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Anion binding properties of 5,5′-dicarboxamido-dipyrrolylmethanes†

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A series of 5,5′-dicarboxamido-dipyrrolylmethanes have been synthesized and in some cases crystallographically characterized. Proton NMR titrations have revealed that these compounds, that contain only four neutral hydrogen bond donors and are acyclic, selectively bind anions in very competitive solvent media such as DMSO-d_6/water mixtures.

Introduction

The design and synthesis of receptors that are selective for oxo-anions is an area of intense current interest due to the roles these ions can play in biological systems,[1] in inhibiting vitrification processes for nuclear waste or as pollutants in the environment[2] and in the selective extraction of transition metals from aqueous solution.[3] The use of pyrrole as an anion receptor moiety was pioneered by Sessler in the early 1990s with a series of papers on the anion complexation properties of expanded porphyrins such as sapphyrin.[4] Pyrrole is an ideal group from which to construct an anion receptor as, unlike other neutral hydrogen bond donor groups such as amides or ureas, it does not contain a hydrogen bond acceptor that could compete with a putative anionic guest for hydrogen bond formation with the NH group.[5] That said, amides are used extensively in synthetic anion receptors as they are synthetically accessible, are relatively stable and are good hydrogen bond donors forming stable complexes with anions.[6] In fact amides in proteins often form hydrogen bonds to oxo-anions which stabilize their three dimensional structures,[7] whilst anion transport proteins such as the sulfate binding protein make extensive use of amide NH groups to hydrogen bond to the anion and also to form charge relays to delocalise the charge on the guest into the protein structure.[8] Very recently a macrocycle containing a dipyrrolylmethane and a 2,6-diamidopyridine group that shows a high affinity for dihydrogen phosphate and hydrogen sulfate in acetonitrile solution has been reported by Sessler, Ustynyuk and co-workers,[9] whilst systems from Schmuck and co-workers have shown that guanidinium groups that contain an appended pyrrole-amide moiety are useful in the enantioselective complexation of amino acids and that guanidinocarbonyl pyrrole carboxylate zwitterions form stable self-assembled dimers in water.[10]

Out of the pyrrole arena, in 1997, Crabtree and co-workers reported that isophthalamide molecules form remarkably strong anion complexes in organic solution (binding chloride and fluoride particularly strongly).[11] In fact analogous groups had been employed in a macrocyclic anion templated system reported in 1996,[12] however Crabtree's work showed that the simple acyclic systems could exhibit very high anion affinities. In fact since this report, this motif (or ones similar to it) has been included in a variety of anion receptors,[13] salt receptors[14] and anion-templated self-assembling systems.[15]

Another class of anion receptor, in this case with high selectivity for oxo-anions, is based on urea or thiourea moieties.[16] Umezawa and co-workers have synthesised ditopic receptors containing two urea or thiourea groups and found these species to be selective for dihydrogenphosphate over other putative anionic guests in DMSO solution.[17]

We had previously studied the anion complexation properties of 2- and 2-,5-carboxamidopyrroles.[18] These compounds, although structurally simple, showed selectivity for oxo-anions in competitive solvent media (DMSO/water mixtures). Whilst, these receptors showed oxo-anion selectivity, the crystal structure of the benzoate complex of dibutyl-3,4-diphenyl-1*H*-pyrrole-2,5-dicarboxamide revealed that whilst one oxygen of the benzoate was bound in the plane of the pyrrole ring by hydrogen bonds from the pyrrole NH group and one of the amides, the other oxygen was not in the plane of the pyrrole ring and the second amide was twisted out of plane by approximately 38° in order to form a hydrogen bond to it.[19] The twisted amide bond in this structure led us to consider replacing the pyrrole unit in these receptors with a dipyrrolylmethane, as twists around the pyrrole–CR_2–pyrrole (R = H, Me) bonds would induce less strain in the receptor than the twist of an amide bond in the first generation systems. This, in addition to the extra pyrrole NH hydrogen bond donor group, should lead to the formation of stronger complexes between 5,5′-dicarboxamido-dipyrrolylmethanes and oxo-anions than were observed with pyrrole-2,5-dicarboxamides. Unlike ureas which have two parallel NH hydrogen bond donor groups, the 2-carboxyamido pyrrole unit has a convergent array of two hydrogen bond donors which may form two linear hydrogen bonds to the same atom. Thus a receptor containing two 2-carboxyamidopyrrole groups may be expected to form a different hydrogen bonding array with an anion such as dihydrogen phosphate than a bis urea receptor. Hence we set out to synthesise and investigate the anion complexation properties of several dipyrrolylmethane based anion receptors.[20]

Discussion

Compounds **1** and **2** were synthesized by reaction of commercially available diethyl-5,5′-methylenebis(4-ethyl-3-methyl-2-pyrrole carboxylate) with aniline or *n*-butylamine in the presence of trimethylaluminium[21] in dry dichloromethane at 35 °C affording the ligands in 40 and 43% respective yields after column chromatography as previously described.[20] Anion binding studies were conducted with **1** and **2** in DMSO-d_6/water mixtures using ^{1}H NMR titration techniques.[22] The results (shown in Table 1) showed that in DMSO-d_6/5% water solution, both **1** and **2** were effective and selective anion binding agents binding oxo-anions and fluoride (K_a = 8990 M^{-1}) strongly. A satisfactory fit could not be obtained with dihydrogen phosphate ($K_a > 10^4$ M^{-1}) hence the experiment was repeated in DMSO-d_6/25% water solution, and the stability constant found to be 234 M^{-1} with compound **1** in this very competitive solvent mixture (compared to 114 M^{-1} with fluoride).

However, disappointingly, these compounds were found to be unstable in solution with a red discoloration appearing over the course of a few days. An electrospray mass spectrum of compound **2** showed that over time in solution, the

† Electronic supplementary information (ESI) available: Figures S1–S39 and Tables S1–S5. See http://www.rsc.org/suppdata/ob/b4/b409115a/

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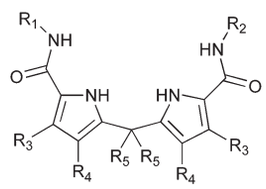
Table 1 Stability constants K_a (M^{-1}) of compounds **1** and **2** with a variety of putative anionic guests (added as tetrabutylammonium salts) at 298 K in DMSO-d_6/5% water (except where noted)[a]

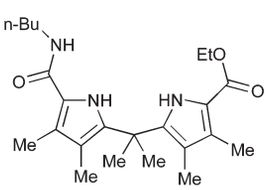
Anion	Compound **1**	Compound **2**
F^-	8990	7560
Cl^-	43	23
Br^-	10	13
HSO_4^-	128	44
Benzoate	424	354
F^{-b}	114	11
$H_2PO_4^{-b}$	234	20

[a] Errors estimated to be no more than ±15%. [b] Measured in DMSO-d_6/25% water.



1 $R_1 = R_2 =$ Ph $R_3 =$ Me $R_4 =$ Et $R_5 =$ H
2 $R_1 = R_2 =$ n-Bu $R_3 =$ Me $R_4 =$ Et $R_5 =$ H

3 $R_1 = R_2 =$ Ph $R_3 = R_4 = R_5 =$ Me
4 $R_1 = R_2 =$ n-Bu $R_3 = R_4 = R_5 =$ Me
5 $R_1 =$ Ph $R_2 =$ n-Bu $R_3 = R_4 = R_5 =$ Me



6

compound lost two mass units, presumably due to oxidation of the dipyrrolylmethane skeleton to dipyrrolylmethene. We therefore decided to synthesize analogous compounds containing two alkyl groups attached to the sp^3 hybridized *meso* carbon (the same strategy used to stabilize porphyrinogens as calix[4]pyrroles[23]) which would not be as susceptible to oxidation. Whilst being more stable, Lightner and co-workers have predicted, using molecular mechanics calculations on dipyrrolylmethanes, that the gem-dimethyl effect present due to the substitution on the *meso* carbon may de-stabilise conformations favourable for the formation of a convergent binding site by the four hydrogen bond donors.[24] Hence whilst the new compounds may be more stable than **1** or **2**, they may also have lower affinities for anions. The question remained whether this effect would preclude these receptors from functioning in partially aqueous DMSO solution.

Compounds **3** and **4** were synthesised by reaction of ethyl 5-(2-(5-(ethoxycarbonyl)-3,4-dimethyl-1*H*-pyrrol-2-yl)propan-2-yl)-3,4-dimethyl-1*H*-pyrrole-2-carboxylate (prepared according Lightner and co-workers' method[24]) with aniline or *n*-butylamine in the presence of trimethylaluminium in dry dichloromethane at 35 °C. After quenching and purification by column chromatography, compounds **3** and **4** were isolated 32 and 11% respective yields. Compound **6** was also isolated during chromatography on the reaction mixture of compound **4** in 20% yield when the reaction time was 4 days. However **6** was isolated in 22% yield as a single reaction product when the reaction time was reduced to 2 days. Compound **5** was synthesised by reaction of **6** with aniline in the presence of trimethylaluminium in dry dichloromethane at 35 °C. After quenching and purification by column chromatography the compound was isolated in 39% yield.

Crystals of compounds **3**, **4** and **6**‡ were obtained by slow evaporation of solutions of the receptors in dichloromethane–methanol mixtures (**3** and **6**) or nitromethane (**4**). The crystal structures presented, especially that of **6**, were obtained from poor quality crystals and as a result the standard *R*-factors are slightly higher than those found from more amenable samples. It was not possible to obtain better quality crystals and, in each case, the structures are unambiguous. The crystal structure of **3** shows that the amide NH groups are *syn* to the pyrrole NH forming a convergent hydrogen bond donor array. One amidopyrrole unit binds to a carbonyl oxygen in an adjacent molecule whilst the other hydrogen bonds to a methanol solvent molecule which in turn is hydrogen bonded to a carbonyl oxygen. Hence a continuous 'zig-zag' tape is formed in the crystal (Fig. 1 and supplementary information).[25]

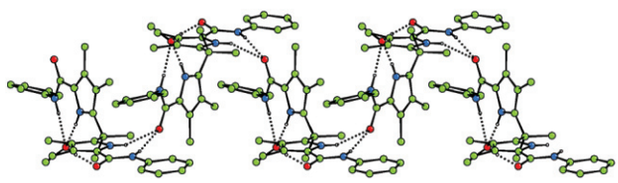


Fig. 1 The X-ray crystal structure of **3**·MeOH. Non-acidic hydrogen atoms have been omitted for clarity. The pyrrole and amide groups are involved in a three dimensional network of hydrogen bonds (see supplementary information for more details).

Compound **4** crystallised from nitromethane forming an extended three dimensional hydrogen bonding array containing three crystallographically distinct units (A-green, B-red, C-blue—Fig. 2) with the third differing from the other two in that one of its pyrrolic amide units is *trans* (*i.e.* the pyrrole and amide NH groups are oriented in opposite directions at one end of the molecule) whilst all the others are *cis.* This allows for a greater structural freedom in the building of the hydrogen bonded network, with the majority of the contacts being convergent double NH···O but also involving one single NH···O. The extended structure is built up from chains of alternating A donors and B acceptors forming slabs two chains thick in the *ab* plane *via* bridging C molecules (see supplementary information for more details).

In the solid state, the amidopyrrole unit of compound **6** adopts a similar conformation to compound **3** and binds to an amide oxygen in an adjacent molecule. The ester functionalized pyrrole dimerizes *via* NH···OC interactions with another pyrrole ester group in another adjacent molecule forming a network of dipyrrolylmethanes (Fig. 3 and also see supplementary information).

The stability constants of compounds **3** (bis-phenylamide), **4** (bis-butylamide) and **5** (mono-phenyl-mono-butylamide) were

‡ Crystal data for **3**. MeOH $C_{30}H_{36}N_4O_3$, $Mr = 500.63$, $T = 120(2)$ K, orthorhombic, space group $P2_12_12_1$, $a = 11.1668(3)$, $b = 11.7777(3)$, $c = 20.3200(6)$ Å, $V = 2672.47(13)$ Å^3, $Z = 4$, reflections collected: 32775, independent reflections: 4702 [*R*int = 0.1689]. Final *R* indices [$F2 > 2s(F2)$]: $R1 = 0.0765$, $wR2 = 0.1793$, *R* indices (all data): $R1 = 0.1061$, $wR2 = 0.1945$.

Crystal data for **4**. $(0.17CH_3NO_2)$, $C_{25.17}H_{40.50}N_{4.17}O_{2.33}$, $Mr = 438.78$, $T = 120(2)$ K, triclinic, space group *P-1*, $a = 13.0112(9)$ Å, $b = 17.310(3)$ Å, $c = 17.729(4)$ Å, $\alpha = 88.460(14)°$, $\beta = 81.647(10)°$, $\gamma = 88.021(10)°$, $V = 3947.3(11)$ Å^3, $Z = 6$ (3 molecules in the asymmetric unit), reflections collected: 66535, independent reflections: 11332 [$R_{int} = 0.0701$], Final *R* indices [$F2 > 2s(F2)$]: $R1 = 0.0904$, $wR2 = 0.2491$, *R* indices (all data): $R1 = 0.1121$, $wR2 = 0.2694$.

Crystal data for **6**. $C_{23}H_{35}N_3O_3$, $Mr = 401.54$, $T = 120(2)$ K, monoclinic, space group $P2_1/c$, $a = 13.788(2)$, $b = 17.251(3)$, $c = 9.9242(10)$ Å, $\beta = 107.786(9)°$ $V = 2247.8(6)$ Å^3, $Z = 4$, reflections collected: 16670, independent reflections: 3195 [*R*int = 0.2070], Final *R* indices [$F2 > 2s(F2)$]: $R1 = 0.1281$, $wR2 = 0.2857$, *R* indices (all data): $R1 = 0.1753$, $wR2 = 0.3148$.

CCDC reference numbers 241871, 241872 and 245224. See http://www.rsc.org/suppdata/ob/b4/b409115a/ for crystallographic data in .cif or other electronic format.

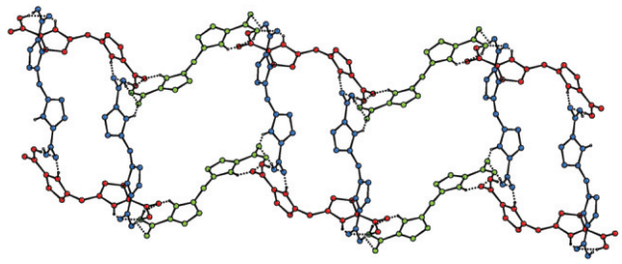


Fig. 2 The X-ray crystal structure of the nitromethane solvate of compound **4** showing the three crystallographically inequivalent molecular sub-units in different colours. Only the molecular core is shown for clarity. See supplementary information for further details.

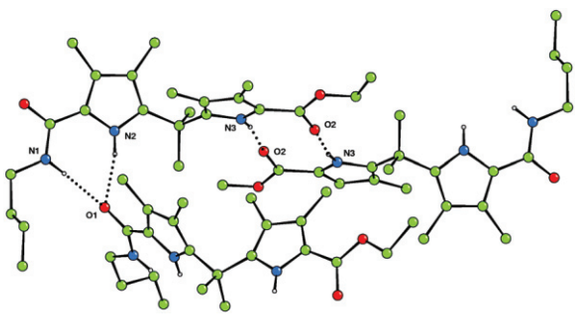


Fig. 3 The X-ray crystal structure of compound **6**. Non-acidic hydrogen atoms have been omitted for clarity. The pyrrole, amide and ester groups are involved in a three dimensional network of hydrogen bonds (see supplementary information for more details).

determined by ^{1}H NMR titration techniques in DMSO-d_6/5% water solution (the titration curves for compound **3** and the various anionic guests are shown in Fig. 4a with a Job plot[26] for compound **3** and dihydrogen phosphate shown in Fig. 4b indicating 1 : 1 receptor : anion stoichiometry). In all cases, 1 : 1 receptor : anion complexation was observed Table 2. Compound **3** was found to be selective for dihydrogen phosphate in this solvent mixture binding this anion with a stability constant of 1092 M^{-1} in DMSO-d_6/5% water (in DMSO-d_6/25% water the stability constant was dramatically reduced to approximately 10 M^{-1}). This is a weaker interaction than that observed between compound **1** and dihydrogen phosphate, but is significant as the receptor is neutral and acyclic and yet binds this anion strongly in DMSO-d_6/5% water. Similar anion selectivity trends are observed in compounds **1** and **3**. Compounds **5** (mono-phenyl-mono-butylamide) and **4** (bis-butylamide) show decreasing affinities for dihydrogen phosphate, presumably due to the difference in basicity between the phenylamide and butylamide groups. The same trend is observed for benzoate, although this anion binds more weakly than dihydrogen phosphate. The trend with fluoride is more difficult to rationalize and it is not yet clear why the highest affinity is observed with this anion and compound **5**. Comparison of the dihydrogen phosphate binding properties of dipyrrolylmethane **3** with an equivalent mono-pyrrole bis-amide namely 3,4-diphenyl-1*H*-pyrrole-2,5-diphenylcarboxamide[18] showed that the dipyrrolylmethane binds dihydrogen phosphate approximately three times more strongly than the bis-amido-pyrrole ($K = 350 \pm 10$ M^{-1} for the monopyrrole binding dihydrogen phosphate in DMSO-d_6/5% water). Attempts to obtain X-ray quality crystals of anion complexes with these species have, up to this point, been unsuccessful. We therefore decided to study the solution conformation of the receptors using NOESY spectroscopy. Compound **5** proved ideal for these studies due its lack of symmetry.

NOESY experiments were carried out in DMSO-d_6 solutions of compound **5** in the absence and presence of five equivalents of dihydrogen phosphate (added as the tetrabutylammonium salt) in order to obtain information about the structure of the free receptor and complex in solution. In the absence of

Table 2 Stability constants K_a (M^{-1}) of compounds **3**, **4** and **5** with a variety of putative anionic guests (added as tetrabutylammonium salts) at 298 K in DMSO-d_6/5% water.[a] No significant shifts were observed upon addition of tetrabutylammonium bromide or hydrogen sulfate

Anion	Compound **3**	Compound **4**	Compound **5**
F^-	124	89	429
Cl^-	<15	b	b
Benzoate	41	20	33
$H_2PO_4^-$	1092	81	307

[a] Errors estimated to be no more than ±15%. [b] No significant shift.

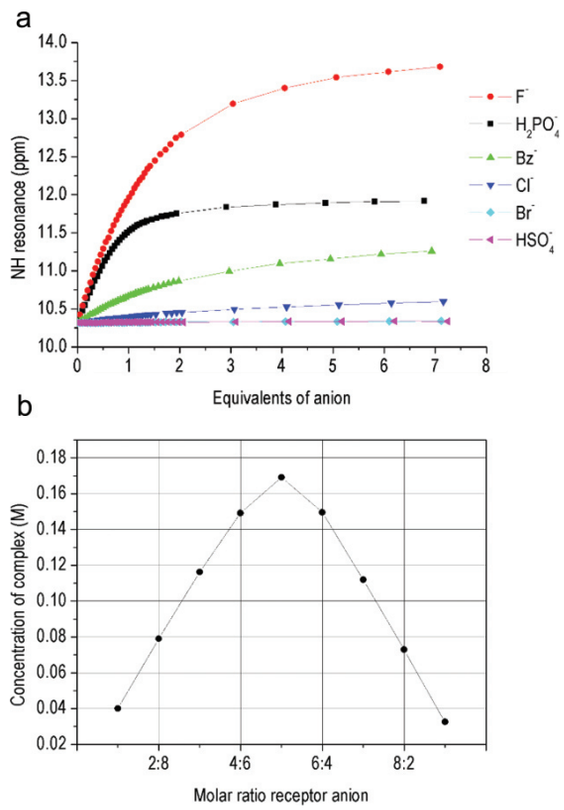


Fig. 4 (a) ^{1}H NMR titration curves for compound **3** with fluoride, chloride, bromide, dihydrogen phosphate and hydrogen sulfate in DMSO-d_6/0.5% water at 298 K. Anions added as their tetrabutylammonium salts and (b) Job plot of compound **3** and tetrabutylammonium dihydrogen phosphate in DMSO-d_6 indicating 1 : 1 receptor : anion stoichiometry.

the anion, a variety of negative cross peaks between methyl groups and pyrrole or amide NH groups were observed (Fig. 5). These couplings suggest that the receptor is adopting a linear conformation in solution. No coupling was observed between NH groups. However, upon addition of dihydrogen phosphate, the cross peaks between the methyl and the NH resonances disappeared and instead, positive cross peaks were observed between the amide NH to adjacent pyrrole NH resonance and between the two pyrrole NH resonances. Additionally, positive cross peaks were observed between the phenylamide NH and the pyrrole NH adjacent to the butylamide group. Weaker coupling was observed between the butylamide NH and the pyrrole NH adjacent to the phenylamide group. These cross peaks are presumably due proton exchange processes. When 100 equivalents of D_2O were added to receptor **5** in the presence of 5 equivalents of dihydrogen phosphate the NH resonances decreased in intensity due to proton–deuterium exchange.

A gas phase DFT geometry optimisation calculation was performed on receptor **5** and dihydrogen phosphate using the Spartan '02 computer program.[27] The resultant structure (Fig. 6) shows the receptor adopting a cleft conformation wherein the receptor binds to two oxygen atoms in the oxo-anion, each by a pyrrole and amide hydrogen bond.

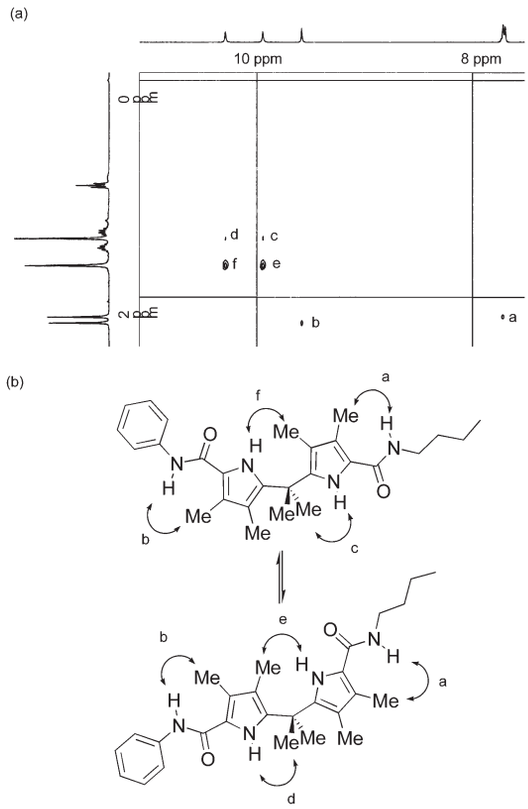


Fig. 5 (a) A portion of the NOESY spectrum of compound **5** in DMSO-d_6 and (b) a schematic showing the through space couplings present in this compound.

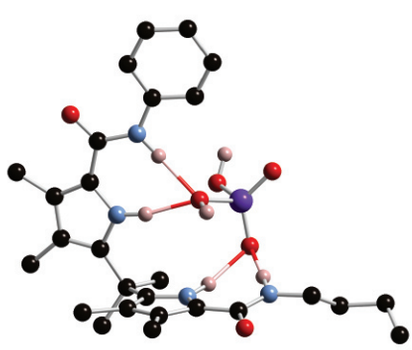


Fig. 6 Structure of the dihydrogen phosphate complex of **5** generated by DFT calculation using Spartan '02.[27]

Titrations with compound **6** were conducted in DMSO-d_6/0.5% water solution as this receptor was found to form considerably weaker complexes with anions than the bis-amides. The results, summarized in Table 3 show that this receptor is selective for fluoride, with dihydrogen phosphate and benzoate forming complexes that are over an order of magnitude less stable. However interestingly, examination of the ^{1}H NMR spectra during the titrations with anions showed that one of the pyrrole NH groups only shifts slightly (upfield) during the titration whilst the other pyrrole and the amide NH shift downfield (see Fig. 7 for the titration with dihydrogen phosphate and the supplementary information for the fluoride titration). This finding is consistent with the ester functionalised pyrrole ring not interacting with the anionic guest (the anion is binding only to the amido-pyrrole group)—a binding mode supported by DFT calculations (Fig. 8) albeit in the gas phase.[27] The possibility exists for the dihydrogen phosphate group to donate a hydrogen bond to the ester and accept one from the adjacent pyrrole. The fact that this does not appear to happen in solution may be due to the poor hydrogen bonding ability of ester carbonyl groups.[28]

Table 3 Stability constants K_a (M^{-1}) of compound **6** with a variety of putative anionic guests (added as tetrabutylammonium salts) at 298 K in DMSO-d_6/0.5% water.[a] No significant shifts were observed upon addition of tetrabutylammonium bromide or hydrogen sulfate

Anion	Stability constant (M^{-1})
F^-	1450
Cl^-	<15
Benzoate	41
$H_2PO_4^-$	83

[a] Errors estimated to be no more than ±15%.

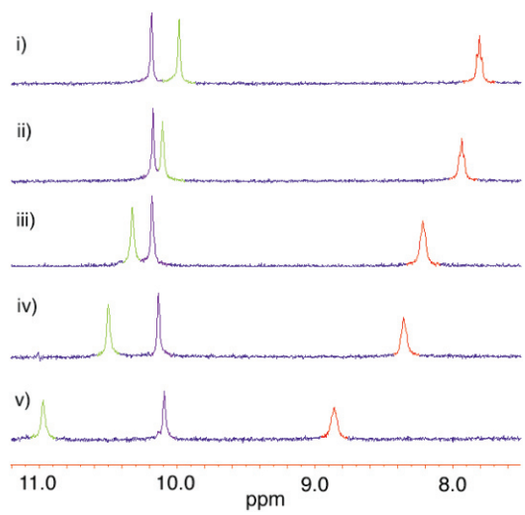


Fig. 7 ^{1}H NMR titration of compound **6** with dihydrogen phosphate i) 0 equiv., ii) 0.24 equiv., iii) 0.58 equiv., vi) 1.2 equiv., v) 3.9 equiv. in DMSO-d_6/0.5% water (amide proton resonance in red, the adjacent pyrrole NH resonance is in green and the pyrrole-ester NH resonance is in blue).

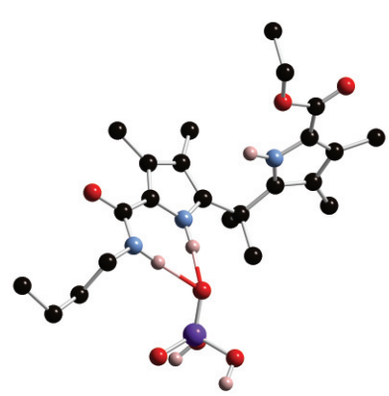


Fig. 8 Structure of the dihydrogen phosphate complex of **6** generated by DFT calculation using Spartan '02.[27]

Conclusions

5,5′-Dicarboxamido-dipyrrolylmethanes have been synthesized and shown to have unusually high affinities for dihydrogen phosphate in partially aqueous DMSO-d_6 solutions. Both compounds **1** and **2** were found to be unstable in solution over short periods of time (days). Therefore the bis-amides **3**, **4** and **5** were synthesized which contained methyl groups attached to the *meso* carbon atom. These compounds were found to be stable under comparable conditions. Compound **3** displayed a high affinity and selectivity for dihydrogen phosphate in competetive solvent media (*e.g.* DMSO-d_6/5% water solution.) Unsymmetrically substituted receptor **5** was used to study the conformation adopted by these species in solution. NOESY spectroscopy studies suggest that the receptor adopts a linear conformation in solution in the absence of an anion. Presumably the presence of dihydrogen phosphate induces a 'cleft-like'

conformation in the receptor resulting in 1 : 1 receptor : anion stoichiometry for the complex in solution. A gas phase DFT calculation on compound **5** with dihydrogen phosphate also results in a 1 : 1 complex wherein the dihydrogen phosphate is bound by four hydrogen bonds from the receptor. Compound **6**, a mono-amide, was found to have lower affinities for anions than the bis-amide receptors. Interestingly, only one of the pyrrole rings was involved in hydrogen bond donation to the anion in this case. The 5,5′-dicarboxamido-dipyrrolylmethane skeleton shows great promise as a new binding motif for phosphates under competitive conditions. We are currently working to incorporate this unit into a variety of selective anion and ion-pair receptors. The results of these studies will be reported in due course.

Experimental

General methods

Reagents were purchased from the Aldrich Chemical Co. Thin layer chromatography data (R_f values) were obtained on Fluka silica gel 60 F_{254} plates using the mobile phases described below. Column chromatography was carried out on Fluka silica gel 60 220–440 mesh. Deuterated solvents were purchased from Apollo Ltd. Chemical shifts are reported in ppm and are referenced to solvent. Proton and ^{13}C NMR spectra were recorded on a Bruker AV-300 NMR spectrometer. Elemental analyses were conducted by Medac Ltd.

Bis-*N*-phenylamide-5,5′-methylenebis(4-ethyl-3-methyl-2-pyrrolecarboxylate) (1)

Aniline (1.45 g, 15.54 mmol) was dissolved in freshly distilled dichloromethane (26 ml), and a 2 M solution of $AlMe_3$ in hexanes (7.78 ml, 15.54 mmol) was added dropwise. After stirring for 30 min, a solution of diethyl-5,5′-methylenebis(4-ethyl-3-methyl-2-pyrrolecarboxylate) (1 g, 2.67 mmol) in freshly distilled dichloromethane (10 ml) was added and the reaction mixture was stirred at 35 °C for 3 days. The reaction was carefully quenched with dilute 0.7 M HCl (100 ml), and extracted with dichloromethane (2 × 40 ml). The organic phases were combined and dried together over $MgSO_4$ and filtered. The volatiles were removed *in vacuo* and the solid obtained was purified by gradient column chromatography on silica gel with dichloromethane–dichloromethane/2% methanol affording the desired compound (0.48 g, 40%). Suitable crystals for X-ray studies were obtained by slow evaporation of a solution of this product in a mixture of dichloromethane/methanol. ^1H NMR 300 MHz in DMSO-d_6 δ (ppm): 0.89 (t, *J* 7.3, 6*H*, CH_3), 2.23 (s, 6H, CH_3), 2.33 (q, *J* 7.3, 4*H*, CH_2), 3.86 (s, 2H, CH_2), 7.02 (t, *J* 7.4, 2H, ArH), 7.30 (t, *J* 7.7, 4H, ArH), 7.64 (d, *J* 8.2, 4H, ArH), 9.26 (s, 2H, NH), 10.90 (s, 2H, NH). ^{13}C NMR 75.4 MHz in DMSO-d_6 δ (ppm): 10.4 (CH_3), 15.5 (CH_2), 16.7 (CH_3), 22.6 (CH_2), 119.7 (C), 120.6 (CH), 122.4 (C), 122.8 (CH), 123.0 (C), 128.4 (CH), 128.6 (C), 139.5 (C), 159.9 (C). ES^+ mass spectrum, *m*/*z*, 491.4 (M + Na^+). $HRES^+$ mass spectrum, *m*/*z* calculated: 491.2417 (M + Na^+), *m*/*z* found: 491.2412 (Δ 1.0 ppm). Anal. Found for $C_{29}H_{32}N_4O_2$·MeOH (Calcd): C, 72.14 (71.97); H, 6.93 (7.25); N, 10.92 (11.19)%. Mp 257–259 °C. R_f 0.06 (dichloromethane : methanol 98 : 2).

Bis-*N*-butylamide-5,5′-methylenebis(4-ethyl-3-methyl-2-pyrrolecarboxylate) (2)

Butylamine (1.14 g, 15.54 mmol) was dissolved in freshly distilled dichloromethane (26 ml), and a 2 M solution of $AlMe_3$ in hexanes (7.78 ml, 15.54 mmol) was added dropwise. After stirring for 30 min, a solution of diethyl-5,5′-methylenebis(4-ethyl-3-methyl-2-pyrrolecarboxylate) (1 g, 2.67 mmol) in freshly distilled dichloromethane (10 ml) was added and the reaction mixture was stirred at 35 °C for 3 days. The reaction was carefully quenched with dilute 0.7 M HCl (100 ml), and extracted with dichloromethane (2 × 40 ml). The organic phases were combined and dried together over $MgSO_4$ and filtered. The volatiles were removed *in vacuo* and the solid obtained was purified by gradient column chromatography on silica gel with dichloromethane–dichloromethane/2% methanol affording the desired compound (0.48 g, 43%). Suitable crystals for X-ray studies were obtained by slow evaporation of a solution of this product in a mixture of dichloromethane/methanol. ^1H NMR 300 MHz in DMSO-d_6 δ (ppm): 0.86 (m, 12H, CH_3), 1.30 (tq, *J* 7.3 *J* 6.7, 4H, CH_2), 1.46 (tt, *J* 7.2 *J* 7.3, 4H, CH_2), 2.13 (s, 6H, CH_3), 2.27 (q, *J* 7.2, 4H, CH_2), 3.19 (dt, *J* 5.4 *J* 7.2, 4H, CH_2), 3.72 (s, 2H, CH_2), 7.11 (t, *J* 5.4, 2H, NH), 10.56 (s, 2H, NH). ^{13}C NMR 75.4 MHz in DMSO-d_6 δ (ppm): 10.4 (CH_3), 13.8 (CH_2), 15.7 (CH_3), 16.8 (CH_2), 19.7 (CH_3), 22.2 (CH_2), 31.7 (CH_2), 38.2 (CH_2), 120.1 (C), 120.9 (C), 121.5 (C), 127.5 (C), 161.6 (C). ES^+ mass spectrum, *m*/*z*, 451.3 (M + Na^+). $HRES^+$ mass spectrum, *m*/*z* calculated: 429.3224 (M + Na^+), *m*/*z* found: 429.3234 (Δ 1.8 ppm). Anal. Found for $C_{25}H_{40}N_4O_2$·½MeOH (Calcd): C, 68.75 (68.88); H, 9.53 (9.52); N, 12.72 (12.60)%. Mp 189–190 °C. R_f 0.1 (dichloromethane : methanol 96.5 : 3.5).

5-(2-(5-(Phenylcarbamoyl)-3,4-dimethyl-1*H*-pyrrol-2-yl)propan-2-yl)-3,4-dimethyl-*N*-phenyl-1*H*-pyrrole-2-carboxamide (3)

Aniline (2.80 g, 30.10 mmol) was dissolved in freshly distilled dichloromethane (50 ml), and a 2 M solution of $AlMe_3$ in hexanes (15.05 ml, 30.10 mmol) was added dropwise. After stirring for 30 min, a solution of ethyl 5-(2-(5-(ethoxycarbonyl)-3,4-dimethyl-1*H*-pyrrol-2-yl)propan-2-yl)-3,4-dimethyl-1*H*-pyrrole-2-carboxylate[24] (1.61 g, 4.30 mmol) in freshly distilled dichloromethane (20 ml) was added and the reaction mixture was stirred at 35 °C for 3 days. The reaction was carefully quenched with dilute 0.7 M HCl (100 ml), and extracted with dichloromethane (2 × 70 ml). The organic phases were combined and dried together over $MgSO_4$ and filtered. The volatiles were removed *in vacuo* and the solid obtained was purified by gradient column chromatography on silica gel with dichloromethane–dichloromethane/2% methanol affording the desired compound (0.64 g, 32%). Suitable crystals for X-ray studies were obtained by slow evaporation of a solution of this product in a mixture of dichloromethane/methanol. ^1H NMR 300 MHz in DMSO-d_6 δ (ppm): 1.43 (s, 6H, CH_3), 1.70 (s, 6H, CH_3), 2.19 (s, 6H, CH_3), 7.04 (t, *J* 7.3, 2H, ArH), 7.33 (dd, *J* 7.3 *J* 8.2, 4H, ArH), 7.66 (d, *J* 8.2, 4H, ArH), 9.58 (s, 2H, NH), 10.31 (s, 2H, NH). ^{13}C NMR 75.4 MHz in DMSO-d_6 δ (ppm): 8.7 (CH_3), 10.6 (CH_3), 27.8 (CH_3), 35.8 (C), 115.3 (C), 118.6 (C), 120.0 (CH), 122.8 (CH), 126.3 (C), 128.6 (CH), 136.9 (C), 139.4 (C), 159.5 (CO). ES^+ mass spectrum, *m*/*z*, 469.3 (M + H^+). $HRES^+$ mass spectrum, *m*/*z* calculated: 469.2598 (M + H^+), *m*/*z* found: 469.2590 (Δ 1.7 ppm). Anal. Found for $C_{29}H_{32}N_4O_2$·½MeOH (Calcd): C, 72.85 (73.11); H, 6.91 (7.07); N, 11.24 (11.56)%. Mp 145–146 °C. R_f 0.34 (dichloromethane : methanol 96 : 4).

5-(2-(5-(Butylcarbamoyl)-3,4-dimethyl-1*H*-pyrrol-2-yl)propan-2-yl)-3,4-dimethyl-*N*-butyl-1*H*-pyrrole-2-carboxamide (4)

Butylamine (1.37 g, 18.69 mmol) was dissolved in freshly distilled dichloromethane (35 ml), and a 2 M solution of $AlMe_3$ in hexanes (9.35 ml, 18.69 mmol) was added dropwise. After stirring for 30 min, a solution of ethyl 5-(2-(5-(ethoxycarbonyl)-3,4-dimethyl-1*H*-pyrrol-2-yl)propan-2-yl)-3,4-dimethyl-1*H*-pyrrole-2-carboxylate (1.00 g, 2.67 mmol) in freshly distilled dichloromethane (13 ml) was added and the reaction mixture was stirred at 35 °C for 4 days. The reaction was carefully quenched with dilute 0.7 M HCl (100 ml), and extracted with dichloromethane (2 × 50 ml). The organic phases were combined and dried together over $MgSO_4$ and filtered. The volatiles were removed *in vacuo* and the solid obtained was purified by gradient column chromatography on silica gel with petroleum ether/10% ethyl acetate–petroleum ether/20% ethyl acetate–petroleum ether/40% ethyl acetate affording the

desired compound (0.13 g, 11%). Compound **6** was isolated as secondary product (214.4 mg, 20%). Suitable crystals for X-ray studies were obtained by slow evaporation of a solution of this product in a mixture of acetonitrile/methanol. ^{1}H NMR 300 MHz in $CDCl_3$ δ (ppm): 0.96 (t, *J* 5.5, 6H, CH_3), 1.40 (tq, *J* 5.5 *J* 3.4, 4H, CH_2), 1.55 (s, 6H, CH_3), 1.57 (tt, *J* 5.3 *J* 3.4, 4H, CH_2), 1.63 (s, 6H, CH_3), 2.16 (s, 6H, CH_3), 3.43 (dt, *J* 5.3 *J* 3.0, 4H, CH_2), 5.67 (s, 2H, NH amide), 8.89 (s, 2H, NH pyrrol). ^{13}C NMR 75.4 MHz in $CDCl_3$ δ (ppm): 9.7 (CH_3), 11.4 (CH_3), 14.3 (CH_3), 20.7 (CH_2), 27.4 (CH_3), 32.5 (CH_2), 36.1 (C), 39.7 (CH_2), 116.5 (C), 119.9 (C), 120.4 (C), 136.1 (C), 162.6 (CO). ES$^+$ mass spectrum, *m*/*z*, 429.3 (M + H$^+$), 451.2 (M + Na$^+$), 857.5 (2M + H$^+$), 879.4 (2M + Na$^+$). HRES$^+$ mass spectrum, *m*/*z* calculated: 429.3224 (M + H$^+$), *m*/*z* found: 429.3218 (Δ 1.4 ppm). Anal. Found for $C_{25}H_{40}N_4O_2 \cdot ⅔$MeOH (Calcd): C, 68.28 (68.51); H, 9.62 (9.56); N, 12.38 (12.45)%. Mp 137–138 °C. R_f 0.33 (ethyl acetate : petroleum ether 80 : 20).

5-(2-(5-(Butylcarbamoyl)-3,4-dimethyl-1*H*-pyrrol-2-yl)propan-2-yl)-3,4-dimethyl-*N*-phenyl-1*H*-pyrrole-2-carboxamide (5)

Aniline (0.36 g, 3.84 mmol) was dissolved in freshly distilled dichloromethane (13 ml), and a 2 M solution of $AlMe_3$ in hexanes (1.92 ml, 3.84 mmol) was added dropwise. After stirring for 30 min, a solution of **6** (0.22 g, 0.55 mmol) in freshly distilled dichloromethane (7 ml) was added and the reaction mixture was stirred at 35 °C for 3 days. The reaction was carefully quenched with dilute 0.7 M HCl (50 ml), and extracted with dichloromethane (2 × 30 ml). The organic phases were combined and dried together over $MgSO_4$ and filtered. The volatiles were removed *in vacuo* and the solid obtained was purified by gradient column chromatography on silica gel with dichloromethane–dichloromethane/0.5% methanol affording the desired compound (95.4 mg, 39%). Suitable crystals for X-ray studies were obtained by slow evaporation of a solution of this product in a mixture of dichloromethane/methanol. ^{1}H NMR 300 MHz in $CDCl_3$ δ (ppm): 0.96 (t, *J* 5.5, 6H, CH_3), 1.41 (tq, *J* 5.5 *J* 3.4, 2H, CH_2), 1.56 (s, 6H, CH_3), 1.57 (tt, *J* 5.3 *J* 3.4, 2H, CH_2),), 1.59 (s, 3H, CH_3), 1.66 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 3.45 (t, *J* 5.3, 2H, CH_2), 5.75 (s, 1H, NH amide), 7.10 (dd, *J* 5.6 *J* 0.8, 1H, CH Ar), 7.34 (dd, *J* 5.7 *J* 5.6, 2H, CH Ar),7.52 (s, 1H, NH), 7.58 (dd, *J* 5.7 *J* 0.8, 2H, CH Ar), 8.99 (s, 1H, NH), 9.06 (s, 1H, NH). ^{13}C NMR 75.4 MHz in $CDCl_3$ δ (ppm): 9.3 (CH_3), 11.1 (CH_3), 13.9 (CH_3), 20.3 (CH_2), 26.9 (CH_3), 32.1 (CH_2), 35.9 (C), 39.5 (CH_2), 116.4 (C), 116.8 (C), 119.4 (C), 119.7 (C), 120.1 (CH), 120.7 (C), 121.3 (C), 124.1 (CH), 129.2 (CH), 136.1 (C), 137.1 (C), 138.4 (C), 160.2 (CO), 162.4 (CO). ES$^+$ mass spectrum, *m*/*z*, 897.8 (2M + H$^+$). HRES$^+$ mass spectrum, *m*/*z* calculated: 471.2730 (M + Na$^+$), *m*/*z* found: 471.2733 (Δ 0.5 ppm). Anal. Found for $C_{25}H_{40}N_4O_2$.MeOH (Calcd): C, 69.67 (69.97); H, 8.23 (8.39); N, 11.43 (11.66)%. Mp 170–171 °C. R_f 0.17 (dichloromethane : methanol 96 : 4).

Ethyl 5-(2-(5-(butylcarbamoyl)-3,4-dimethyl-1*H*-pyrrol-2-yl)propan-2-yl)-3,4-dimethyl-1*H*-pyrrole-2-carboxylate (6)

Butylamine (2.38 g, 32.30 mmol) was dissolved in freshly distilled dichloromethane (50 ml), and a 2 M solution of $AlMe_3$ in hexanes (15.05 ml, 32.30 mmol) was added dropwise. After stirring for 30 min, a solution of ethyl 5-(2-(5-(ethoxycarbonyl)-3,4-dimethyl-1*H*-pyrrol-2-yl)propan-2-yl)-3,4-dimethyl-1*H*-pyrrole-2-carboxylate (1.73 g, 4.62 mmol) in freshly distilled dichloromethane (20 ml) was added and the reaction mixture was stirred at 35 °C for 2 days. The reaction was carefully quenched with dilute 0.7 M HCl (100 ml), and extracted with dichloromethane (2 × 50 ml). The organic phases were combined and dried together over $MgSO_4$ and filtered. The volatiles were removed *in vacuo* and the solid obtained was purified by gradient column chromatography on silica gel with dichloromethane–dichloromethane/0.4% methanol affording the desired compound (0.41 g, 22%). Suitable crystals for X-ray studies were obtained by slow evaporation of a solution of this product in a mixture of dichloromethane/methanol. ^{1}H NMR 300 MHz in DMSO-d_6 δ (ppm): 0.91 (t, *J* 7.3, 3H, CH_3), 1.28 (t, *J* 7.3, 3H, CH_3), 1.34 (s, 6H, CH_3), 1.37 (m, 2H, CH_2), 1.48 (m, 2H, CH_2), 1.61 (s, 6H, CH_3), 3.20 (dt, *J* 5.5 *J* 6.4, 2H, CH_2), 4.23 (q, *J* 7.3, 2H, CH_2), 7.70 (t, *J* 5.5, 1H, NH), 9.89 (s, 1H, NH), 10.19 (s, 1H, NH). ^{13}C NMR 75.4 MHz in DMSO-d_6 δ (ppm): 8.8 (CH_3), 8.8 (CH_3), 10.4 (CH_3), 10.5 (CH_3), 13.8 (CH_3), 14.5 (CH_3), 19.8 (CH_3), 27.6 (CH_3), 31.7 (CH_2), 35.8 (CH_2), 38.1 (CH_2), 58.9 (CH_2), 114.5 (C), 115.5 (C), 115.6 (C), 118.9 (C), 124.1 (C), 126.9 (C), 135.4 (C), 139.5 (C), 161.0 (CO), 161.2 (CO). ES$^+$ mass spectrum, *m*/*z*, 402.4 (M + H$^+$), 424.4 (M + Na$^+$), 803.5 (2M + H$^+$). HRES$^+$ mass spectrum, *m*/*z* calculated: 424.2570 (M + Na$^+$), *m*/*z* found: 424.2568 (Δ 0.5 ppm). Anal. Found for $C_{23}H_{35}N_3O_3$ (Calcd): C, 68.60 (68.80); H, 8.82 (8.79); N, 10.28 (10.46)%. Mp 90–91 °C. R_f 0.58 (dichloromethane : methanol 96 : 4).

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