Pergamon

Tetrahedron 55 (1999) 4709–4720

TETRAHEDRON

Novel Furan-, Thiophene- and Benzo[b]thiophene Bridged Macrocycles of 4,4'-Bipyridine[1]

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Received 10 December 1998; accepted 9 February 1999

Abstract

Eight novel heterocyclic bridged phanes of the paraquat type were synthesized by a simple two-step procedure. Starting from furan bridged bis(4,4'-bipyridinium) dication **2** and the corresponding bis(bromomethyl)arenes furanophanes of 4,4'-bipyridine were obtained in moderate to high yields. In similar manner thiophenophane **9** was synthesized in low yield using dication **8** as precursor. The spectroscopic properties of furanophane **4** and thiophenophane **9** were compared. Cycloadditions on the furan ring failed, which is attributed to the decrease of electron density of the furan ring caused by neighbouring electron-accepting bipyridinium groups. The syntheses of the benzo[b]thiophene bridged phanes were performed starting from dibromide **10** and bis(4,4'-bipyridinium) dications **12-14** since the instability of the required bis(4,4'-bipyridinium) dication **11** did not allow its use in aqueous solution.

Keywords: 4,4'-Bipyridine; Furan; Thiophene; Benzo[b]thiophene; Macrocycles

Introduction

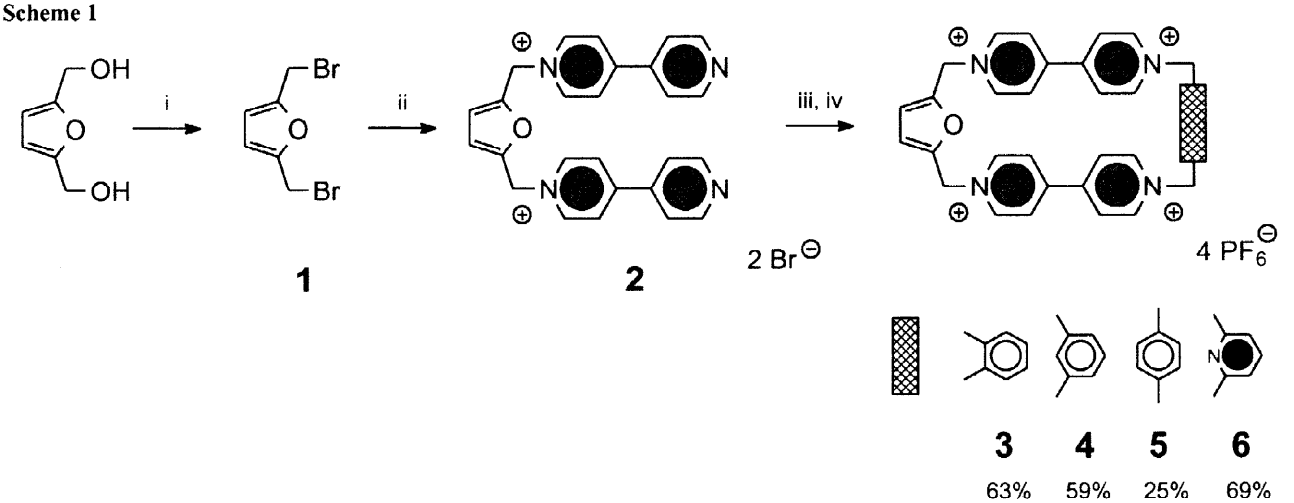
During the last decade macrocyclic compounds of paraquat type have intensively been studied in view of their host-guest chemistry [2], redox behaviour [3], catalytic activity [4], and incorporation into supramolecular architectures [5]. Separation of enantiomers by chiral 4,4'-bipyridine phanes has recently been achieved [6]. For use of this type of phanes as stationary phase in chromatography reactive positions are required allowing selective functionalizations. In this account we report syntheses of several novel heterophanes of 4,4'-bipyridine which are bridged by π-electron-rich aromatic units such as furan, thiophene and benzo[b]thiophene. We also present examples for the functionalization of furanophanes and investigations on the spectroscopic properties of the new macrocyclic compounds.

0040-4020/99/$ - see front matter
PII: S0040-4020(99)00144-1

Furano- and Thiophenophanes

Retrosynthetic analysis of furanophanes based on 4,4'-bipyridine reveals that bis(4,4'-bipyridinium) dication **2** and dibromide **1** should be precursors. Although side-chain brominated furan derivative **1** is occasionally mentioned in the literature, no detailed procedure for its preparation was available [7] and no physical and chemical data were reported. We prepared **1** according to the procedure by Bergmann et al. [8], by nucleophilic substitution of the commercially available diol with phosphorous tribromide in benzene. Thus, **1** was obtained as a colourless and unstable solid in low yield. Its subsequent reaction with an excess of 4,4'-bipyridine afforded the desired dication **2** in excellent yield as an air- and thermostable solid. Furanophanes **3-6** were then synthesized in moderate to good overall yields by simple heterogeneous reaction of **2** with the corresponding bis(bromomethyl)arenes [9,12,13] followed by chromatographic work-up and counterion exchange (Scheme 1).

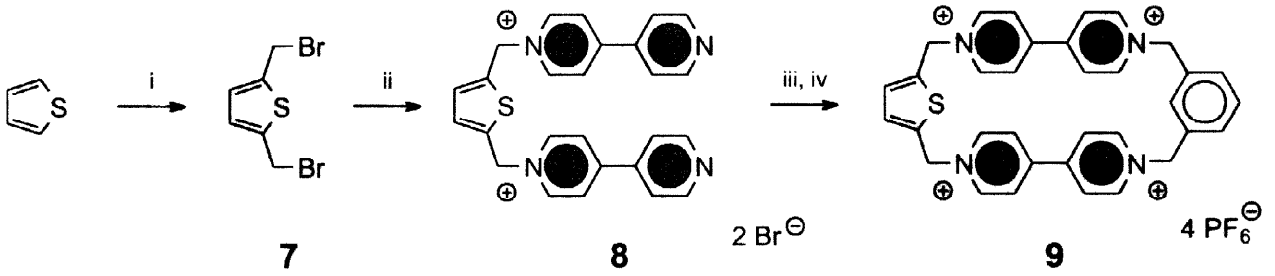
Scheme 1



Reagents and conditions: i) PBr_3, C_6H_6, reflux, 14%; ii) 4,4'-bipyridine, CH_3CN, reflux, 94%; iii) bis(bromomethyl)arene, CH_3NO_2/H_2O, r.t., 30-60d; iv) NH_4PF_6, H_2O.

For comparison thiophenophane **9** was prepared in the way depicted in Scheme 2. Synthesis of 2,5-bis(bromomethyl)thiophene **7** has been reported [10,11], but we prepared **7** by bis(bromomethylation) of thiophene which is easier to perform albeit the yield is very low. Dication **8** was obtained by reaction of **7** with an excess of 4,4'-bipyridine in acetonitrile as reported by Stoddart et al. [11], however, our yield was considerably higher. Thiophenophane **9** was synthesized by the method described above in low yield. The decreased efficiency of the ring closure reaction is ascribed to geometric effects: the bulkier sulfur atom in **8** (compared with the oxygen atom in **2**) causes an expansion of the intramolecular CH_2/CH_2 distance and therefore makes ring closure less probable. In accordance with this assumption we failed to cyclize **8** with 1,2-bis(bromomethyl)benzene which had provided furanophane in high yield starting from **2**.

Scheme 2



Reagents and conditions: i) 2 eq. $(CH_2O)_n$, HBr, HOAc, 4%; ii) 4,4'-bipyridine, CH_3CN, reflux, 79%; iii) 1,3-bis(bromomethyl)benzene, CH_3NO_2/H_2O, r.t., 30d; iv) NH_4PF_6, H_2O, 11%.

Macrocycles **3**, **4**, and **6** were isolated in remarkably high yields. Hünig and coworkers [12] observed a similar effect in their syntheses of related carbophanes: best results in the macrocyclization were obtained by use of *high* concentrations of the dications and the side-chain brominated arenes. This effect was explained by the advantage of the principle of rigid groups. In the series of heterophanes the furan moiety apparently offers optimal geometric preconditions which will be discussed in detail with pyridinophane **6**.

While structures of furanophanes **3-5** were unambiguously confirmed by spectroscopic methods (^1H, ^{13}C, multidimensional NMR), pyridinophane **6** does not contain a suitable anchor unit for unequivocal proof of its macrocyclic nature. Hence, its structure was determined by an X-ray analysis (Figure 1).

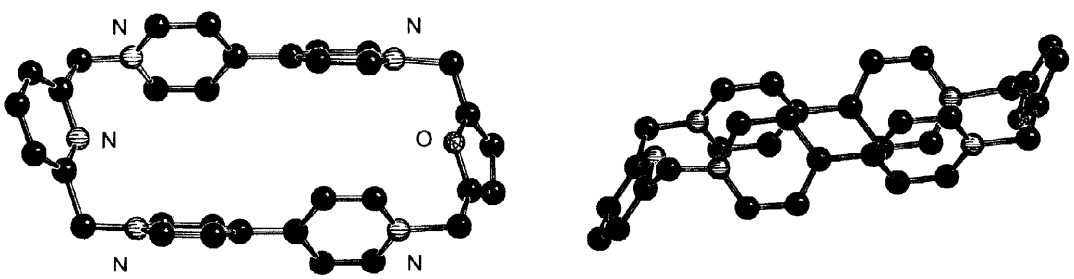


Figure 1. X-ray crystal structure of **6**-4PF_6 (supervision and side-view, counterions and hydrogen atoms were omitted for clarity).

The solution of the crystal structure was entailed with some difficulties due to almost identical geometric dimensions of the spacer groups (see Experimental Part). The intramolecular distances of the methylene units amount to 4.69 Å at the furan side, and 4.92 Å at the pyridine part, respectively. Thus, the free pyridine rings of dication **2** are in optimal distance for the ring closure reaction, which is also expressed in the remarkably high yield of pyridinophane **6**. Only lone pairs are located in the cavity of phane **6**. The strain is transferred to the bipyridinium groups exclusively as revealed by an unusually high torsion angle of 52.5° between the pyridinium rings. This value is comparable to that obtained for the twofold pyridine bridged phane where a torsion angle of 54° was recorded [13].

Comparison of the spectroscopic properties of related phanes **4** and **9** delivered surprising results. The intraannular proton H_i can be chosen as an excellent indicator for the macrocyclic structure: this proton appeared at $\delta = 7.09$ for furanophane **4** whereas a value of $\delta = 7.93$ was observed for thiophenophane **9** (Figure 2). Apparently, the chemical shift of H_i responds very sensitively to the spacer dimension as implied by differing CH_2/CH_2 distances. The formal exchange of sulfur by an oxygen atom causes a difference in chemical shifts of $\Delta\delta = 0.84$!

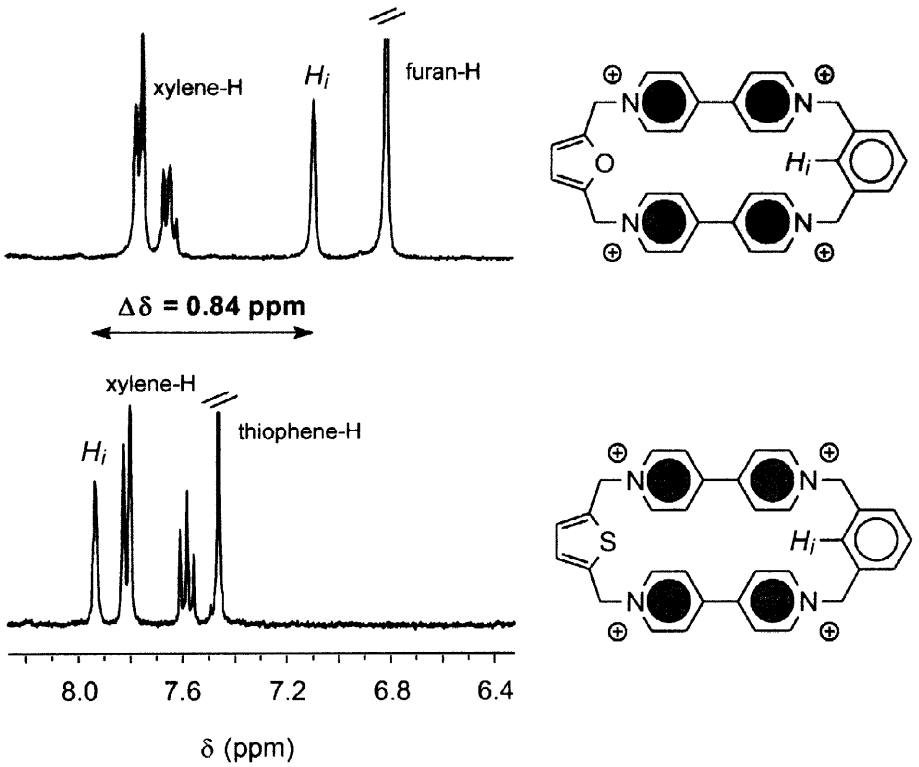


Figure 2. ^1H NMR spectra (300 MHz, $[D_6]$DMSO) of furanophane **4** and thiophenophane **9** (region of aromatic protons)

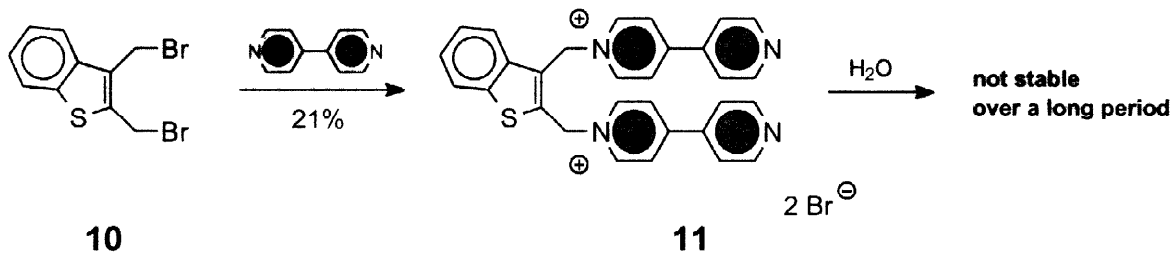
Extraploratory attempts to perform cycloadditions of tetracyanoethene or dimethyl acetylenedicarboxylate with furanophane **3** at room temperature failed. Even forced conditions (acetonitrile, reflux or DMF, 10 kbar, r.t.) did not furnish Diels-Alder products. Although hybridization change from sp^2 to sp^3 at C-2 and C-5 of the furan unit should result in a considerable decrease of the phane strain, the electron deficient bipyridinium units probably reduce the electron density of the furan ring thus preventing the cycloaddition for kinetic reasons.

Diels-Alder reactions in aqueous solution are now well established in organic synthesis [14]. However, dication **2** underwent no cycloadditions at room temperature neither with maleic acid nor its anhydride in water. On reflux the starting material rapidly decomposed to 4,4'-bipyridine and undefined spacer fragments, which is attributed to the instability of **2** under acidic conditions.

Benzo[b]thiophenophanes

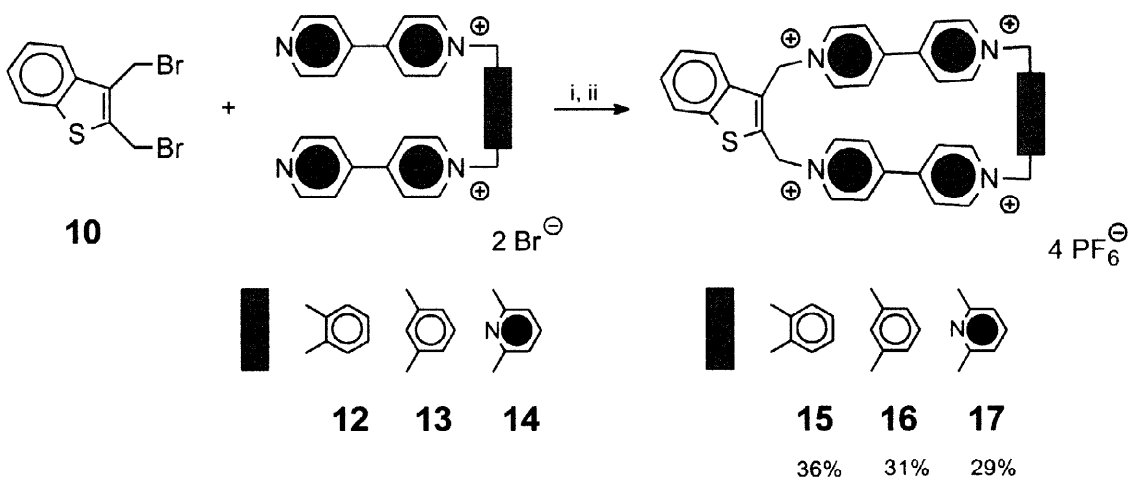
Application of the general synthetic procedure of furano- or thiophenophanes to preparation of benzo[b]thiophenophanes **15-17** was not successful. Although the required dication **11** could be obtained by alkylation of 4,4'-bipyridine with dibromide **10** [15] in low yield (see Scheme 3), intermediate **11** is too unstable for further cyclization in aqueous solution [16].

Scheme 3



Alternatively, macrocyclization could be executed by alkylation of bis(4,4'-bipyridinium) dications **12-14** [12,13] with dibromide **10** under the proven reaction conditions. Benzo[b]thiophenophanes **15-17** were isolated as yellow solids in approximately 30% yield after chromatographic work-up and counterion exchange (Scheme 4).

Scheme 4



Reagents and conditions: i) CH_3NO_2/H_2O, r.t., 30d; ii) NH_4PF_6, H_2O.

Characterization of these phanes by NMR spectroscopy was difficult with reference to their low symmetry expressed in overlap and signal broadening in the NMR spectra. The incorporated benzo[b]thiophene bridge is *rigid* at room temperature, and no conformational change due to frozen flip movements is observed.

In the case of phane **15** the mobility of *both* bridges is frozen. The *syn-anti* ratio could not be determined due to line broadening in the ^{1}H NMR spectrum. This result is comparable to that observed in and reported for the corresponding carbophane including *ortho*-xylene units as spacer units [12].

In phanes **16** and **17** only the benzo[b]thiophene spacer is frozen, while the larger bridges are flexible. This is indicated by singlets in the ^{1}H NMR spectra for their methylene protons. The intraannular proton H_i of **16** is a significant indicator for successful macrocyclization. Its chemical shift was determined to δ = 6.27, whereas the related carbophane with an *ortho*-xylene bridge instead of the bis(methylene)benzo[b]thiophene bridge shows this proton at δ = 6.26 [12,17]. The unusual yellow colour of compounds **15-17** is attributed to a weak *inter*molecular charge transfer from the benzo[b]thiophene system to the electron-deficient bipyridinium groups in the solid state. In aqueous solutions the compounds are transparent in the UV-Vis spectra above 270 nm.

Conclusion

We could demonstrate that furanophanes of 4,4'-bipyridine are readily prepared by the standard two-phase procedure starting from a furan bridged dication and several bis(bromomethyl)arenes. Yields up to 70% could be obtained for the crucial macrocyclization step. A thiophenophane was synthesized in the same way. The formal exchange of oxygen against sulfur not only influenced the efficiency of ring closure but also caused changes in the spectroscopic properties of the phanes. Diels-Alder reactions of a furanophane failed, probably due to the decreased electron density of the furan moiety caused by the neighbouring bipyridinium groups. Because of the instability of the corresponding benzo[b]thiophene bridged bis(4,4'-bipyridinium) dication in water the syntheses of benzo[b]thiophenophanes were alternatively performed by combining arene bridged dications and 2,3-bis(bromomethyl)-benzo[b]thiophene. The desired phanes could then be isolated in moderate yields. The electrochemical behaviour of the new phanes will be reported in a separate communication [18].

Experimental Part

General techniques: Melting points were determined on a Kofler-Boëtius apparatus and are corrected. NMR spectra were recorded on Bruker DRX-500 or AC-300 instruments with CHD_2SOCD_3 (in [D_6]DMSO; δ = 2.50 (^{1}H), δ = 39.56 (^{13}C)] and $CHCl_3$ [in $CDCl_3$; δ = 7.25 (^{1}H)] as internal standards; signals are quoted as s (singlet), d (doublet), t (triplet), m (multiplet), br (broad), vbr (very broad). UV-Vis spectra were recorded on a Cary-3 double-beam spectrometer. Elemental analysis were carried out on a Carlo Erba CHN-S analyzer.

All reactions were monitored by thin-layer chromatography (TLC) carried out on Macherey-Nagel silica gel precoated plates Polygram Sil G/UV_{254} with UV light and iodine (iodine chamber) as developing reagent. Merck silica gel (G60, particle size 0.063-0.200 mm) was used for column chromatography, Merck silica gel precoated glass-plates KG 60/KIESELGUR F_{254} (20 × 20 cm, thickness 0.25 mm) were used for PTLC; as eluent a mixture of methanol

and 2M aqueous NH_4Cl solution (3:2 v/v) was used. The non-aqueous alkylation reactions were performed with exclusion of moisture. Yields refer to chromatographically homogeneous materials. All reagents were obtained from Aldrich, Fluka and Acros and used as received. 2,6-Bis(bromomethyl)pyridine was prepared as described in the literature [9].

2,5-Bis(bromomethyl)furan (1) [7]**:** To a vigorously stirred suspension of 1.28 g (10.0 mmol) of 2,5-bis(hydroxymethyl)furan in dry benzene (20 mL) was slowly added 3.00 ml (8.55 g, 31.0 mmol) of phosphorous tribromide in benzene (10 mL) at -15 °C. The yellowish solution was warmed to room temperature and then heated under reflux for 30 minutes. After quenching with ice water (20 mL) and filtration over celite® the organic layer was separated, and the aqueous phase was extracted twice with benzene (20 mL each). The combined organic phases were dried over Na_2SO_4 and the solvent was removed in vacuo. The residual solid was recrystallized from *n*-hexane affording 346 mg (14%) of **1** as colourless needles. **CAUTION! Product 1 is a very strong lachrymator and an unstable solid, which can decompose under explosion! Therefore it is not advisable to store 1 in a closed vessel!** Characterization of **1**: M.p. 43 °C; UV-Vis (CH_2Cl_2): λ_{max} (ε) = 267 nm (14100); ^1H NMR (300 MHz, $CDCl_3$): δ = 4.48 (s, 4 H, CH_2), 6.35 (s, 2 H, Ar-H); $C_6H_6Br_2O$ (253.9): calcd C 28.38, H 2.38; found C 28.56, H 2.37.

1,1''-[2,5-Bis(methylene)furan]bis-4,4'-bipyridinium Dibromide (2): To a boiling solution of 624 mg (4.00 mmol) of 4,4'-bipyridine in dry acetonitrile (20 mL) was added slowly 254 mg (1.00 mmol) of **1** in acetonitrile (10 mL). The solution was refluxed for two hours, cooled to room temperature, and stored overnight at 7 °C. The yellow precipitate was collected, washed with acetonitrile and dried at 80 °C affording 549 mg (94%) of **2**-2Br as greenish-yellow needles. M.p. >240 °C (decomp.); R_f = 0.275 (silica gel); UV-Vis (H_2O): λ_{max} (ε) = 259 (30200), 221 nm (18200); ^1H NMR (300 MHz, [D_6]DMSO): δ = 6.06 (s, 4 H, CH_2), 6.94 (s, 2 H, Ar-H), 8.02 (d, J = 5.7 Hz, 4 H, pyridine-3-H), 8.71 (d, J = 6.5 Hz, 4 H, pyridinium-3-H), 8.84 (d, J = 5.7 Hz, 4 H, pyridine-2-H), 9.36 (d, J = 6.5 Hz, 4 H, pyridinium-2-H); ^{13}C NMR (75.5 MHz, [D_6]DMSO): δ = 55.41 (t), 113.65 (d), 121.96 (d), 125.78 (d), 140.66 (s), 145.36 (d), 148.54 (s), 150.98 (d), 153.01 (s); $C_{26}H_{22}Br_2N_4O \cdot H_2O$ (584.3): calcd C 53.44, H 4.14, N 9.56; found C 53.44, H 3.92, N 9.36.

General procedure for preparation of furanophanes **3-6**

Dication **2** was dissolved in water (5 mL), the bis(bromomethyl)arene was dissolved in nitromethane (5 mL). Both solutions were combined and vigorously shaken for 30 days (with exception of **5**: 60 days). The aqueous layer was separated and the organic phase was washed twice with water (0.5 mL each). The combined aqueous solutions were purified by column chromatography (25 g of silica gel). From the fraction containing the phane the solvent was removed in vacuo and the residual solid (ammonium chloride, tetrabromide of the phane) was dissolved in a minimum of water. A saturated aqueous NH_4PF_6 solution was added until no further precipitation was observed. The precipitate was collected, washed thoroughly with water and dried at 80 °C.

(2,5)Furanophane (3): From 117 mg (0.20 mmol) of **2**-2Br and 80 mg (0.30 mmol) of 1,2-bis-(bromomethyl)benzene was obtained 137 mg (63%) of **3**-4PF_6 as colourless crystals. M.p. 261-264 °C (decomp.); R_f = 0.37 (silica gel); UV-Vis (H_2O): λ_{max} (ε) = 254 (60200), 214 nm (36300); ^{1}H NMR (500 MHz, [D_6]DMSO): δ = 5.97 (s, 4 H, CH_2), 6.02, 6.38 (2 d, *J* = 15.2 Hz, 2 H each, CH_2, AB), 6.76 (s, 2 H, Ar-H), 7.91, 8.02 (2 m, 2 H each, Ar-H), 8.21, 8.50 (2 d, *J* = 6.8, 7.0 Hz, 4 H each, bipy-3-H), 8.80, 9.22 (2 d, *J* = 6.0, 6.8 Hz, 4 H each, bipy-2-H); ^{13}C NMR (125.7 MHz, [D_6]DMSO): δ = 56.67 (t), 61.20 (t), 112.46 (d), 126.46 (d), 126.74 (d), 131.46 (s), 132.26 (d), 135.71 (d), 144.73 (d), 145.96 (d), 147.84 (s), 148.16 (s), 148.28 (s); $C_{34}H_{30}F_{24}N_4OP_4$ (1090.5): calcd C 37.45, H 2.77, N 5.14; found C 37.32, H 2.73, N 4.95.

(2,5)Furanophane (4): From 117 mg (0.20 mmol) of **2**-2Br and 80 mg (0.30 mmol) of 1,3-bis-(bromomethyl)benzene was obtained 128 mg (59%) of **4**-4PF_6 as colourless crystals. M.p. >275 °C (decomp.); R_f = 0.30 (silica gel); UV-Vis (H_2O): λ_{max} (ε) = 253 (44700), 202 nm (46800); ^{1}H NMR (500 MHz, [D_6]DMSO): δ = 5.95, 5.99 (2 s, 4 H each, CH_2), 6.81 (s, 2 H, Ar-H), 7.09 (s br, 1 H, Ar-H), 7.64 (t, *J* = 7.7 Hz, 1 H, Ar-H), 7.76 (dd, *J* = 0.8, 7.7 Hz, 2 H, Ar-H), 8.48, 8.53 (2 d, *J* = 6.8 Hz, 4 H each, bipy-3-H), 9.25, 9.27 (2 d, *J* = 6.8, 6.9 Hz, 4 H each, bipy-2-H); ^{13}C NMR (125.7 MHz, [D_6]DMSO): δ = 56.39 (t), 63.27 (t), 113.00 (d), 125.99 (d), 126.54 (d br), 130.19 (d), 130.25 (d), 135.76 (s), 145.78 (d), 145.84 (d), 148.02 (s), 148.63 (s), 148.78 (s); $C_{34}H_{30}F_{24}N_4OP_4$ (1090.5): calcd C 37.45, H 2.77, N 5.14; found C 37.51, H 2.76, N 4.97.

(2,5)Furanophane (5): From 115 mg (0.197 mmol) of **2**-2Br and 80 mg (0.30 mmol) of 1,4-bis(bromomethyl)benzene was obtained 53 mg (25%) of **5**-4PF_6 as colourless crystals. M.p. >260 °C (decomp.); R_f = 0.25 (silica gel); UV-Vis (H_2O): λ_{max} (ε) = 258 (20000), 209 nm (16600); ^{1}H NMR (500 MHz, [D_6]DMSO): δ = 5.89, 5.97 (2 s, 4 H each, CH_2), 6.84 (s, 2 H, Ar-H), 7.75 (s, 4 H, Ar-H), 8.43, 8.45 (2 d, *J* = 6.6 Hz, 4 H each, bipy-3-H), 9.31, 9.42 (2 d, *J* = 6.3 Hz, 4 H each, bipy-2-H); ^{13}C NMR (125.7 MHz, [D_6]DMSO): δ = 56.04 (t), 63.79 (t), 113.82 (d), 126.74 (d), 127.14 (d), 129.94 (d), 137.33 (s), 144.92 (d), 145.62 (d), 148.10 (s), 148.78 (s), 148.96 (s); $C_{34}H_{30}F_{24}N_4OP_4$ (1090.5): calcd C 37.45, H 2.77, N 5.14; found C 37.25, H 2.88, N 5.16.

(2,5)Furanophane (6): From 117 mg (0.20 mmol) of **2**-2Br and 81 mg (0.30 mmol) of 2,6-bis-(bromomethyl)pyridine was obtained 151 mg (69%) of **6**-4PF_6 as colourless crystals. M.p. >275 °C (decomp.); R_f = 0.34 (silica gel); UV-Vis (H_2O): λ_{max} (ε) = 253 (37200), 208 nm (29500); ^{1}H NMR (500 MHz, [D_6]DMSO): δ = 6.00, 6.06 (2 s, 4 H each, CH_2), 6.82 (s, 2 H, Ar-H), 7.75 (d, *J* = 7.9 Hz, 2 H, Ar-H), 8.14 (t, *J* = 7.9 Hz, 1 H, Ar-H), 8.54, 8.55 (2 d, *J* = 6.6 Hz, 4 H each, bipy-3-H), 9.25, 9.27 (2 d, *J* = 7.0 Hz, 4 H each, bipy-2-H); ^{13}C NMR (125.7 MHz, [D_6]DMSO): δ = 56.62 (t), 63.25 (t), 112.73 (d), 123.61 (d), 125.91 (d), 126.54 (d), 139.32 (d), 145.96 (d), 146.89 (d), 148.08 (s), 148.45 (s), 148.77 (s), 152.05 (s); $C_{33}H_{29}F_{24}N_5OP_4$ (1091.5): calcd C 36.31, H 2.68, N 6.42; found C 36.61, H 2.67, N 6.11.

2,5-Bis(bromomethyl)thiophene (7) [10,11]: **CAUTION! During the reaction the strongly carcinogenic bis(bromomethyl)ether is generated** [15b]**. Skin contact with the reaction**

mixture has to be avoided strictly! After use all glass-wares have to be cleaned thoroughly with ammonia solution. To a solution of 0.63 g (21.0 mmol) of paraformaldehyde in hydrobromic acid (5 mL, 5.7M in glacial acetic acid) was added 0.84 g (10.0 mmol) of freshly distilled thiophene. The red solution was stirred at room temperature for 30 minutes, then heated to 50 °C for 15 minutes. After cooling to room temperature a colourless solid precipitated which was collected, washed with water, 2% sodium bicarbonate solution, again with water and dried in vacuo thus affording 106 mg (4%) of **7** as colourless crystals. **CAUTION! (7) is a strong lachrymator and an unstable solid, which can decompose under explosion!** Characterization of **7**: M.p. 70-75 °C (Lit.[10]: 78 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.67 (s, 4 H, CH_2), 6.94 (s, 2 H, Ar-H).

1,1''-[2,5-Bis(methylene)thiophene]bis-4,4'-bipyridinium Dibromide (8) [11]**:** To a boiling solution of 241 mg (1.54 mmol) of 4,4'-bipyridine in dry acetonitrile (10 mL) was added slowly 84 mg (0.31 mmol) of **7** in a mixture of acetonitrile and CH_2Cl_2 (10 mL; 9:1 v/v). The solution was refluxed for two hours, and cooled to room temperature. The precipitate was collected, washed thoroughly with acetonitrile and dried at 70 °C affording 143 mg (79%, Lit.[11]: 16%) of **8**-2Br as yellow crystals. A pure sample for the elemental analysis was obtained by counterion exchange with aqueous NH_4PF_6 solution. M.p. 223 °C (decomp., dibromide), 213-218 °C [decomp., bis(hexafluorophosphate), Lit.[11]: 198 °C (decomp.)]; R_f = 0.29 (silica gel); UV-Vis (H_2O): λ_{max} (ε) = 261 nm (44700); ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 6.21 (s, 4 H, CH_2), 7.56 (s, 2 H, Ar-H), 8.02 (d, J = 5.8 Hz, 4 H, pyridine-3-H), 8.69 (d, J = 6.6 Hz, 4 H, pyridinium-3-H), 8.74 (d, J = 5.9 Hz, 4 H, pyridine-2-H), 9.45 (d, J = 6.7 Hz, 4 H, pyridinium-2-H); ^{13}C NMR (75.5 MHz, [D_6]DMSO): δ = 57.00 (t), 121.93 (d), 125.86 (d), 130.89 (d), 137.99 (s), 140.71 (s), 145.02 (d), 150.88 (d), 152.97 (s); $C_{26}H_{22}F_{12}N_4P_2S{\cdot}2H_2O$ (748.5): calcd C 41.72, H 3.50, N 7.49, S 4.28; found C 41.83, H 3.41, N 7.35, S 4.15.

(2,5)Thiophenophane (9): The synthesis was performed as described above for the furanophanes. Starting from 50 mg (0.086 mmol) of **8**-2Br and 45 mg (0.17 mmol) of 1,3-bis(bromomethyl)benzene, the aqueous solution was purified by preparative TLC affording after counterion exchange 10 mg (11%) of **9**-4PF_6 as colourless crystals. M.p. >270 °C (decomp.); R_f = 0.28 (silica gel); UV-Vis (H_2O): λ_{max} (ε) = 255 (33100), 209 nm (20900); ^{1}H NMR (500 MHz, [D_6]DMSO): δ = 5.91, 6.13 (2 s, 4 H each, CH_2), 7.46 (s, 2 H, Ar-H), 7.58 (t, J = 7.7 Hz, 1 H, Ar-H), 7.81 (d, J = 7.7 Hz, 2 H, Ar-H), 7.93 (s, 1 H, Ar-H), 8.48, 8.50 (2 d, J = 6.3, 6.4 Hz, 4 H each, bipy-3-H), 9.28, 9.44 (2 d, J = 6.7 Hz, 4 H each, bipy-2-H); ^{13}C NMR (125.7 MHz, [D_6]DMSO): δ = 58.86 (t), 63.61 (t), 126.97 (d), 127.08 (d), 128.61 (d), 130.55 (d br), 130.98 (d), 135.81 (s), 140.99 (s), 145.23 (d), 145.36 (d), 148.78 (s), 148.95 (s); $C_{34}H_{30}F_{24}N_4P_4S$ (1106.5): calcd C 36.90, H 2.73, N 5.06, S 2.90; found C 37.21, H 2.77, N 5.07, S 2.74.

General procedure for the preparation of the benzo[b]thiophenophanes **15-17**

2,3-Bis(bromomethyl)benzo[b]thiophene **10** [15] was dissolved in nitromethane (5 mL), the bis(4,4'-bipyridinium) dication (**12** [12], **13** [12] or **14** [13]) was dissolved in water (5 mL). The further procedure and work-up was performed as described above for the furanophanes.

(2,3)Benzo[b]thiophenophane (15): From 144 mg (0.25 mmol) of **12**-2Br and 112 mg (0.35 mmol) of **10** was obtained 56.7 mg of a crude product, which contained open-chained impurities. 38 mg of the crude product was stirred with 2N hydrochloric acid for one hour. The residual solid was collected, washed with water and dried at 70 °C affording 31 mg (36%, based on conversion and purification step) of pure **15**-4PF_6 as yellow crystals. In a second fraction 98 mg (56%) of **12** was recovered as bis(hexafluorophosphate). Characterization of **15**-4PF_6: M.p. 236-238 °C (decomp.); R_f = 0.45 (silica gel); UV-Vis (H_2O): λ_{max} (ε) = 256 (66100), 203 nm (58900); ^1H NMR (300 MHz, [D_6]DMSO): δ = 6.02 (d, J = 15.3 Hz, 2 H, CH_2, part of AB), 6.3-6.7 (series of d + s, 6 H, CH_2, parts of AB), 7.6-8.7 (series of m, 20 H, Ar-H, bipy-3-H, bipy-2-H), 9.3-9.6 (s br, 4 H, bipy-2-H); ^{13}C NMR (75.5 MHz, [D_6]DMSO): δ = 53.38 (t br), 55.65 (t), 61.17 (t), 61.42 (t), 122.65 (d br), 123.59 (d), 125.96 (d), 126.25 (d), 126.75 (d), 126.88 (d br), 127.02 (d), 128.00 (s), 131.11 (s br), 132.27 (d br), 135.80, 136.03 (2 d), 137.23 (s), 139.36 (s), 139.93 (s), 143.87, 144.49, 145.30, 145.72 (4 d), 147.92, 148.01, 148.19, 148.30 (4 s); $C_{38}H_{32}F_{24}N_4P_4S$ (1156.6): calcd C 39.46, H 2.79, N 4.84, S 2.77; found C 38.94, H 3.01, N 4.80, S 2.46.

(2,3)Benzo[b]thiophenophane (16): From 144 mg (0.25 mmol) of **13**-2Br and 112 mg (0.35 mmol) of **10** was obtained 71 mg (31%, based on conversion) of **16**-4PF_6 as yellow crystals. 38 mg (22%) of **13** was recovered as bis(hexafluorophosphate). Characterization of **16**-4PF_6: M.p. 233-234 °C (decomp.); R_f = 0.39 (silica gel); UV-Vis (H_2O): λ_{max} (ε) = 259 (79400), 202 nm (132000); ^1H NMR (300 MHz, [D_6]DMSO): δ = 5.96, 5.98 (2 s, 2 H each, CH_2), 6.27 (s, 1 H, Ar-H), 6.3-6.8 (2 d br, 2 H, CH_2, AB), 6.54 (s, 2 H, CH_2), 7.67 (m, 5 H, Ar-H), 8.23, 8.34 (2 d, J = 6.9 Hz, 2 H each, bipy-3-H), 8.29, 8.38 (2 d, J = 9.0 Hz, 1 H each, Ar-H), 8.51 (m, 4 H, bipy-3-H), 8.71, 9.06, 9.19, 9.20 (4 d, J = 6.7 Hz, 2 H each, bipy-2-H); ^{13}C NMR (75.5 MHz, [D_6]DMSO): δ = 53.34, 55.52 (2 t), 63.11 (t br), 122.66 (d), 123.63 (d), 123.75 (d), 126.00 (d), 126.20 (d), 126.41, 126.70, 126.79, 126.86 (4 d), 127.27 (s), 129.20, 129.26, 129.90 (3 d), 135.89, 136.17 (2 s), 137.13 (s), 139.29 (s), 140.09 (s), 144.53, 145.18 (2 d), 146.35 (d br), 147.65, 147.94 (2 s), 148.27 (s br); $C_{38}H_{32}F_{24}N_4P_4S$ (1156.6): calcd C 39.46, H 2.79, N 4.84, S 2.77; found C 39.87, H 3.00, N 4.83, S 2.56.

(2,3)Benzo[b]thiophenophane (17): From 236 mg (0.39 mmol) of **14**-2Br and 160 mg (0.50 mmol) of **10** was obtained 88 mg (29%, based on conversion) of **17**-4PF_6 as yellow crystals. 91 mg (33%) of **14** was recovered as bis(hexafluorophosphate). Characterization of **17**-4PF_6: M.p. 222-224 °C (decomp.); R_f = 0.42 (silica gel); UV-Vis (H_2O): λ_{max} (ε) = 258 (57500), 202 nm (102000); ^1H NMR (500 MHz, [D_6]DMSO): δ = 6.08, 6.09 (2 s, 2 H each, CH_2), 6.40, 6.63 (2 d vbr, 1 H each, CH_2, AB), 6.50 (s, 2 H, CH_2), 7.70 (m, 4 H, Ar-H), 8.13 (dd, J = 7.9, 7.7 Hz, 1 H, Ar-H), 8.27, 8.34 (2 d, J = 6.1, 6.8 Hz, 2 H each, bipy-3-H), 8.30, 8.38 (2 m, 1 H each, Ar-H), 8.52 (m, 4 H, bipy-3-H), 8.70 (s br, 2 H, bipy-2-H), 9.01 (d br, J = 5.4 Hz, 2 H, bipy-2-H), 9.15 (m, 4 H, bipy-2-H); ^{13}C NMR (125.7 MHz, [D_6]DMSO): δ = 53.48, 55.69 (2 t), 63.07 (t br), 122.65 (d), 122.75, 122.79 (2 d), 123.59 (d), 126.13 (d br), 126.18 (d), 126.45, 126.80 (2 d), 126.95 (d), 128.02 (s), 136.96 (s), 138.99 (d), 139.44 (s), 140.09 (s), 144.53, 145.38 (2 d), 147.08 (d br), 147.30, 147.54, 148.24, 148.37 (4 s), 152.00, 152.07 (2 s);

$C_{37}H_{31}F_{24}N_5P_4S$ (1157.6): calcd C 38.39, H 2.70, N 6.05, S 2.77; found C 38.50, H 2.58, N 5.96, S 2.31.

Crystal structure determination for (6) [19]: Colourless single crystals were obtained by slow vapor diffusion of diisopropyl ether in acetonitrile solution of **6**-4PF_6. Diffraction data were collected on a Nonius CAD4 diffractometer ($Mo_{K\alpha}$ radiation, graphite monochromator) in the ω-scan mode. The structure was solved by direct methods (SHELXS97 [20]) and refined by full-matrix least squares (SHELXL97 [20]) based on F^2 with all reflections. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were geometrically placed and refined in a riding model. The PF_6 counterions are disordered and were refined in 50:50 split positions. The bridging bis(methylene)heterocycles are statistically distributed in the molecule and were refined with an occupation factor of 0.5 each. Crystallographic data and details of the refinement procedure: Empirical formula: $C_{33}H_{29}F_{24}N_5OP_4$; M = 1091.5 g mol^{-1}; crystal size: 0.36 × 0.29 × 0.11 mm; crystal system: *monoclinic*; space group: $P2_1/a$ (No. 14); a = 11.354(1), b = 16.885(2), c = 11.462(1) Å; β = 102.08(1)°; V = 2148.8(3) Å^3; D_x = 1.687 g cm^{-3}; Z = 2; F_{000} = 1092; T = 293(2) K; $\mu(Mo_{K\alpha})$ = 0.317 mm^{-1}; unique refl. measured: 2137; refl. observed ($I > 2\sigma|I|$): 1987; refined parameters: 459; restraints: 132; $R1$ = 0.0535; wR_2 = 0.1512 (observed data); $GooF$ = 0.890; $(\Delta\rho)_{max}$ = 0.19(8) e Å^{-3}, $(\Delta\rho)_{min}$ = -0.25(5) e Å^{-3}.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (Graduiertenkolleg "Struktur-Eigenschafts-Beziehungen bei Heterocyclen") and the Fonds der Chemischen Industrie. H. S. is grateful to the Studienstiftung des Deutschen Volkes e.V. for a fellowship. The recording of multidimensional NMR spectra by Dr. M. Gruner is most gratefully acknowlegded.

References and Notes

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[17] We have synthesized the mentioned carbophane in a similar procedure starting from dication **13**-2Br and 1,2-bis(bromomethyl)benzene in 64% yield. In our product the resonance of the intraannular proton was determined to $\delta = 6.14$ (500 MHz, [D_6]DMSO).

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[19] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-103287. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk.).

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