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ORIGINAL ARTICLE

Amide-based tripodal receptors for selective anion recognition

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Abstract In order to improve efficiency and reduce waste production; the microwaves offer mild methods to prepare amides based neutral tripodals receptors directly from non activated carboxylic acids and amines in the absences of coupling reagents and solvents, with high yield and very short time. The preliminary 1H NMR titration experiments revealed that tripodals receptor **1** and **2** can recognize $H_2PO_4^-$ and $C_6H_5CO_2^-$ through a 1:1 binding-stoichiometry in preference over other anions (PF_6^-, ClO_4^-, HSO_4^- and Br^-). The tripodal receptor **2** showed higher binding to the all examined anions than the tripodal receptor **1**.

Keywords Anion recognition · Tripodal receptor · Amides · Microwave · NMR titration

Introduction

A great deal of attention has recently been focused on the selective recognition of anions by means of synthetic receptors due to their potential applications in many fields, ranging from environmental monitoring, industrial purposes to clinical diagnostics [1, 2]. More specifically anions play important roles in medicinal chemistry (maintenance of phosphate and sulphate concentration during dialysis [3]) and catalysis (such as anion templated synthesis [4]). Same anions have been linked to waterway pollution (from runoff of nitrate- and phosphate-containing fertilizer [5]) and carcinogenesis (metabolites of nitrate [6]).

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The selectivity of a synthetic receptor towards a specific analyte is determined by multiple interactions between host and guest in a complementary fashion. The receptor may contain a variety of functionalities, which must be organised to complement the size and shape of the analyte. The topology of the receptor is of importance in determining the overall receptor-anion interactions. The tripodal synthetic receptors constitute a special class of acyclic ionophores, which consist of multi-armed ligands that can coordinate with the target anion. The tripodal molecular platform provides three arms to which ligating groups are tailored or attached. The molecular design allows the rational control of binding properties such as complex stability and selectivity. The selectivity of tripodal synthetic receptors relates greatly to the rigidity of its arms and its cavity size [7–9].

The main aims of designing tripodal anion receptors are: (i) there are a sufficient number of positively charged or neutral electron deficient groups in the ligand to serve as interaction sites. (ii) Receptors with a flexible tripodal structure have a strong affinity for trigonal oxoanions, such as phosphate, carbonate and chlorate, because the geometry and orientation of the host molecules favour the formation of stable host guest complexes [10]. The host molecules can be ensured interactions with guest based on non-covalent interactions. The non-covalent interactions include electrostatic interactions, hydrogen bonding, hydrophobicity, π–π-stacking and a combination of these interactions. In addition, for the anions itselves, the size, shape, H-bonding capability, acid/base properties and the number of interaction sites are also important.

There has been extensive effort devoted to the development of synthetic anion receptors with a multitude of review articles written on the subject [1, 11–16]. Among these anion receptor compounds, bearing as binding sites

amides [17, 18], ureas [19, 20] and thiureas [21, 22] groups are the dominant structures.

Generally, many observable signal such as redox potential changes, NMR and UV-vis spectral changes, colour changes, and emission fluorescence changes have been used as indication of host guest interactions. In particular, NMR most widely used techniques for measuring interactions between host and guest [23, 24].

The application of microwave technology in organic chemistry has been explored extensively within the last decade and a large number of publication and reviews have clearly shown that many types of chemical transformation can be carried out successfully under microwave condition. Most importantly, microwave irradiation processing frequently leads to dramatically reduced reaction times, higher yields, less formation of by products, easier work up matching with the goal green chemistry, solvent-free organic transformations, atom economy and selective of reactions [25–30].

This study reports the synthesis of tripodal amides receptors **1** and **2** by microwave and evaluated their binding properties of anions such as $H_2PO_4^-$, $C_6H_5CO_2^-$, PF_6^-, ClO_4^-, HSO_4^- and Br^- by ^1H NMR titration. It has been found that especially both tripodals receptor **1** and **2** show high affinity to dihydrogenphosphate and benzoate anions. However, tripodal receptor **2** show higher recognition towards dihydrogenphosphate and benzoate than tripodal receptor **1**.

Result and Discussion

Synthesis of Tripodal Receptors

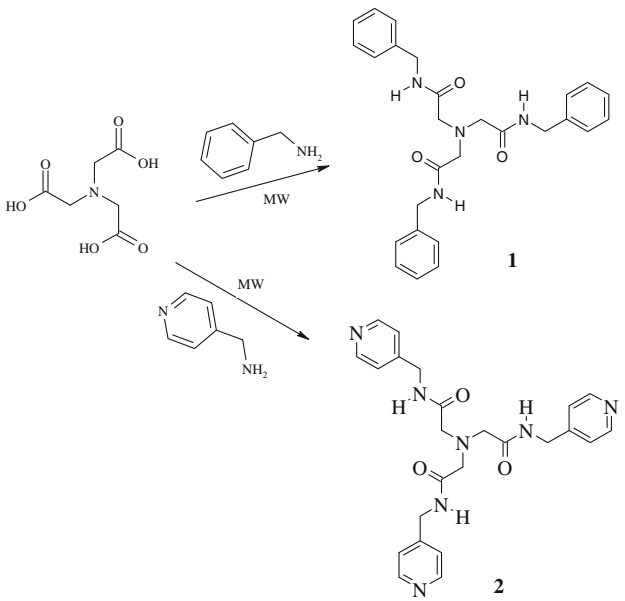
In this study, in order to improve efficiency and reduce waste production; the microwaves offer mild methods to prepare amides directly from non activated carboxylic acids and amines in the absences of coupling reagent and solvents. The application of microwave technology in the amide solvent-free synthesis is not frequently described in literature [31–36]. The most popular methods for the synthesis of carboxyamides involve the conversation of carboxylic acid to more reactive functional group or in situ activation by using coupling reagents. Although good results are obtained with both approaches, they need often expensive coupling reagents, which lead to the formation of by products requiring further separation [37].

In the present study, amides-based tripodal receptors **1** and **2** were synthesised by microwave with high yield and in very short time. The synthesis of amide-based tripodal receptor **1** was previously reported in the literature [38]. A similar procedure was followed for the synthesis of tripodal receptor **2**. Nitrilotriacetic acid was directly treated with benzyl amine and picolyl amine under microwave condition to give amide-based tripodal receptors **1** and **2**, respectively as shown in Scheme 1. Despite the simplicity of the reaction procedure, few examples have been reported on the direct synthesis of amides-based tripodals from carboxylic acids under microwave irradiation in the absences of the solvent. The structures proposed for these amide-based tripodal receptors are consistent with data obtained from ^1H, ^{13}C NMR, IR and elemental analyses. All ^1H and ^{13}C NMR signals were assigned on the basis of DEPT and ^1H-^{13}C correlation experiment.

Anion Binding in Solution

NMR has become a routine tool in the study of host–guest supramolecular chemistry and there are now hundreds of studies where ^1H NMR titration was used to measure intermolecular association. A major advantage of the NMR method over other techniques is that the results are not greatly affected by the presence of minor impurities and valuable structural information can be obtained [23]. In this paper, the abilities of tripodal receptors **1** and **2** to bind anions such as $H_2PO_4^-$, $C_6H_5CO_2^-$, PF_6^-, ClO_4^-, HSO_4^- and Br^- were investigated using ^1H NMR titration method.

The differences in chemical shifts in ^1H NMR spectra of the free and the complexed state of either host receptor or guest may suffice to estimated thermodynamics of molecular recognition. The technique is based on addition of varying concentration of guest anions in the prescience of



Scheme 1 Microwave assisted synthesis of amide-based tripodal receptors

constant receptor concentration resulted in shifting of some ^{1}H NMR signals up field or downfield. The complexation of anions [G] with receptors [H] is expressed by Eq. 1

$$H + G \overset{K}{\leftrightarrows} H \cdot G \quad (1)$$

Tetrabutylammonium form of anions such as $H_2PO_4^-$, $C_6H_5CO_2^-$, PF_6^-, ClO_4^-, HSO_4^- and Br^- were used as guest molecules. The association constant of the supramolecular system formed was calculated according to the modified Benesi–Hildebrant equation of (Eq. 2) derived from (Eq. 1), where $[H]_o$ and $[G]_o$ refer to the total concentration of tripodal receptors and tetrabutylammonium salts, respectively. The original Benesi–Hildebrant experiment was an optical spectroscopy study of the association of iodine with aromatic hydrocarbons [39]. The key feature of this method is that by working with a large excess of component H, the concentration of uncomplexed H can be set equal to the initial concentration, $[H] = [H]_o$. Relationships between known quantities (initial concentrations) and experimental observations can now be derived, Marthur [40] and Ashbaugh [41] have independently derived the NMR version of the Benesi–Hildebrant equation. For all the anions examined, plots of calculated $1/\delta$ values as a function $1/[G]_o$ values give a linear relationship with a slop of calculated $1/K_a \cdot \Delta\delta_{max}$ and intercept $1/\Delta\delta_{max}$ supporting 1:1 complex formation.

$$\frac{1}{\Delta\delta} = \frac{1}{(K_a \cdot \Delta\delta_{max} \cdot [G]_o)} + \frac{1}{\Delta\delta_{max}}$$

where

$$\Delta\delta = (\delta_H - \delta_{obs}) \text{ and } \Delta\delta_{max} = (\delta_H - \delta_{HG}) \quad (2)$$

The binding properties of tripodal receptors **1** and **2** were examined toward tetrabuthylammonium form of anions such as $H_2PO_4^-$, PF_6^-, HSO_4^-, ClO_4^-, $C_6H_5CO_2^-$, Br^- by using ^{1}H NMR titration. The concentration of tripodal receptors was kept constant at 1×10^{-3} M in $DMSOd_6$. The binding constants were calculated from chemical schifts in the ^{1}H NMR peak of NH in the tripodal receptors against addition of various concentrations ($0–6 \times 10^{-3}$ M) of tetrabuthylammonium form of anions. The addition of tetrabuthylammonium salts of $H_2PO_4^-$ and $C_6H_5CO_2^-$ to the solution of tripodal receptors **1** and **2** caused significant downfield shifts in amide NH signals and upfields shifts in N–C$\underline{H_2}$–C=O (see Fig. 1) signals indicating fast equilibrium between complexed and free receptor and also suggesting that the encapsulation of anions inside the receptor through N–H…A^- hydrogen bonding interactions. But the addition of HSO_4^- to receptor **1** shows small changes in chemical shifts and PF_6^-, $ClO_4^-$and Br^- basically leads to no changes in chemical shifts. For the receptor **2**, the addition of $H_2PO_4^-$, $C_6H_5CO_2^-$ and HSO_4^- leads to significant chemical shifts, but the addition of PF_6^-, HSO_4^-, and

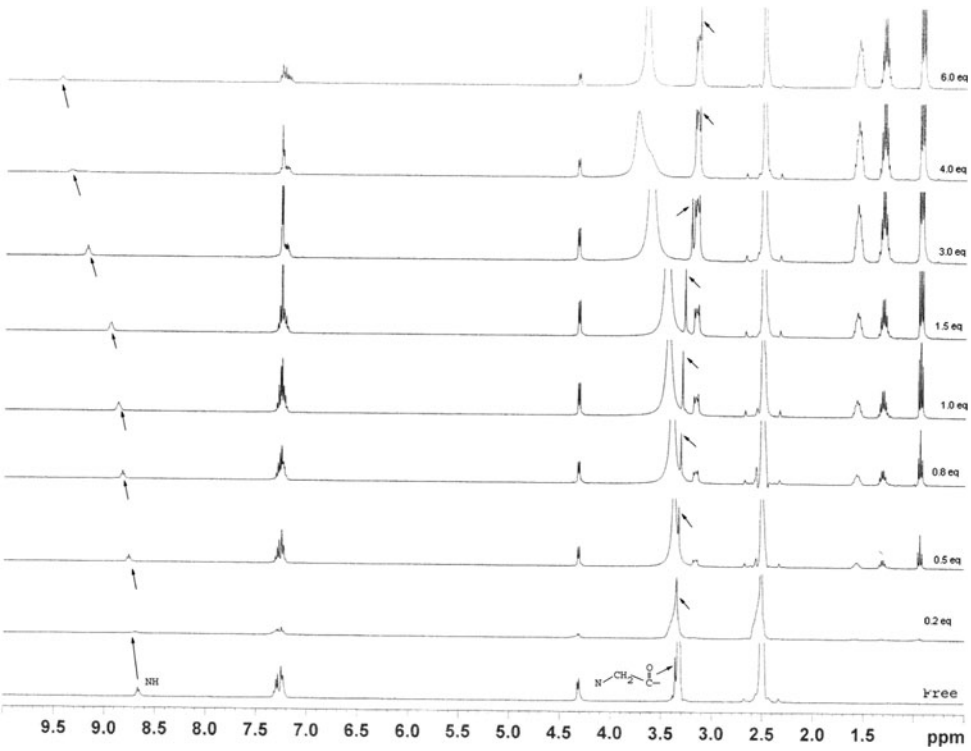


Fig. 1 Typical ^{1}H NMR spectral changes upon addition of various concentrations ($0 - 6 \times 10^{-3}$ M) of $Bu_4NH_2PO_4$ to the constant concentration (1×10^{-3} M) of tripodal receptor **1** in [D6] DMSO

ClO_4^- shows small chemical shifts and the addition Br^- showed basically no shift, indicating that the association constant cannot be determined using the data. Typical ^1H NMR spectral changes upon addition of tetrabuthylammonium form of $H_2PO_4^-$ anion to tripodal receptor **1** are shown in Fig. 1 while typical plots are shown for the complexation of the same anion and tripodal receptor **2** in Fig. 2. In the Fig. 3, the Job's Plot of receptor **1** and $H_2PO_4^-$ anion in $DMSOd_6$ shows the maximum at a molar fraction of 0.5. This result indicated that the receptor **1** binds $H_2PO_4^-$ anion guest with a 1:1 ratio. Moreover, similar results were obtained for tripodal receptor **2** and for both tripodal receptors **1** and **2** with other anions. It can be thought that the occurrence of protonation equilibria between the protic anions, such as $H_2PO_4^-$ and HSO_4^-, and the pyridine substituents of **2** is possible. However, if this was the case the NMR spectrum of **2** was going to be changed. As it can be seen that just some signals has shifted, on the other hand the main peaks still remains same. This proposed that this type of interactions can not occure. Therefore, this possibility has been ignored.

The binding constant, K_a, of the complexes of the tripodal receptors **1** and **2** with tetrabuthylammonium form of anions ($H_2PO_4^-$, PF_6^-, HSO_4^-, ClO_4^-, $C_6H_5CO_4^-$, Br^-) were determined by the Benessi–Hildebrant equation on the basis of the ^1H NMR spectrum of the complexes in $DMSOd_6$ collected at 25 ± 0.1 °C. Binding constant (K_a)

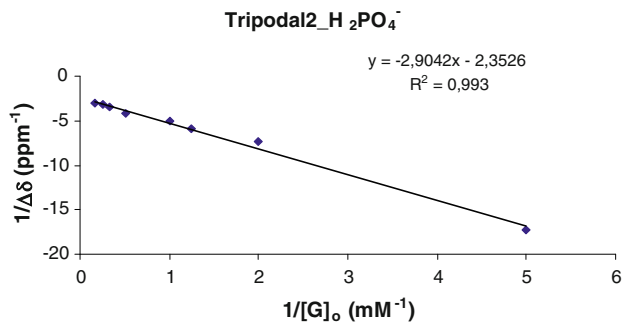


Fig. 2 Typical plot of $1/\Delta\delta$ versus $1/[G]_o$ for host–guest complexation of tripodal receptor **2** and $Bu_4NH_2PO_4$

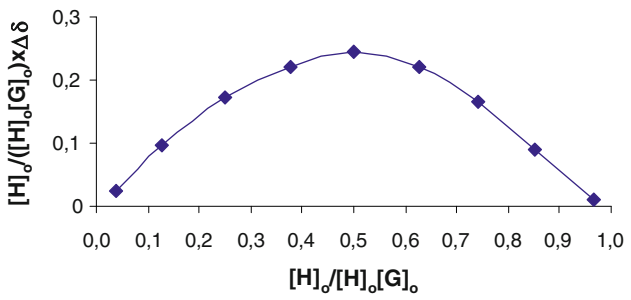


Fig. 3 Job's Plot for tripodal receptor **1** with $Bu_4NH_2PO_4$

Table 1 Binding constants (K_a) and binding free energies ($\Delta G°$) for 1:1 complexes of tripodal receptors 1 and 2 with anions in [D6] DMSO at 298 K

Receptor	Anion	K_a ($dm^3\ mol^{-1}$)[a]	$-\Delta G°$ (kJ mol^{-1})
Tripodal 1	$H_2PO_4^-$	241	13.6
	PF_6^-	ND	–
	HSO_4^-	43	9.3
	ClO_4^-	ND	–
	$C_6H_5CO_2^-$	110	11.7
	Br^-	ND	–
Tripodal 2	$H_2PO_4^-$	810	16.6
	PF_6^-	73	10.6
	HSO_4^-	39	9.1
	ClO_4^-	59	10.1
	$C_6H_5CO_2^-$	286	14.0
	Br^-	ND	–

The guest anions were used as the salts of $Bu_4NH_2PO_4$, Bu_4NPF_6, Bu_4NHSO_4, Bu_4NClO_4, Bu_4NBr, $Bu_4NC_6H_5O_2$

ND indicated that the spectra showed little or no change with the addition of anion so that the binding constants cannot be determined using the spectra

[a] Binding constant were represented as the average of three experiments, errors were ±10%

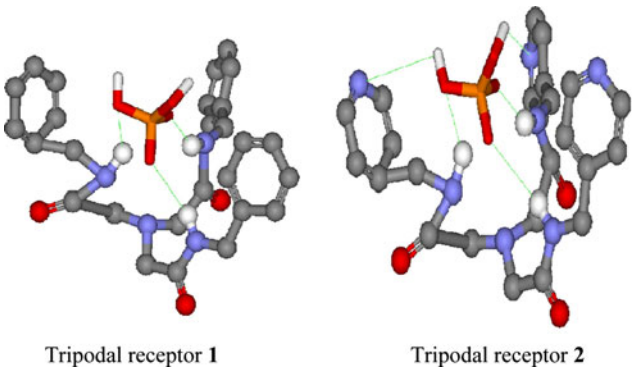
and the Gibbs free energy changes ($-\Delta G°$) of these tripodal receptors with anions obtained from usual curve-fitting analyses ($R^2 > 0.993$) of the observed chemical shift changes are summarized in Table 1. As shown in Table 1, the selectivity trends of binding affinity of anions for tripodal receptor **1** was in order of $H_2PO_4^- > C_6H_5CO_2^- > HSO_4^-$ and for tripodal **2** the order was $H_2PO_4^- > C_6H_5CO_2^- > ClO_4^- > PF_6^- > HSO_4^-$ in $DMSOd_6$. The study clearly demonstrated that the spacer of tripodal-type receptor influences the recognition for anions. Replacing the spacer of phenyl with pyridine moiety, the binding ability for desired anions strongly improve. As it can be seen from Table 1, the tripodal receptor **2** showed much better binding for all examined anions than the tripodal receptor **1**. This showed the benefit of a multidentate binding site. Although a full understanding of the principles that govern anion recognition has not yet been achieved, it already becomes clear that the selectivity of receptors for special anions can be rationalized on the basis of the anion basicity and shape complementarity between the receptor and the anionic guests [42]. In particular, multiple hydrogen bonding interaction are necessary in high-affinity anion binding sites. As expected from the basicity of anions, $H_2PO_4^-$ and $C_6H_5CO_2^-$ gave stronger complexation than other anions. Basicity of $C_6H_5CO_2^-$ and its capable π-π interaction with aromatic moiety of tripodal receptors may also play important role as a cooperatively and an additional binding force for recognition.

A plausible structure of the complexes

The proposed a plausible structure of the complexes of the tripodal receptors **1** and **2** with $H_2PO_4^-$ guest anion (scheme 2) are the simplest one that can account for the experimental data. Some general conclusions for interactions of tripodal hosts with anions have been proposed and confirmed [43, 44]. There are three main factors affecting the stability of the tripodal receptor-anion complexes. First, there are at least three hydrogen bonding sites in the complexes of tripodal receptors with oxoanions, namely the three H-bond donor sites of tripodal receptors (three NH). These sites enable a strong binding affinity between tripodal receptors and oxoanions, as reported in literatures [45]. Second, the flexible, three-dimensional molecular structure of tripodal receptors allows the shape and preorganization of the receptors to guide the recognition process. Last, the fit size and shape of anionic species favour formation of a stable receptor-anion complex. In addition, tripodal receptor **2** pyridine nitrogen may provide additional donor sites for receptor with acceptors. Tripodal receptor **2** has at least two additional hydrogen bonding sites that ensure the receptor **2** stronger binding to the all examined guest anions than the tripodal receptor **1**.

Conclusion

In summary, we have reported the synthesis of tripodal amides receptors **1** and **2** by microwave and their calculated binding properties with anions such as $H_2PO_4^-$, $C_6H_5CO_2^-$, PF_6^-, ClO_4^-, HSO_4^- and Br^- by ^1H NMR titration. The results indicate that tripodals **1** and **2** possess higher affinity for dihydrogenphosphate and benzoate anions. However, tripodal receptor **2** shows higher selectivity for dihydrogenphosphate and benzoate compared with tripodal receptor **1**. The results demonstrated that electrostatic interaction, hydrogen bonding, and preorganization of binding sites of receptors and the nature of anions play essential roles in the anion recognition.



Scheme 2 Three dimensional structures are droved by DS visualizer program

Experimental section

Tripodal receptor 2 (2,2′,2″ nitrilotris (N-4-picolyl acetamide))

Nitrilotriacetic acid (0.50 g, 2.62 mmol) and picolyl amine (0.843 g, 7.80 mmol) were taken in the reaction vessel. The resultant mixture was subjected to microwave irradiation. The temperature of mixture was reached to 150 °C within 2 min at 600 W and remained at 150 °C for 40 min at 600 W. The mixture was then cooled to room temperature and extracted with chloroform (3 × 50 mL). The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was recrystallised from mixture of ethylacetate and diethylether (4:1) to give tripodal receptor **2** as a white solid (0.99 g, 82%). Mp.96–97 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 3.45 (s, 6H), 4.60 (d, 6H, $J = 6$ Hz), 7.15 (t, 3H, $J = 3.4$ Hz), 7.27 (t, 3H, $J = 6.8$ Hz), 7.61–7.65 (m, 3H), 8.43 (t, 3H, $J = 2.2$ Hz), 8.81 (t, 3H, $J = 6$ Hz); ^{13}C NMR (100 Hz, $CDCl_3$): δ 44.10, 59.14, 121.98, 122.35, 136,97, 148.74, 157.26, 170.37; IR (KBr) : 3287(NH), 3030, 3060 (Ar–H), 1645(C=O) 1066 (C–N); Anal.Calcd for: $C_{24}N_7H_{27}O_3$: C, 62.46; H, 5.90; N, 21.24;. Found: C, 62.43; H, 5.95; N, 21.17.

The synthesis of tripodal receptor **1** (2,2′,2″nitrilotris (N-benzyl acetamide)) was previously reported in the literature [38].

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