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Adamantane–dipyrromethanes: novel anion receptors

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Abstract—New adamantane–dipyrromethanes (AdD **1**–**4**) were synthesized and their anion binding properties investigated. AdD **1**–**3** form 2:1 complexes with F^- (AdD:F = 2:1) characterized by high association constants, and 1:1 complexes with Cl^-, Br^-, HSO_4^- and $H_2PO_4^-$. The binding of Cl^-, Br^-, $HSO_4^-$and $H_2PO_4^-$ by AdD **1**–**3** is 2–3 times stronger than for the reference compound, *meso*-phenyldipyrromethane (**5**). However, AdD **4** forms complexes with F^- characterized by 1:1 and 1:2 stoichiometry (AdD:F = 1:2).

Anions play key roles in chemical and biological processes. Many anions act as nucleophiles, bases, redox agents or phase transfer catalysts, while most enzymes bind anions as either substrates or cofactors.[1] Additionally, it is of great importance to detect anionic pollutants such as phosphates and nitrates in ground and wastewater. Consequently, it is highly desirable to obtain anion sensors which would be characterized by high binding constants and selectivity. This demand has fueled research in the field of anion sensing during the last 20 years, which has resulted in numerous publications which have been reviewed.[2]

A significant number of molecules which are used as anion sensors include pyrrole subunits. Pyrroles have acidic NH protons to which an anion can be attached by two or more hydrogen bonds. Among these molecules, anion sensing has been reported for the derivatives of amidopyrroles,[2f,3] amidodipyrromethanes,[4] calix-pyrroles,[5] sapphyrins[6] and porphyrins,[7] as well as dipyrroquinoxalines.[8] The highest selectivity of binding was observed for fluoride. Sensing of fluoride has a significant importance due to its role in preventing dental caries and osteoporosis.[9]

Since the presence of two NH protons is sufficient to accomplish the binding of an anion with high association constants (as in the case of dipyrroquinoxalines), we were prompted to investigate the applicability of dipyrromethanes as anion sensors. Dipyrromethanes are simple molecules which can be easily synthesized,[10] and therefore are good candidates for the study of anion binding. Moreover, the crystal structure of a dipyrromethane Cl^- complex has been reported.[11]

In the context of our work on the synthesis of macrocycles (bearing polycyclic units such as adamantane or PCU)[12] capable of selective recognition of different guest molecules, we turned our attention to anion sensors. In this Letter, we report the synthesis of four new adamantane–dipyrromethane derivatives (AdD) **1**–**4**, as well as an investigation of their anion binding properties.[13] It was anticipated that incorporation of the bulky adamantane units would hinder the rotational mobility of the pyrrole moieties in the AdD, and thus increase the stability of complexes with anions, as compared to dipyrromethanes bearing phenyl substituents in the *meso* positions (5-phenyldipyrromethane, **5**). Moreover, adamantane derivatives are characterized by lipophilicity which might assist the applicability of the AdD molecules as anion phase transfer agents. In this study, we present the results of the binding with F^-, Cl^-, Br^-, HSO_4^- and $H_2PO_4^-$.

The AdD derivatives **1**–**4** were prepared in moderate yields according to the standard procedure for the synthesis of dipyrromethanes,[10] from pyrrole and the corresponding adamantane carbonyl derivatives: adamantane-1-carbaldehyde (**6**), adamantan-2-one (**7**),

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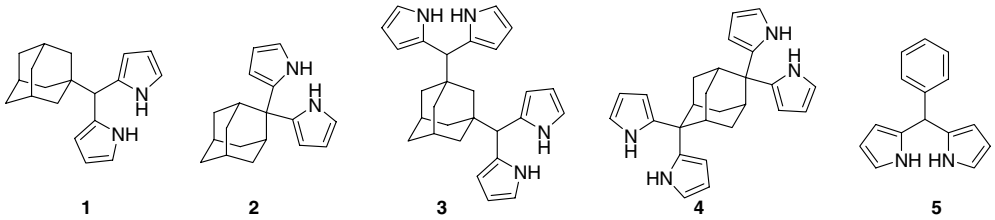
adamantane-1,3-dicarbaldehyde (**8**), and adamantan-2,6-dione (**9**), respectively. The syntheses were carried out in the presence of TFA, in an excess of pyrrole, which was used as the solvent.[14] AdD derivatives **1**–**4** were chemically stable and resistant to oxidation with strong oxidizing agents such as DDQ.



1 **2** **3** **4** **5**

The anion binding properties were investigated by NMR titrations. The titrations were performed at rt (20 °C) by recording spectra in $CDCl_3$ solution, except for AdD **3** and **4** (because of solubility problems, see Table 1). The concentration of the AdD or **5** in the NMR experiment was typically 0.05 M. The anions were added in the form of tetrabutylammonium salts. The concentrations of the anions ranged from 0.01 to 0.1 M, reaching the maximal ratio of anion:AdD = 2:1. One example of the changes in ^{1}H NMR spectra upon addition of anion to AdD is presented in Figure 1.

As can be seen in Figure 1, upon addition of F^-, the signal of the free NH protons at δ 7.8 ppm disappeared and a new signal at 10.0 ppm appeared which was assigned to the bound NH protons, in a fast exchange with the unbound NH resonances. With increasing concentration of F^-, this signal shifted to lower magnetic field, reaching the maximum value at ~12.2 ppm. Additionally, in AdD **2** some changes were also observed to the chemical shift of the bridgehead C2–H and C3–H protons (downfield shift of 0.52 ppm), and pyrrole C3–H and C4–H protons (upfield shift of 0.25 ppm).

In order to estimate the association constants of the complex with F^- and determine the stoichiometry, we used the EQNMR program.[15] The fitting clearly indicated the formation of a 2:1 complex (AdD:F^- = 2:1) characterized by a relatively high association constant of 4.4×10^3 mol^{-2} dm^6. The stoichiometry of the complex was additionally verified by a Job plot.[16] The results obtained by NMR titrations for **1**, **3** and **5** with Bu_4NF showed similar behavior. Besides the shift of the NH signal, a smaller effect was also observed in the chemical shift of the pyrrole C–H protons, as well as in the *meso* C–H (downfield shift of 0.1 ppm). However, a careful analysis of the results by the EQNMR program revealed that AdD **1** and **3** form only 2:1 complexes, while **5** formed two complexes characterized by the stoichiometries 2:1 and 1:1. The association constant of the 1:1 complex is two orders of magnitude lower than that for the 2:1 complex. The values of the estimated constants are compiled in Table 1.

AdD **3** has two potential anion binding sites, and therefore, it may theoretically form complexes characterized by the stoichiometries (AdD:anion) 2:1, 1:1 and 1:2. Moreover, AdD is characterized by a structure in which two types of 1:1 complexes may be formed. An anion could be bound to two NH protons, leaving the other binding site unaffected, or it could be bound by four NH protons. However, analysis of the experimental data obtained in $CDCl_3$ pointed to the presence of only one complexed species characterized by the stoichiometry of 2:1 and an exceptionally high association constant. On the other hand, NMR titration in DMSO indicated the presence of 1:1 and 2:1 complexes. However, we could not estimate the association constants (in DMSO) with an acceptable precision.

The titration for AdD **4** was performed in DMSO-d_6. Therefore, the estimated association constant is not directly comparable to those obtained for the complexes in $CDCl_3$. However, the result indicates to which H

Table 1. The association constants of the complexes of dipyrromethanes with anions determined by NMR titration[a]

Compound	F^-[c]	Cl^-	Br^-	HSO_4^-	$H_2PO_4^-$
1	$(1 \pm 0.1) \times 10^4$ (2:1)	80 ± 10 (1:1)	22 ± 4 (1:1)	65 ± 3 (1:1)	150 ± 10 (1:1)
2	$(4.4 \pm 0.1) \times 10^3$ (2:1)	68 ± 6 (1:1)	38 ± 3 (1:1)	22 ± 2 (1:1)	182 ± 9 (1:1)
3	$(4.8 \pm 0.5) \times 10^5$ (2:1), $\sim 1 \times 10^4$ (2:1) and $\sim 1 \times 10^3$ (1:1)[f]	ND[e]	ND[e]	$(1.4 \pm 0.8) \times 10^3$ (1:1)	ND[d,e]
4[b]	150 ± 40 (1:1) $(3.3 \pm 0.7) \times 10^3$ (1:2)	ND[f]	ND[g]	ND[g]	74 ± 20 (1:1)
5	170 ± 20 (1:1) $(2.3 \pm 0.2) \times 10^4$ (2:1)	22 ± 2 (1:1)	4.8 ± 0.8 (1:1)	6 ± 1 (1:1)	32 ± 2 (1:1)

The complexes were formed in 1:1 stoichiometry giving K_{11} (mol^{-1} dm^3), 2:1 giving K_{21} (mol^{-2} dm^6) and 1:2 (AdD **4** × 2F^-) giving K_{12} (mol^{-2} dm^6).

[a] The titrations were performed in $CDCl_3$ solution unless stated otherwise. The anions were added as tetrabutylammonium salts. The association constants were determined by fitting the dependence of the chemical shift of the NH signal ($\Delta\delta$) to the anion concentration, using EQNMR program.

[b] The titration was performed in DMSO-d_6 because of insolubility in $CDCl_3$.

[c] Content of water was at <5 wt %.

[d] The titration was performed in CD_3CN because of precipitation during the titration in $CDCl_3$.

[e] The titration data could not be fitted to 1:1 or 1:2 stoichiometries or their combination.

[f] The titration was performed in DMSO-d_6; the data could not be fitted well, indicating the presence of 1:1 and 2:1 complexes.

[g] No binding was observed.

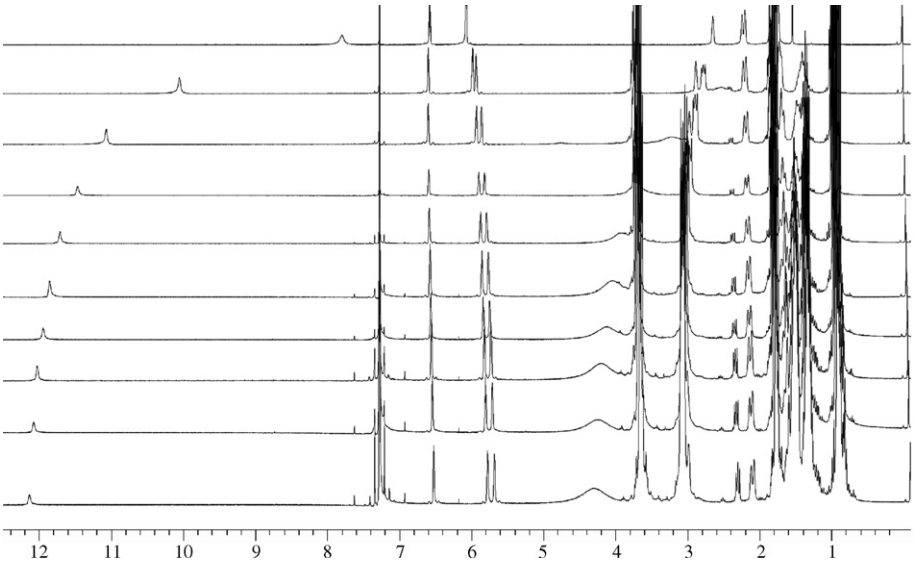


Figure 1. ^{1}H NMR spectra ($CDCl_3$) of AdD **2** ($c = 0.05$ M) with varying concentrations of Bu_4NF (added as 1 M solution in THF). The top spectrum corresponds to the pure AdD **2**, while the other spectra correspond to AdD **2** and the following F^- concentrations: 0.011, 0.022, 0.033, 0.044, 0.055, 0.066, 0.077, 0.088, and 0.11 M.

atoms the anion is being bound as well as the stoichiometry of the complex. The analysis revealed formation of two complexed species characterized by stoichiometries 1:1 and 1:2 (AdD:$F^- = 1:2$).

The addition of other anions (Cl^-, Br^-, HSO_4^- and $H_2PO_4^-$) to the solutions of AdDs **1**–**4** and **5** also showed shifting of the NH signal. Additionally, we observed significant downfield shifts of the *meso* C–H (**1**, **3** and **5**) and the bridgehead H signal (AdD **2** and **4**). These shifts were more pronounced in the case of Cl^- than F^-. For an example, upon addition of 2 equiv of Cl^- the signal of the bridgehead H shifted for 0.39 ppm, whereas upon addition of F^- the shift was 0.26 ppm. Consequently, we assume that the binding of the bigger (and softer) anions is accomplished by formation of two medium–strong hydrogen bonds between the anion and the NH protons and one additional weak H-bond between the anion and the H-atom attached to the bridgehead carbon or *meso* H-atom. The hydrogen bond of an anion with a C–H is not usual, and has been previously reported.[17] However, an influence on the chemical shift of the C–H due to through-space polarization by anions can not be excluded.

The association constants of the complexes with anions Cl^-, Br^-, HSO_4^-, and $H_2PO_4^-$ were 2–3 orders of magnitude lower than with F^- and characterized by 1:1 stoichiometries (additionally verified by the Job plot of AdD **1** and Cl^-). Formation of 1:1 complexes characterized by lower association constants for these anions is not surprising taking into account that they are bigger, less basic and less nucleophilic, and is in accordance with the similar behavior of the anion sensors with other pyrrole derivatives.

AdD derivatives showed 2–3 times stronger binding of Cl^-, Br^-, HSO_4^-, and $H_2PO_4^-$ than **5**. The higher binding constants in the case of AdD can be rationalized by preorganization of the molecule for the complexation imposed by the bulky adamantane and the availability of the hydrogen attached to carbon (*meso* C–H or bridgehead C–H) for the complexation. Moreover, in the case of **5** there is most likely a repulsion between the anion and the phenyl ring which results in the formation of weaker complexes characterized by the geometry, with the anion further away from the phenyl ring and *meso* C–H.

The NMR titrations for AdD **3** and most of the anions showed, after the addition of 0.25 equiv of anion, line broadening of the pyrrole C–H signals, while the NH signal at $\delta \approx 7.9$ ppm disappeared and a new very broad signal at ≈9.5 appeared. This was accompanied by the formation of precipitates which made it difficult to record the spectra. Upon the next addition of anion (0.5 equiv), line broadening disappeared and the N–H signal appeared at $\delta \approx 11$ ppm. The following addition of anion (0.75 equiv) had only a negligible influence, shifting the NH signal only slightly downfield. Similar behavior was observed also in some cases for AdD **4**. These findings indicate that AdD **3** and **4** most probably also form higher, rod-like aggregates, which may be considered supramolecular oligomeric molecules and which may provide important applications of AdD **3** and **4** in supramolecular synthesis.

In summary AdD derivatives **1**–**4** were prepared for the first time and their binding with anions was examined. The highest binding was observed for F^- yielding 2:1 complexes, except for AdD **4** which gave a 1:2 complex. AdD derivatives form complexes with Cl^-, Br^-, HSO_4^- and $H_2PO_4^-$ characterized by 1:1 stoichiometry and 2–3 orders of magnitude smaller association constants. We are continuing to study the binding of the anions by AdD molecules, and particularly, the formation of the complexes with the unexpected stoichiometries, as in the case of AdD **3** and **4**.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.08.122.

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14. 1-*Di*(*pyrrole*-2-*yl*)*methyladamantane* (**1**): 51%; colorless crystals, mp 168–169 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.56–1.69 (m, 12H), 1.97 (br s, 3H), 3.57 (s, 1H), 6.08–6.23 (m, 4H), 6.60–6.69 (m, 2H), 7.97 (br s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 28.6 (d, 3C), 36.7 (t, 3C), 36.9 (s, 1C), 40.4 (t, 3C), 51.4 (d, 1C), 106.5 (d, 2C), 108.2 (d, 2C), 115.7 (d, 2C), 130.1 (s, 2C); IR (KBr) 3369 (s), 2927 (m), 2903 (m), 2864 (m) cm^{-1}; MS *m*/*z* (%) 279 (100, M−H$^+$); HRMS, calculated for $C_{19}H_{23}N_2$: 279.1861; observed: 279.1859.
2,2-*Di*(*pyrrole*-2-*yl*)*adamantane* (**2**): 29%; colorless crystals, mp 183.4–185.2 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.69–1.87 (m, 8H), 2.16–2.26 (m, 4H), 2.64 (br s, 2H), 6.04–6.07 (m, 4H), 6.56–6.58 (m, 2H), 7.78 (br s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 27.3 (d, 2C), 33.6 (t, 4C), 33.9 (d, 2C), 38.1 (t, 1C), 45.0 (s, 1C), 103.9 (d, 2C), 107.3 (d, 2C), 116.1 (d, 2C), 137.9 (s, 2C); IR (KBr) 3382 (s), 3097 (w), 2950 (m), 2924 (m), 2890 (m), 2894 (m), 1107 (m), 1028 (m), 787 (m), 727 (s) cm^{-1}; MS *m*/*z* (%): 265 (100, M−H$^+$); HRMS, calculated for $C_{18}H_{21}N_2$: 265.1705; observed: 265.1706.
1,3-*Bis*[*di*(*pyrrole*-2-*yl*)*methyl*]*adamantane* (**3**): 37%; colorless crystals, mp 110–112 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.38–1.55 (m, 12H), 1.96–2.02 (m, 2H), 3.57 (br s, 2H), 6.00–6.19 (8H), 6.58–6.65 (m, 4H), 7.94 (br s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.8 (d, 2C), 35.8 (t, 1C), 37.8 (s, 2C), 39.3 (t, 4C), 43.8 (t, 1C), 50.9 (d, 2C), 106.5 (d, 4C), 108.2 (d, 4C), 115.8 (d, 4C), 129.9 (s, 4C); IR (KBr) 3382 (s), 2901 (s), 2847 (m), 720 (s) cm^{-1}; MS *m*/*z* (%): 423 (100, M−H$^+$); HRMS, calcd for $C_{28}H_{31}N_4$: 423.2549; observed: 423.2542.
2,2,6,6-*Tetra*(*pyrrole*-2-*yl*)*adamantane* (**4**): 15%; colorless crystals, decomposition above 215 °C; ^{1}H NMR (DMSO-

d_6, 300 MHz) δ 1.83–1.95 (m, 8H), 2.68 (br s, 4H), 5.73–5.86 (m, 8H), 6.42–6.50 (m, 4H), 10.09 (br s, 4H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 29.2 (t, 4C), 31.2 (d, 4C), 44.3 (s, 2C), 103.7 (d, 4C), 106.5 (d, 4C), 115.2 (d, 4C), 138.2 (s, 4C); ^{13}C NMR (CD_3CN, 75 MHz) δ 30.4 (t, 4C), 33.1 (d, 4C), 45.6 (s, 2C), 104.6 (d, 4C), 108.0 (d, 4C), 116.5 (d, 4C), 139.2 (s, 4C); IR (KBr) 3409 (s), 3379 (s), 2959 (m), 2925 (m), 2899 (m), 2861 (m), 720 (s) cm^{-1}; MS m/z (%): 395 (75, M$-$H$^+$), 328 (100); HRMS, calcd for $C_{26}H_{27}N_4$: 395.2236; observed: 395.2236.

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