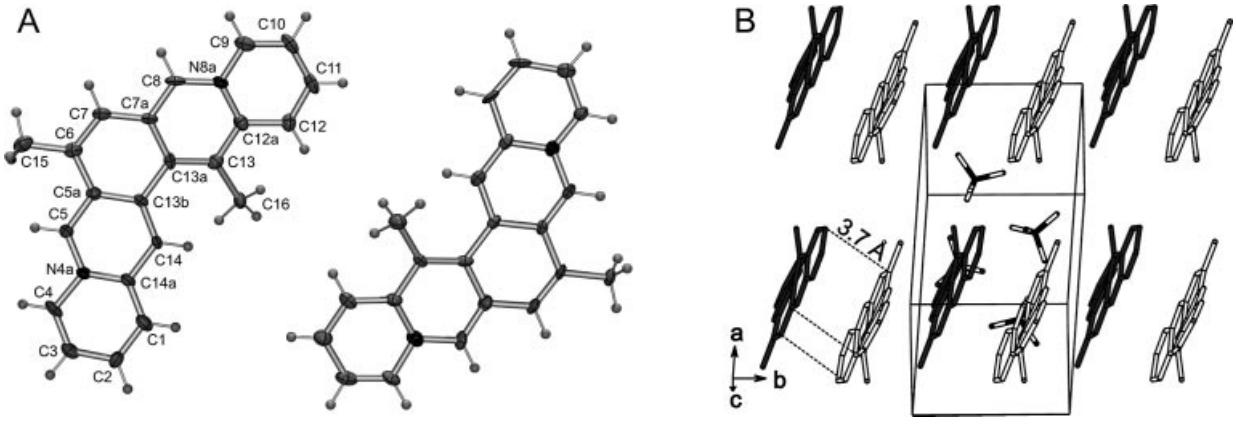


Figure 1. (A) The molecular structure (ORTEP view) of an enantiomeric pair of **4a** in the solid state. The thermal ellipsoids for non-H atoms are shown with 50% probability. (B) Crystal packing of **4a** extending along the *b* axis. The hydrogen atoms and selected BF_4^- anions have been omitted for clarity. Enantiomers are shown in different colors.

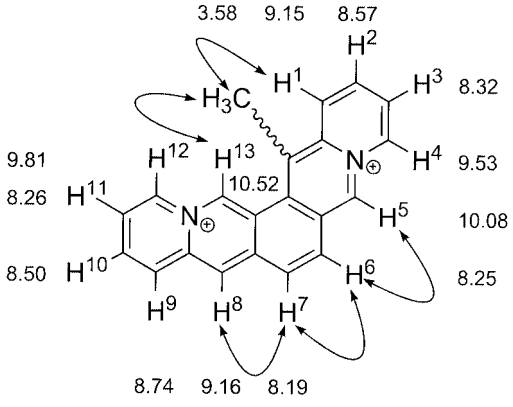
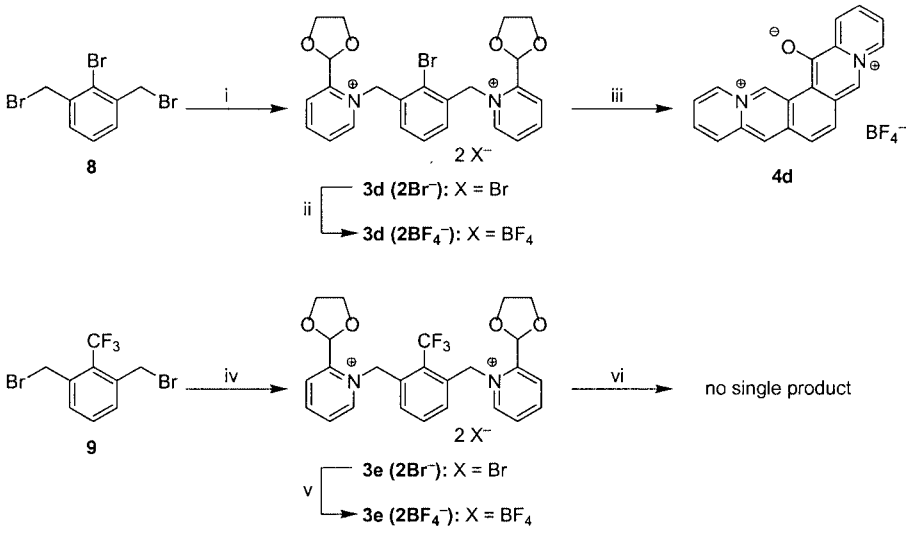


Figure 2. ^1H NMR shifts and characteristic NOE effects in **4b**.

property of the trifluoromethyl group deactivates the benzene ring and suppresses the *ipso*- and *ortho*-substitution, so that electrophilic substitution to give the angular pentaphene derivative and the linear pentacene derivative does not take place.

Mechanism of the Cyclodehydration of 3a, 3b, and 3d

The formation of the diazoniapentaphene derivatives **4a**–**b** may be rationalized by a cyclodehydration which involves an *ipso*-addition of the protonated aldehyde group followed by a methyl migration. Thus, after aldehyde deprotection and the first cyclodehydration sequence, the benzo[*b*]quinolizinium derivative **10a** is the proposed intermediate (Scheme 4). Apparently, the methyl groups do not protect

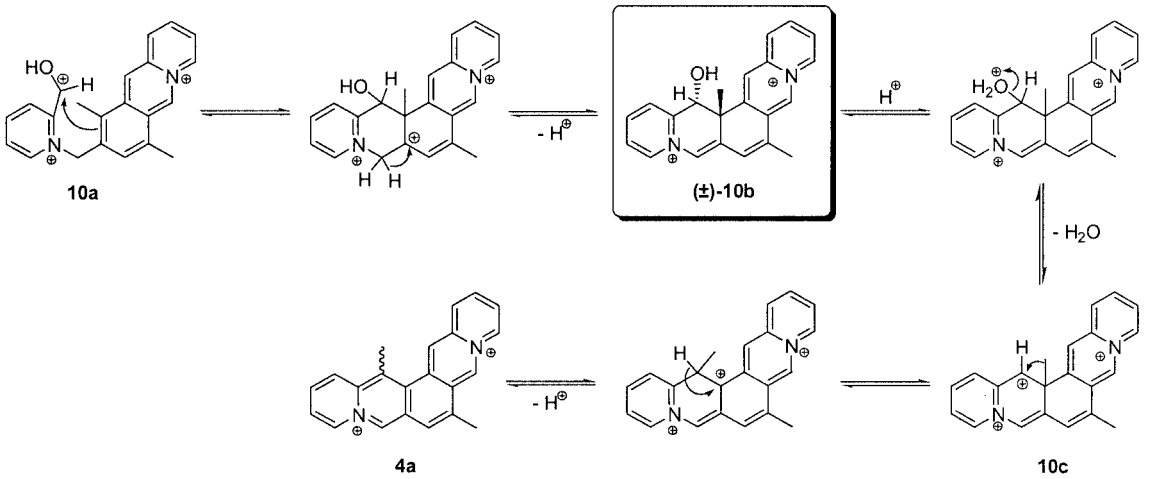


Scheme 3. Reagents and conditions: (i) **6**, NMP, room temp., 7 days (91%); (ii) aq. $NaBF_4$ (80%); (iii) PPA, 150 °C, 72 h (56%); (iv) **6**, NMP, room temp., 7 days (72%); (v) aq. $NaBF_4$ (75%); (vi) PPA, 160 °C, 48 h.

these positions from electrophilic *ipso* addition, so that an angular annelation takes place along with subsequent deprotonation to give the intermediate **10b**. Although there are only few examples for an *ipso* substitution of an *ortho*-alkyl group in the presence of a second hydrogen-substituted *ortho'* position,[16] this addition is in agreement with theoretical and experimental studies which show that benzo[*b*]quinolizinium derivatives exhibit a significantly higher reactivity towards electrophiles at positions 7 and 10 as compared to positions 8 and 9.[7c] Thus, sulfonation and bromination of the benzo[*b*]quinolizinium cation are reported to occur at position 10,[17] whereas chlorination results in the 7,10-disubstituted product.[18] Under the employed acidic conditions, the hydroxy functionality is protonated and water acts as a leaving group to give the cation **10c**. Finally, a Wagner–Meerwein [1,2]-methyl migration followed by deprotonation leads to a fully aromatic diazoniapentaphene. Although alkyl migrations are observed extremely rarely upon aromatic *ipso* substitution,[19] the energetically favorable aromatization is probably the driving force for this methyl shift. The proposed mechanism is supported by the isolation of intermediate **10b (2BF$_4^-$)**, which was formed when the dibromide salt **3a** was cyclized under slightly milder reaction conditions, i.e. in refluxing aq. HBr (48%). Although compound **10b** was isolated in rather low yield (35%), the ^{1}H NMR spectrum of the crude product, obtained by precipitation of the reaction mixture with acetone, did not reveal the presence of any side products. This indicates that the competing nucleophilic substitution of the pyridinium residue with bromide does not take place under these conditions.

The structure of **10b (2BF$_4^-$)** is confirmed by ^{1}H- and ^{13}C NMR, mass-spectrometric and elemental analyses. Especially characteristic is the coupling of the hydroxyl proton with 13-H [^3J(H,H) = 4.7 Hz] and the NOE effect between the latter and the methyl group at C13a.

Compound **10b** has two stereogenic centers, and therefore the formation of four stereoisomers is possible. How-



Scheme 4. Mechanism of formation of **10b** and **4a**.

ever, NMR spectra give evidence that only one diastereomer (as a racemate) has formed. Indeed, the integration of NOE spectra showed that the distance between 13-H and the methyl group at C13a is consistent with the structure of the *anti*-isomer shown on Scheme 4. This structure was further confirmed by the X-ray diffraction analysis (Figure 3, A). Thus, the racemate of *anti*-**10b** crystallizes in the chiral space group $P2_1/n$ as a crystalline hydrate containing one water molecule per cation and forming ordered layers of enantiomers (Figure 3, B).

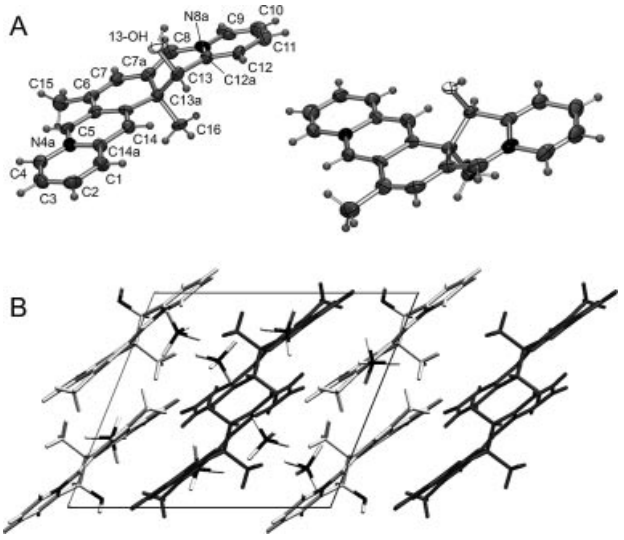


Figure 3. (A) The molecular structure (ORTEP view) of the enantiomeric pair of **10b** in the solid state. The thermal ellipsoids for non-H atoms are shown with 50% probability. (B) Crystal packing of **10b** extending along the *c* axis. Selected BF_4^- anions and water molecules have been omitted for clarity. Enantiomers are shown in different colors.

The proposed mechanism in Scheme 4 is further supported by the fact that dehydration of **10b** in PPA at 150 °C gives the product **4a** in high yield (91%), without formation of any side products.

At the moment, no explanation for the medium effect of acid employed can be provided. It is noteworthy that a related effect was observed in the acid-mediated rearrangements of dienones, such as 10-methyl-2-keto-$\Delta^{1:9,8:4}$-hexahydronaphthalene.[20] However, in that case, aqueous HBr induced a single [1,2]-methyl shift, while the use of the vigorously hygroscopic medium (H_2SO_4 in acetic anhydride) resulted in several consecutive electrophilic rearrangements. In contrast, upon treatment of **3a** with aq. HBr the methyl shift does not take place, and the reaction provides the intermediate **10b**.

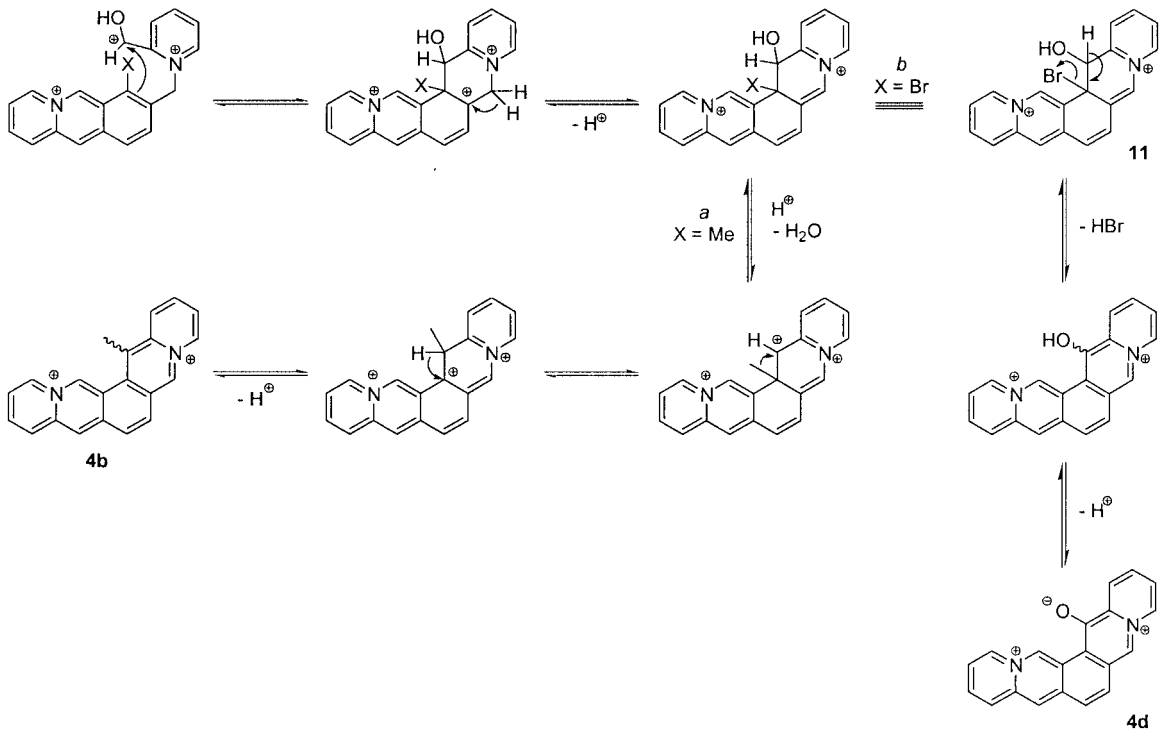
In the case of the formation of **4b**, a similar mechanism is likely to take place (Scheme 5, path *a*); however, with a bromo substituent the aromatization takes place from intermediate **11** by HBr elimination (Scheme 5, path *b*). Obviously, the hydroxy group bound to a doubly charged aromatic system is acidic enough to be deprotonated, giving the semi-betaine **4d** as a final product.

Electronic Spectra of Diazoniapentaphene Derivatives

Diazoniapentaphene salts are known to have strong absorption in the UV region of the electromagnetic spectrum and significant fluorescence properties.[9] To study the effect of the substituents on their electronic spectra, we have compared the spectral properties of the compounds **4a**–**b** with those of the unsubstituted diazoniapentaphenes. Absorption spectra of **4a** and **4b** (Figure 4) resemble the ones of the parent compounds and confirm the assignment of diazoniapentaphene structure to these compounds. Absorption spectra consist of several strong *p*- and *β*-absorption bands in the UV region ($\varepsilon_{max} > 4 \times 10^4$ cm^{-1} M^{-1}) and much weaker *α*-bands in the visible region (400–500 nm). However, derivative **4a** shows much less pronounced fine structure in the UV region than the parent compound (Figure 4, A). This confirms the deviation from the planar structure, as it had been shown for methyl-substituted phenanthrenes.[21] In case of derivative **4b**, this effect is less pronounced (Figure 4, B).

Compounds **4a**–**b** are strongly fluorescent in most solvents, such as water, alcohols and acetonitrile (Table 1). The fluorescence emission spectra resemble the ones of the parent diazoniapentaphenes, while introduction of two methyl groups in **4a** leads to a bathochromic shift of the emission maximum of about 25 nm and reduction of the vibrational structure as compared to the unsubstituted analogue. At the same time, the introduction of one methyl group in **4b** results in a bathochromic shift of only 7 nm, and the shape of the emission spectrum is identical with that of **4c**. The largest fluorescence quantum yields are observed in water solution (Φ_F = 0.32 and 0.41 for **4a** and **4b**, respectively). They are about 20% smaller than the values for the unsubstituted diazoniapentaphene salts (Φ_F = 0.38 for 4a,8a-diazoniapentaphene and 0.50 for 4a,12a-diazoniapentaphene in aqueous solutions, the latter being determined with authentic samples). In contrast, in dimethyl sulfoxide (DMSO) the fluorescence is strongly quenched (Φ_F = 0.01–0.03 for unsubstituted and methyl-substituted diazoniapentaphenes), and the emission spectra are structureless. A similar decrease of fluorescence in DMSO was observed for the related 3a,9a-diazaperylenium dication[23] as well as for benzo[*b*]quinolizinium salts,[24] and it was correlated with the high electronic donor strength of this solvent in combination with the low reduction potential of the chromophore.[24]

Notably, compound **10b**, where the fused aromatic system is disrupted by two methylene groups, also shows reasonably strong UV absorption and fluorescence properties. Thus, its structureless, broad long-wavelength absorption band is located at 386 nm and has log ε = 4.29 (Figure 5). The fluorescence emission spectrum is also very broad with a maximum centered at around 480–500 nm. As in the case of the diazoniapentaphenes, the fluorescence intensity is strongest in aqueous solution (Φ_F = 0.21), whereas in DMSO it is essentially quenched ($\Phi_F < 0.01$). The absorption and emission maxima are comparable to the ones of the protonated 1-pyridyl-4-phenylbutadienes.[25] Thus, with



Scheme 5. Mechanism of formation of **4b** and **4d**.

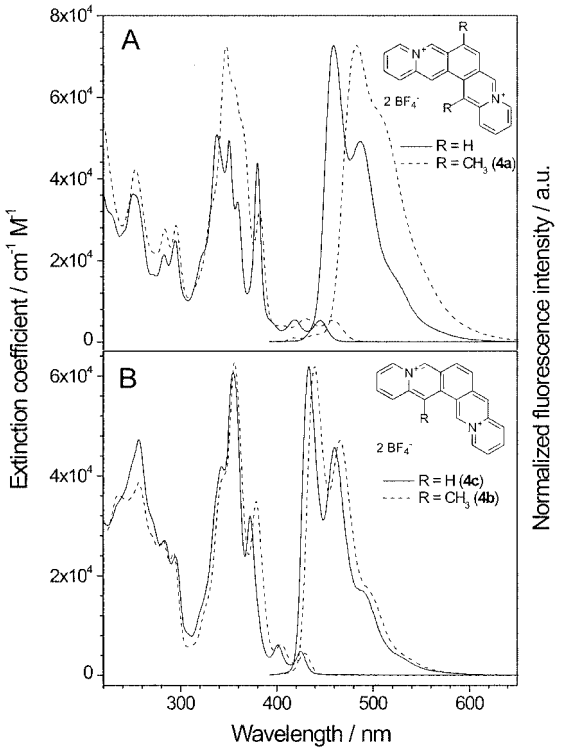


Figure 4. (A) Absorption (left part) and normalized fluorescence emission (right part, λ_{ex} = 380 nm in all cases) spectra of 4a,8a-diazoniapentaphene bis(tetrafluoroborate) (solid line) and of compound **4a** (dashed line) in water. (B) Absorption (left part) and normalized fluorescence emission (right part) spectra of 4a,12a-diazoniapentaphene bis(tetrafluoroborate) **4c** (solid line) and its 14-methyl derivative **4b** (dashed line) in water.

Table 1. Fluorescence properties of diazoniapentaphenes **4a**–**b**.

Solvent[a]	**4a**		**4b**	
	λ_{max}[b]	Φ_F[c]	λ_{max}[b]	Φ_F[c]
DMSO	523	0.02	469	0.03
Acetonitrile	485	0.24	442 468	0.21
Ethanol	– [d]	– [d]	443 470	0.15
Methanol	487	0.26	442 469	0.26
Water	483	0.32	440 466	0.41

[a] In order of their increasing E_T^N values.[22] [b] Fluorescence emission maximum, nm, c(**4**) = 5 μM; excitation wavelength λ_{ex} = 380 nm for all compounds. [c] Fluorescence quantum yield relative to Coumarin 1, estimated error ± 10%. [d] Not determined.

respect to the electronic transitions, **10b** may be regarded as a bridged diarylbutadiene derivative, whereas the conformational restrictions exclude the photoisomerisation, consequently enhancing the quantum yield of fluorescence.

Electronic absorption spectra of the semi-betaine **4d** in most solvents consist of a broad band of moderate intensity (log $\varepsilon \approx 4.0$) at 460–490 nm and a stronger (log $\varepsilon \approx 4.4$–4.6), somewhat structured band in the UV region of the spectrum.[26] In contrast to the diazoniapentaphenes **4a**–**c**, which exhibit only negligible solvatochromism, the positions and intensities of absorption bands of **4d** are strongly solvent-dependent (see part A of Figure 6 and Table 2). Moreover, the energy of the long-wavelength transition shows an almost linear correlation with the Gutmann's acceptor number (AN)[22] of the solvent (r = 0.993, Figure 6,

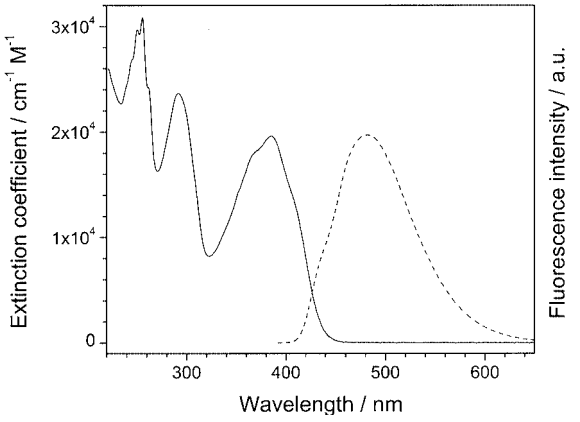


Figure 5. Absorption (solid line) and normalized fluorescence emission (dashed line) spectra of **10b** in water. Excitation wavelength λ_{ex} = 380 nm.

B) as well as with the Swain's "acity" parameter *A* (r = 0.996, data not shown), thus illustrating the ability of the solvent to interact with the negative charge localized at the oxygen atom. Thus, the long-wavelength band undergoes a hypsochromic shift by 30 nm when changing form acetone (AN = 12.5) to water (AN = 54.8). Unfortunately, the limited solubility of **4d** in solvents with lower AN values excluded investigations therein. As an extreme case, in trifluoroacetic acid (TFA; AN = 105.3) the spectrum loses the aforementioned structure completely and attains a typical aromatic character, similar to that of unsubstituted diazoniapentaphenes, with a structured β-band (λ_{max} = 266 nm) and α-band (430 nm; S_0–S_1 transition). To a certain extent the latter overlaps with the strongest *p*-band (λ_{max} = 357 nm). We assume that this spectrum represents the fully protonated dicationic form of **4d**. This drastic change, however, is not observed either in acetic acid or in water, indicating that the acidity is less important for the stabilization of the semi-betaine **4d** than the overall electrophilic properties characterized by the value of AN. Thus, acetic acid is more acidic than water, however, the spectrum is more blue-shifted in water as compared to acetic acid. Addition of e.g. perchloric acid to aqueous solutions of **4d** does not result in such a severe effect as neat TFA, either.

Salt **4d** exhibits weak orange-red fluorescence in most solvents, with a broad emission band centered at 620–660 nm (Table 2) and quantum yields in the range of 0.03 to 0.07. Similar to the absorption maxima, the emission maxima are solvent-dependent, but do not show any evident correlation with the empiric solvent parameters (solvent polarity function E_T^N, donor- or acceptor numbers). In trifluoroacetic acid, dual fluorescence is observed, with a structured part located at 420–480 nm (blue emission) and a broader band at 580–600 nm (red emission). We attribute the blue emission, similar to that of diazoniapentaphenes, to the fully protonated dicationic form of **4d**. The red emission, observed in all solvents investigated including TFA, is attributed to the electronic charge-transfer (CT) from the phenolate oxygen to the diazoniapentaphene core. The CT character of this emission is supported by the broadness of

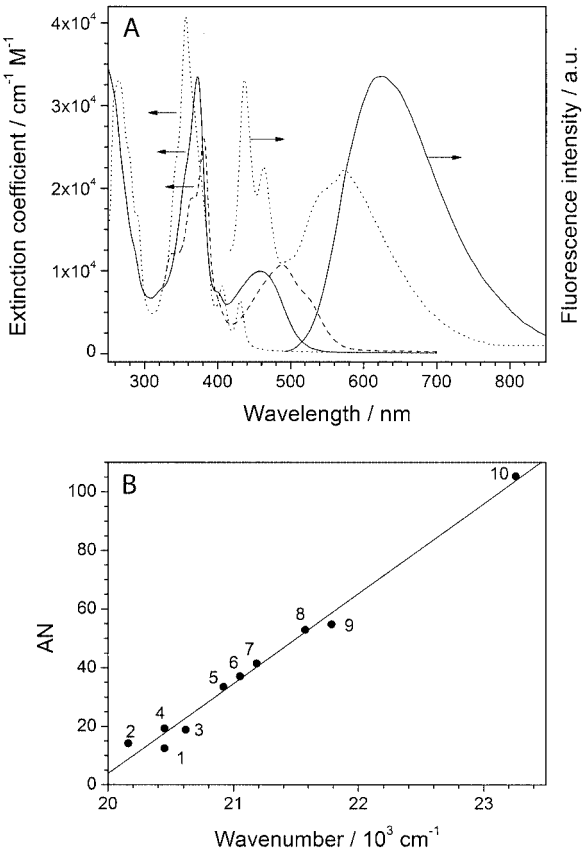


Figure 6. (A) Absorption (left part) and normalized fluorescence emission (right part) spectra of 4a,12a-diazoniapentaphene-14-olate tetrafluoroborate **4d** in water (solid lines), acetone (dashed line) and trifluoroacetic acid (dotted lines). Experimental conditions see footnotes to Table 2. (B) Correlation of the position of the lowest-energy absorption band of **4d** with the donor number of the solvent: (1) acetone, (2) pyridine, (3) acetonitrile, (4) DMSO, (5) 2-propanol, (6) ethanol, (7) methanol, (8) acetic acid, (9) water, (10) TFA.

the fluorescence band ($\Delta\lambda_{1/2} \approx 140$ nm) and large Stokes shift values (140–180 nm).

In summary, we have shown that diazoniapentacene derivatives are not available by the established cyclodehydration route. Instead, the corresponding diazoniapentaphene derivatives are formed, even when the positions for electrophilic addition are blocked by methyl or bromo substituents. Moreover, we elucidated the reaction mechanisms by the isolation of a reaction intermediate. We showed that one of the reaction products, namely the betaine-like derivative **4d** exhibits solvatochromic absorption properties and a relatively large Stokes shift, which represents a useful feature for optical sensors. Further studies along these lines are presently under investigation.

Experimental Section

All commercially available chemicals were reagent grade and used without further purification. Solvents were purified and dried according to standard procedures. The melting points were measured with a melting point apparatus (Büchi 510K) and are uncorrected.

Table 2. Solvatochromic properties of compound **4d**.

Solvent[a]	λ_{abs}[b] (log ε[c])	λ_{em}[d]	Φ_F[e]
Acetone	338 (sh[f]) 365 (4.27) 381 (4.42) 489 (4.03)	650	3.9×10^{-2}
Pyridine	343 (4.00) 369 (4.11) 387 (4.25) 496 (3.97)	634	7.1×10^{-2}
Acetonitrile	335 (4.13) 363 (sh) 380 (4.41) 485 (4.03)	641	2.8×10^{-2}
DMSO	337 (sh) 370 (4.23) 385 (4.31) 406 (sh) 489 (3.90)	667	3.3×10^{-2}
2-Propanol	380 (4.31) 403 (sh) 478 (3.87)	635	4.4×10^{-2}
Ethanol	334 (sh) 379 (4.37) 402 (sh) 475 (3.94)	642	5.4×10^{-2}
Methanol	378 (4.35) 400 (sh) 472 (3.90)	644	6.5×10^{-2}
Acetic acid	376 (4.51) 464 (3.95)	629	3.8×10^{-2}
Water	373 (4.52) 400 (sh) 459 (4.00)	626	3.0×10^{-2}
Trifluoroacetic acid	266 (4.52) 357 (4.61) 406 (3.92) 430 (3.81)	437[g] 463 573	[h]

[a] In order of their increasing AN value.[27] [b] Absorption maximum, nm, c(**4d**) = 50 μM. [c] Molar decadic extinction coefficient (cm^{-1} M^{-1}). [d] Fluorescence emission maximum, nm, c(**4d**) = 10 μM; excitation wavelength λ_{ex} = 480 nm. [e] Fluorescence quantum yield relative to Cresyl Violet, estimated error ± 10%. [f] Shoulder. [g] Excitation wavelength λ_{ex} = 405 nm. [h] Not determined.

Mass spectra (ESI in the positive-ion mode) were recorded with a Finnigan LCQ Deca instrument (source voltage 6 kV). NMR spectra were measured on a Bruker AC200 (^{1}H: 200 MHz, ^{13}C: 50 MHz) and Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) spectrometer at 20 °C; chemical shifts are given in ppm (δ) values (internal standards TMS for ^{1}H- and ^{13}C NMR spectroscopy and hexafluorobenzene, δ_F = –162.8 ppm, for ^{19}F NMR spectroscopy). Infrared spectra were obtained with a Perkin–Elmer 1750 Fourier-transform spectrometer in KBr pellets; only significant frequencies are given. Elemental microanalyses of all new compounds were performed by Mr. H. Bodenstedt (Institut für Organische Chemie, University of Siegen).

The following compounds were obtained according to the published procedures: 2-(1,3-dioxolan-2-yl)pyridine (**6**),[28] 2-methylisophthalic acid (**7a**),[29–31] 1-bromo-2,6-bis(bromomethyl)benzene (**8**),[32] 2,6-bis(bromomethyl)trifluoromethylbenzene (**9**).[33] Repeated attempt to prepare 1,4-bis(bromomethyl)-2,5-dimethylbenzene (**5**) by bromomethylation of *p*-xylene in 48% aq. HBr[34] gave maximum 40% yield in contrast to 97% yield claimed by the authors. We have found that reaction with 33% HBr in glacial acetic acid gives better yield of this product.[35]

Although compound **7b** was previously prepared by esterifiction of the 2-methylisophthalic acid followed by reduction of the diester with lithium aluminium hydride,[29,31] or by two-step reduction of 2,6-dicyanotoluene,[36] we have chosen to reduce the acid **7a** directly by the action of borane–THF complex.[37] Indeed, this reduction procedure has proved to be less laborious and gave the desired product in 92% yield, thus improved with respect to the 87% obtained by the two-step sequence.

4a,12a-Diazoniapentaphene **4c** and 4a,8a-diazoniapentaphene bis(tetrafluoroborates)[9,10] were prepared from 1,4- and 1,3-bis(bromomethyl)benzenes, respectively, following the general procedures (vide infra). The overall yields over 3 synthetic steps were 47 and 48%, correspondingly; spectroscopic data were in agreement with those given in ref.[10].

2,6-Bis(hydroxymethyl)toluene (7b): A solution of 2-methylisophthalic acid **7a** (7.21 g, 40.0 mmol) in dry THF (100 mL) was cooled to 0 °C and deoxygenated by passing a stream of argon. To a stirred solution, borane (100 mL of 1 M THF complex, 100 mmol) was added dropwise under argon atmosphere within 4 h, whereas the reaction mixture has turned into a jelly-like bulk. After 18 h at room temperature, water (100 mL) was added carefully. After hydrogen evolution has ceased, the solution was saturated with solid potassium carbonate. The organic layer was separated; the aqueous layer was extracted with diethyl ether (3 × 30 mL) and the combined organic layers were washed with water and dried over anhydrous magnesium sulfate. After removal of the solvents in vacuo, **7b** (5.60 g, 92%) was obtained as a white solid, m.p. 116–118 °C (ref.[29,36] 122–124 °C), which was used without further purification. ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 2.15 (s, 3 H, CH$_3$), 4.49 (d, ^3J = 5.3 Hz, 4 H, CH$_2$), 5.05 (t, ^3J = 5.3 Hz, 2 H, OH), 7.11 (m, 1 H, 4-H), 7.25 (m, 2 H, 3-H, 5-H). ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 13.8 (CH$_3$), 62.1 (CH$_2$OH), 125.9 (C4), 127.0 (C3, C5), 134.0 (C1), 140.3 (C2, C6).

2,6-Bis(bromomethyl)toluene (7c) was prepared from 2,6-bis(hydroxymethyl)toluene **7b** as described in the literature; m.p. 85–87 °C (ref.[29,31] 94–95 °C), and used in the next step without purification.

General Procedure for Quaternizations of Bis(bromomethyl)arenes with 2-(1,3-Dioxolan-2-yl)pyridine: To a solution of bis(bromomethyl) derivative (20 mmol) in a minimal amount of *N*-methyl-2-pyrrolidone (usually 15–20 mL), 2-(1,3-dioxolan-2-yl)pyridine (**6**) (7.2 g, 48 mmol) was added. The reaction mixture was stirred for 5-7 days under moisture protection, whereas a white precipitate has formed. The reaction mixture was poured into ethyl acetate (300 mL), the solid was separated, washed several times with ethyl acetate and dry diethyl ether, and dried in vacuo/P_2O_5, to give the white amorphous dibromide salt **3 (2Br$^-$)**.

A part of it (10 mmol) was dissolved in minimal amount of water (ca. 10 mL) and treated with concentrated aqueous solution of $NaBF_4$ (4.4 g, 40 mmol). The milky reaction mixture was heated gently until a clear solution was obtained. Upon slow cooling to +5 °C, a crystalline bis(tetrafluoroborate) **3 (2BF$_4^-$)** separated almost quantitatively. It was separated, washed with a plenty of cold water, and dried in vacuo/P_2O_5.

1,4-Bis{[1-(1,3-dioxolan-2-yl)pyridinium]methyl}-2,5-dimethylbenzene Dibromide [3a (2Br$^-$)]: Yield 11.3 g (95%); m.p. (decomp.) 186–188 °C (EtOH). **3a (2BF$_4^-$):** M.p. 240–242 °C (EtOH/MeCN). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.20 (s, 6 H, CH$_3$), 4.11 [s, 8 H, CH(OC*H*$_2$)$_2$], 5.95 (s, 4 H, CH$_2$N$^+$), 6.46 [s, 2 H, C*H*(OCH$_2$)$_2$], 6.73 (s, 2 H, 3-H, 6-H), 8.20 (dd, $^3J_1$ = 7, $^3J_2$ = 6.3 Hz, 2 H, 5′-H), 8.37 (d, ^3J = 7 Hz, 2 H, 3′-H), 8.74–8.90 (m, 4 H, 4′-H, 6′-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 18.1 (CH$_3$), 57.8 (CH$_2$N$^+$),

65.6 [CH(O*C*H$_2$)$_2$], 97.1 [*C*H(OCH$_2$)$_2$], 126.2 (CH), 128.7 (CH), 129.9 (CH), 132.4 (C$_q$), 134.7 (C$_q$), 146.7 (CH), 147.4 (CH), 152.2 (C$_q$) ppm. $C_{26}H_{30}B_2F_8N_2O_4$ (608.1): calcd. C 51.35, H 4.97, N 4.61; found: C 51.14, H 4.90, N 4.64.

2,6-Bis{[1-(1,3-dioxolan-2-yl)pyridinium]methyl}toluene Dibromide [3b (2Br$^-$)]: Yield 11.1 g (96%); m.p. (decomp.) 130–133 °C (EtOH). **3b (2BF$_4^-$):** M.p. 174–176 °C (water). ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 2.23 (s, 3 H, CH$_3$), 4.11 [s, 8 H, CH(OC*H*$_2$)$_2$], 6.07 (s, 4 H, CH$_2$N$^+$), 6.50 [s, 2 H, C*H*(OCH$_2$)$_2$], 6.86 (d, ^3J = 7.8 Hz, 2 H, 3-H, 5-H), 7.29 (t, ^3J = 7.8 Hz, 1 H, 4-H), 8.20 (dd, $^3J_1$ = 8, $^3J_2$ = 6 Hz, 2 H, 5′-H), 8.38 (d, ^3J = 8 Hz, 2 H, 3′-H), 8.74–8.78 (m, 4 H, 4′-H, 6′-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 14.2 (CH$_3$), 58.4 (CH$_2$N$^+$), 65.6 [CH(O*C*H$_2$)$_2$], 97.1 [*C*H(OCH$_2$)$_2$], 126.2 (CH), 127.3 (CH), 128.7 (CH), 128.8 (CH), 132.7 (C$_q$), 135.3 (C$_q$), 146.5 (CH), 147.4 (CH), 152.3 (C$_q$) ppm. $C_{25}H_{28}B_2F_8N_2O_4$ (594.1): calcd. C 50.54, H 4.75, N 4.72; found: C 50.57, H 4.52, N 4.72.

2,6-Bis{[1-(1,3-dioxolan-2-yl)pyridinium]methyl}bromobenzene Dibromide [3d (2Br$^-$)]: Yield 11.7 g (91%); m.p. 175–178 °C (EtOH). **3d (2BF$_4^-$):** M.p. 196–200 °C (water). ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 4.07 [s, 8 H, CH(OC*H*$_2$)$_2$], 6.11 (s, 4 H, CH$_2$N$^+$), 6.49 [s, 2 H, C*H*(OCH$_2$)$_2$], 6.91 (d, ^3J = 7.8 Hz, 2 H, 3-H, 5-H), 7.44 (t, ^3J = 7.8 Hz, 1 H, 4-H), 8.26 (dd, $^3J_1$ = 8, $^3J_2$ = 6.1 Hz, 2 H, 5′-H), 8.39 (d, ^3J = 8 Hz, 2 H, 3′-H), 8.80 (dd, ^3J = 8 Hz, 2 H, 4′-H), 8.96 (d, ^3J = 6.1 Hz, 2 H, 6′-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]-DMSO): δ = 60.6 (CH$_2$N$^+$), 65.6 [CH(O*C*H$_2$)$_2$], 97.2 [*C*H(OCH$_2$)$_2$], 123.2 (C$_q$), 126.4 (CH), 128.8 (CH), 129.1 (CH), 129.8 (CH), 134.4 (C$_q$), 147.3 (CH), 147.8 (CH), 152.3 (C$_q$) ppm. $C_{24}H_{25}B_2BrF_8N_2O_4$ (659.0): calcd. C 43.74, H 3.82, N 4.25; found: C 4.34, H 3.80, N 4.21.

2,6-Bis{[1-(1,3-dioxolan-2-yl)pyridinium]methyl}trifluoromethylbenzene Dibromide [3e (2Br$^-$)]: Yield 9.2 g (72%); m.p. 149–151 °C (EtOH). **3e (2BF$_4^-$):** M.p. 196–198 °C (water). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.05 [m, 8 H, CH(OC*H*$_2$)$_2$], 6.27 (s, 4 H, CH$_2$N$^+$), 6.43 [s, 2 H, C*H*(OCH$_2$)$_2$], 6.85 (d, ^3J = 8.0 Hz, 2 H, 3-H, 5-H), 7.62 (t, ^3J = 8.0 Hz, 1 H, 4-H), 8.29 (dd, $^3J_1$ = 8.0, $^3J_2$ = 6.0 Hz, 2 H, 5′-H), 8.40 (d, ^3J = 8.0 Hz, 2 H, 3′-H), 8.82 (dd, ^3J = 8.0 Hz, 2 H, 4′-H), 9.01 (d, ^3J = 6.0 Hz, 2 H, 6′-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 58.3 (q, $^4J_{C,F}$ = 6 Hz, CH$_2$N$^+$), 65.5 [CH(O*C*H$_2$)$_2$], 97.1 [*C*H(OCH$_2$)$_2$], 124.4 (q, $^2J_{C,F}$ = 30 Hz, C$_q$), 124.5 (q, $^1J_{C,F}$ = 277 Hz, CF$_3$) 126.5 (CH), 128.9 (CH), 129.4 (CH), 133.5 (C$_q$), 133.8 (CH), 147.8 (CH), 148.0 (CH), 152.3 (C$_q$) ppm. ^{19}F NMR (376 MHz, [D$_6$]DMSO): δ = –144.0 (BF$_4^-$), –48.1 (CF$_3$) ppm. $C_{25}H_{25}B_2BrF_{11}N_2O_4$ (648.1): calcd. C 46.33, H 3.89, N 4.32; found: C 46.57, H 3.69, N 4.35.

General Procedure for Ring Closure Reactions in PPA: The corresponding bis(tetrafluoroborate) **3a–d (2BF$_4^-$)** (2.00 g) in PPA (20 g) was slowly heated under argon atmosphere to 150 °C, and the reaction mixture was stirred at this temperature for 24–36 h. After cooling to about 100 °C, water (40 mL) was carefully added and the mixture was stirred at this temperature for 30 min for hydrolysis of the PPA. The mixture was cooled to room temperature and treated with excess of NaBF$_4$ (15–30 mmol, concentrated aqueous solution). The dark solution (sometimes containing small amounts of dark precipitate) was extracted with nitromethane (4×40 mL). The organic phases were combined, washed with water (20 mL) and the solvents evaporated in vacuo; the residue was recrystallized from a suitable solvent.

6,13-Dimethyl-4a,8a-diazoniapentaphene Bis(tetrafluoroborate) (4a): Yield 0.44 g (30%), recrystallization from MeCN/water, brown crystalline solid; m.p. > 300 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.83 (s, 3 H, C6–CH$_3$), 3.53 (s, 3 H, C13–CH$_3$), 7.94 (s, 1 H, 7-H), 8.31 (dd, ^3J = 7 Hz, 1 H, 10-H), 8.35 (dd, ^3J = 7 Hz, 1 H, 3-H), 8.54 (dd, $^3J_1$ = 9, $^3J_2$ = 7 Hz, 1 H, 11-H), 8.56 (dd, $^3J_1$ = 9, $^3J_2$ = 7 Hz, 1 H, 2-H), 9.05 (d, ^3J = 9 Hz, 1 H, 1-H), 9.13 (d, ^3J = 9 Hz, 1 H, 12-H), 9.54 (d, ^3J = 7 Hz, 1 H, 9-H), 9.66 (d, ^3J = 7 Hz, 1 H, 4-H), 9.78 (s, 1 H, 14-H), 9.90 (s, 1 H, 8-H), 10.19 (s, 1 H, 5-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 18.8 (CH$_3$), 19.8 (CH$_3$), 124.7, 125.2, 125.8, 126.5, 126.9, 128.3, 128.4, 130.7, 133.1, 133.5, 134.3, 135.2, 135.9, 136.2, 136.3, 136.3, 137.0, 139.4, 140.6 ppm. MS (ESI): *m*/*z* (%) = 155 (100) [*M*$^{2+}$], 309 (48) [M – H]$^+$, 320 (25) [*M* + F]$^+$, 397 (26) [*M* + BF$_4$]$^+$, 881 (38) [2*M* + 3BF$_4$]$^+$, 1364 (6) [3*M* + 5BF$_4$]$^+$. IR (KBr): $\tilde{\nu}_{max}$ = 524 (BF$_4^-$), 792 s, 1062 s (BF$_4^-$), 1389 s, 1502, 1646 s cm^{-1}. $C_{22}H_{18}B_2F_8N_2$ (484.0): calcd. C 54.59, H 3.75, N 5.79; found: C 54.46, H 3.61, N 5.85.

14-Methyl-4a,12a-diazoniapentaphene Bis(tetrafluoroborate) (4b): Yield 0.81 g (51%), recrystallization from MeCN/water, dark-brown fine crystalline solid; m.p. > 300 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.58 (s, 3 H, CH$_3$), 8.19 (d, ^3J = 9.2 Hz, 1 H, 7-H), 8.25 (d, ^3J = 9.2 Hz, 1 H, 6-H), 8.26 (dd, ^3J = 7 Hz, 1 H, 11-H), 8.32 (dd, ^3J = 7 Hz, 1 H, 3-H), 8.50 (dd, $^3J_1$ = 9, $^3J_2$ = 7 Hz, 1 H, 10-H), 8.57 (dd, $^3J_1$ = 9, $^3J_2$ = 7 Hz, 1 H, 2-H), 8.74 (d, ^3J = 9 Hz, 1 H, 9-H), 9.15 (d, ^3J = 9 Hz, 1 H, 1-H), 9.16 (s, 1 H, 8-H), 9.53 (d, ^3J = 7 Hz, 1 H, 4-H), 9.81 (d, ^3J = 7 Hz, 1 H, 12-H), 10.08 (s, 1 H, 5-H), 10.52 (s, 1 H, 13-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]-DMSO): δ = 18.3 (CH$_3$), 121.0, 122.3, 123.3, 123.4, 124.4, 125.0, 125.5, 127.9, 129.8, 130.0, 133.1, 134.0, 135.6, 135.9, 136.0, 136.4, 137.1, 138.8, 139.7, 139.8 ppm. MS (ESI): *m*/*z* (%) = 148 (59) [*M*]$^{2+}$, 295 (100) [M – H]$^+$, 315 (21) [*M* + F]$^+$, 383 (13) [*M* + BF$_4$]$^+$, 853 (18) [2*M* + 3BF$_4$]$^+$. IR (KBr): $\tilde{\nu}_{max}$ = 523 (BF$_4^-$), 1056 s (BF$_4^-$), 1343, 1449, 1641 w cm^{-1}. $C_{21}H_{16}B_2F_8N_2$ (470.0): calcd. C 53.67, H 3.43, N 5.96; found: C 53.73, H 3.43, N 6.31.

4a,12a-Diazoniapentaphen-14-olate Tetrafluoroborate (4d): Yield 0.65 g (56%), recrystallization from nitromethane, purple needles, m.p. > 300 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 7.53 (d, ^3J = 9.0 Hz, 1 H, 7-H), 7.58 (d, ^3J = 9.0 Hz, 1 H, 6-H), 7.77–7.82 (m, 3 H, 2-H, 3-H, 11-H), 7.97 (dd, $^3J_1$ = 8.5, $^3J_1$ = 7.8 Hz, 1 H, 10-H), 8.15 (d, ^3J = 8.5 Hz, 1 H, 9-H), 8.23 (s, 1 H, 5-H), 8.37–8.39 (m, 2 H, 1-H, 8-H), 8.80–8.84 (m, 1 H, 4-H), 9.28 (d, ^3J = 6.5 Hz, 1 H, 12-H), 11.46 (s, 1 H, 13-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]-DMSO): δ = 110.2 (C$_q$), 113.6 (CH, C5), 122.5 (CH), 122.6 (CH), 123.9 (CH), 124.1 (CH), 125.3 (C$_q$), 126.1 (CH, C9), 127.4 (CH, C7), 128.6 (C$_q$), 129.8 (CH), 132.9 (CH, C6), 133.0 (CH), 133.3 (CH), 133.9 (CH, C4), 135.6 (CH, C12), 137.0 (C$_q$), 138.1 (C$_q$), 164.2 (C$_q$, C14) ppm. MS (ESI): *m*/*z* (%) = 297 (100) [M]$^+$, 329 (24) [*M* + O$_2$]$^+$. IR (KBr): $\tilde{\nu}_{max}$ = 480, 522 (BF$_4^-$), 1061 s (BF$_4^-$), 1185, 1459 s, 1510, 1552 s (C–O phenolate), 1640 w cm^{-1}. $C_{20}H_{13}BF_4N_2O$ (384.1): calcd. C 62.53, H 3.41, N 7.29; found: C 62.66, H 3.34, N 7.49.

6,13a-Dimethyl-13,13a-dihydro-4a,8a-diazoniapentaphen-13-ol Bis(tetrafluoroborate) (10b): A solution of the dibromide **3a (2Br$^-$)** (3.57 g, 6.00 mmol) in 48% aq. HBr (35 mL) was stirred under reflux for 2 h, and 20 mL of liquid were distilled off. The residue was poured into acetone (200 mL); the yellow precipitate was collected and washed with acetone. It was dissolved in 5% aq. HBr (5 mL) and diluted with 96% ethanol (500 mL); the turbid solution was filtered and the filtrate concentrated in vacuo. The residue was diluted with water (15 mL) and treated with 50% aq. HBF$_4$ (3 mL), to afford **9b** (1.05 g, 35%) as yellow crystalline solid. An analytical sample was recrystallized from acetonitrile/water. Brown prisms, decomp. at > 200 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.36 (s, 3 H, C13a–CH$_3$), 2.43 (s, 3 H, C6–CH$_3$), 5.86 (d, ^3J = 4.7 Hz, 1 H, 13-H), 6.83 (d, ^3J = 4.7 Hz, 1 H, OH), 6.95 (s, 1 H, 7-H), 7.81 (s, 1 H, 8-H), 8.10–8.14 (m, 1 H, 3-H), 8.19 (d, ^3J = 7.7 Hz, 1 H, 12-H), 8.24 (dd, $^3J_1$ = 6, $^3J_1$ = 9 Hz, 1 H, 10-H), 8.37-8.40 (m, 2

Table 3. Crystal data and structure refinement details of the compounds **4a** and **10b**.

	4b	**10a**
Molecular formula	$C_{22}H_{18}B_2F_8N_2$	$C_{22}H_{22}B_2F_8N_2O_2$
Temperature [K]	173(2)	123(2)
Wavelength [Å]	0.71073	0.71073
Space group	$P\bar{1}$ (No. 2)	$P\,2_1/n$ (No. 14, cell choice 2)
Unit cell dimensions	a = 10.538(1) Å	a = 11.921(1) Å
	b = 7.4098(7) Å	b = 15.150(1) Å
	c = 13.373(1) Å	c = 13.503(1) Å
	α = 93.29(1)°	α = 90°
	β = 102.77(1)°	β = 112.15(1)°
	γ = 86.60(1)°	γ = 90°
Volume [Å^3]	1015.5(2)	2258.7(3)
Z	2	4
Calculated density [g cm^{-3}]	1.583	1.529
Absorption coefficient [mm^{-1}]	0.144	0.141
F(000)	492	1064
Crystal size	0.3 mm × 0.3 mm × 0.2 mm	0.3 mm × 0.3 mm × 0.2 mm
Measured θ range	$2.76 \geq \theta \geq 30.44$	$2.11 \geq \theta \geq 27.16$
Limiting indices	$-14 \geq h \geq 14$	$-15 \geq h \geq 15$
	$-10 \geq k \geq 10$	$-19 \geq k \geq 19$
	$-18 \geq l \geq 18$	$-17 \geq l \geq 17$
Reflections collected/unique	15232/5598	19635/4803
R_{int}	0.0475	0.0731
Data/restraints/parameters	5598/0/309	4803/0/349
Goodness of fit on F^2	0.943	0.918
R values [$I^2 \geq 2\sigma(I)$]	R_1 = 0.0440, wR_2 = 0.0746	R_1 = 0.0628, wR_2 = 0.1549
R values (all data)	R_1 = 0.0746, wR_2 = 0.1209	R_1 = 0.1212, wR_2 = 0.1759
Final Fourier residuals	0.686 and –0.305 e/Å^3	0.690 and –0.519 e/Å^3

H, 1-H, 2-H), 8.69 (dd, $^3J_1$ = 7.8, $^3J_1$ = 9 Hz, 1 H, 11-H), 8.76 (s, 1 H, 14-H), 9.08 (d, ^3J = 6 Hz, 1 H, 9-H), 9.35 (d, ^3J = 6.7 Hz, 1 H, 4-H), 9.46 (s, 1 H, 5-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 18.8 (C6–*C*H$_3$), 26.1 (C13a–*C*H$_3$), 41.7 (C$_q$, C13a), 69.4 (CH, C13), 123.0 (CH), 124.0 (CH), 125.0 (CH), 126.3 (CH), 126.5 (CH), 128.2 (CH), 128.8 (C$_q$), 128.9 (CH), 132.8 (CH), 134.1 (C$_q$), 135.5 (C$_q$), 137.0 (CH), 137.6 (CH), 141.7 (C$_q$), 143.4 (CH), 146.2 (C$_q$), 147.1 (CH), 147.2 (C$_q$) ppm. MS (ESI): *m*/*z* (%) = 148 (16) [M – OH – CH$_3$]$^{2+}$, 327 (100) [M – H]$^+$, 415 (14) [M + BF$_4$]$^+$, 917 (14) [2M + 3BF$_4$]$^+$. IR (KBr): $\tilde{\nu}_{max}$ = 485, 522 (BF$_4^-$), 1054 s (BF$_4^-$), 1374, 1413, 1502 s, 1637 s cm^{-1}. $C_{22}H_{20}B_2F_8N_2O$ (502.0): calcd. C 52.63, H 4.02, N 5.58; found: C 52.73, H 3.92, N 5.67.

Dehydration of 10b in PPA: Compound **10b** (0.251 g, 0.50 mmol) in PPA (2.50 g) was stirred under argon atmosphere for 18 h at 150 °C. After cooling to 100 °C, a solution of $NaBF_4$ (0.11 g, 1.0 mmol) in water (6 mL) was added, and the reaction mixture was stirred at 80–100 °C for 15 min. After cooling to room temperature, the solution was extracted with nitromethane (4 × 5 mL). The combined organic layers were washed with water (2 × 5 mL), and the solvent was removed in vacuo, to give pure **4a** (0.220 g, 91%) as a yellow solid; spectroscopic data being identical with those given above.

Spectrophotometric Measurements: UV/Visible spectra were recorded on a Varian Cary 100 double-beam spectrophotometer; corrected steady-state emission spectra were recorded on a Varian Cary Eclipse fluorescence spectrometer. All spectrophotometric measurements were performed in thermostatted quartz sample cells at 20 °C, using spectral grade solvents (Fluka, Riedel-de Haën). Working solutions were freshly prepared by dilution of stock solutions (1×10^{-3} M in acetonitrile). If not stated otherwise, the solution concentrations were 20 μM for absorption spectroscopy and 5.0 μM for fluorescence spectroscopy. Spectrophotometer slit widths were kept 2 nm for absorption spectroscopy and 5/5 nm for emission spectroscopy. The relative fluorescence quantum yields were determined by the standard method[38] with Coumarin 1 (Aldrich, Φ_F = 0.73 in ethanol)[39] or Cresyl Violet (Radiant Dyes, Φ_F = 0.54 in methanol)[40] as references; refractive indices of the solvents were taken into account.

X-ray Structure Analysis: Single crystals of **4a** and **10b** were obtained by crystallization from acetontrile/water. The single crystal measurements were performed with a STOE IPDS. The program SHELXS-97[41] was used to perform the structure solutions, applying direct methods. The structures were refined with the program SHELXL-97.[42] The hydrogen atoms were placed with a constant C–H distance of 0.98 Å in geometrically idealized positions, using a riding model. For **10b**, the hydrogen atoms belonging to crystallization water molecules could not be refined. Crystal data and structure refinement details of the compounds **4a** and **10b** are given in Table 3. CCDC-275724 (for **4a**) and -275725 (for **10b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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