Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Extending the Hydrogen-bonding Array in *ortho*-Phenylenediamine Based Bis-ureas

Simon J. Brooks[a]; Philip A. Gale[a]; Mark E. Light[a]
[a] School of Chemistry, University of Southampton, Southampton, UK

To cite this Article Brooks, Simon J. , Gale, Philip A. and Light, Mark E.(2007) 'Extending the Hydrogen-bonding Array in *ortho*-Phenylenediamine Based Bis-ureas', Supramolecular Chemistry, 19: 1, 9 — 15
To link to this Article: DOI: 10.1080/10610270600879076
URL: http://dx.doi.org/10.1080/10610270600879076

Supramolecular Chemistry, January–March 2007 Vol. 19 (1–2), pp. 9–15

Taylor & Francis
Taylor & Francis Group

Extending the Hydrogen-bonding Array in *ortho*-Phenylenediamine Based Bis-ureas

SIMON J. BROOKS, PHILIP A. GALE* and MARK E. LIGHT

School of Chemistry, University of Southampton, Southampton SO17 1BJ, UK

(Received 22 May 2006; Accepted 21 June 2006)

Two new *ortho*-phenylenediamine based bis-urea compounds have been synthesized with pendant amide groups. The stability constants of the new compounds with a variety of anionic guests have been measured by ^{1}H NMR titration techniques and compared to the parent bis-urea. The X-ray crystal structure of the acetate and benzoate complexes of a bis-amide functionalized system have been solved and reveal the receptor forming a dimer with two anions bound at the termini of the hydrogen bonded assembly.

Keywords: Anion receptors; Amides; Urea; Crystallography

INTRODUCTION

Amides and urea groups have been employed in a wide variety of anion receptor systems over recent years [1–13]. We have been interested in the anion complexation properties of a variety of simple linear hydrogen bond donor molecules [14,15]. In 2000, Reinhoudt and co-workers reported the anion binding ability of cyclic and acyclic receptors containing two *ortho*-phenylenediamine based bis-urea units with the receptor showing selectivity for dihydrogen phosphate anions in DMSO solution [16]. We have synthesised a variety of simple acyclic *ortho*-phenylenediamine systems e.g. **1** and demonstrated a general selectivity of these receptors for carboxylates in DMSO-d_6/0.5% water solution [17–19]. In this short paper we report the synthesis of two new bis-urea compounds **2** and **3** (Schemes 1 and 2) that have appended amide groups. We wished to ascertain whether the extra hydrogen bond donor groups in these receptors would contribute to the stability of the oxo-anion complexes.

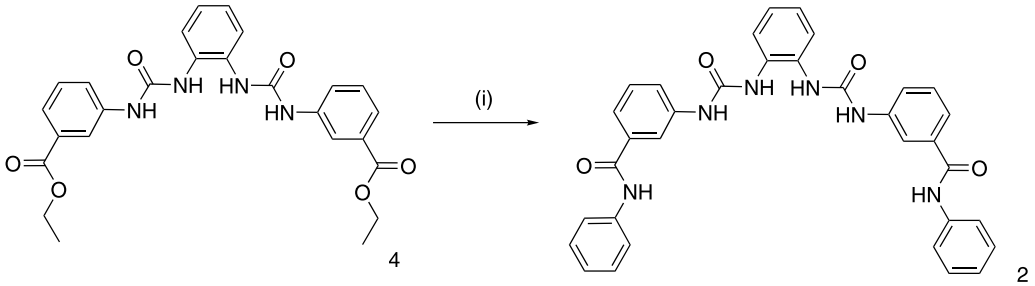
EXPERIMENTAL

Compound 6: 1,1′-(1,2-Phenylene) bis(3-(2-aminophenyl)urea)

10% Pd/C (0.04 g, 0.1 mmol) and hydrazine monohydrate (1.4 mL) was added to a stirring suspension of compound **5** (1.33 g, 3.0 mmol) in EtOH (200 mL) and the reaction was heated to reflux for 16 hours under a nitrogen atmosphere. The reaction was then removed from reflux and allowed to cool to room temperature and the resulting white precipitate and Pd/C removed *via* filtration. The product was redissolved in a small volume of DMF (5 mL) and filtered to remove Pd/C. Removal of DMF under reduced pressure yielded a white precipitate in a green oil. The product was removed *via* filtration and washed with H_2O (3 × 10 mL) followed by methanol (3 × 10 mL) before drying under high vacuum affording the product as a white powder. Mass of product = 0.88 g. Yield = 78%. ^{1}H NMR — 300 MHz (DMSO-d_6) δ (ppm): 8.37 (s, 2H, urea NH), 8.29 (s, 2H, urea NH), 7.64 (dd, 2H, J = 5.6 and 3.4 Hz, ArH), 7.36 (d, 2H, J = 7.9 Hz, ArH), 7.02 (dd, 2H, J = 5.6 and 3.8 Hz, ArH), 6.82 (t, 2H, J = 7.1 Hz, ArH), 6.71 (d, 2H, J = 7.5 Hz, ArH), 6.55 (t, 2H, J = 7.5 Hz, ArH), 4.90 (bs, 4H, NH_2). ^{13}C NMR — 75 MHz (DMSO-d_6) δ (ppm): 153.7 (CO), 140.8 (C), 131.1 (CH), 124.5 (CH), 124.2 (C), 123.7 (C), 123.2 (CH), 116.4 (CH), 115.5 (CH). IR (cm^{-1}): 3353, 3295, 1728, 1664, 1579, 1492, 1431, 1338, 1262, 1184, 1141. LRMS (ES +): 376.9 $[M + H]^+$, 398.9 $[M + Na]^+$, 439.9 $[M + Na + MeCN]^+$, 753.1 $[2M + H]^+$, 775.1 $[2M + Na]^+$, 1129.2 $[3M + Na]^+$, 1152.3 $[3M + Na]^+$. HRMS (ES +): Calculated Mass = 377.1721. Observed Mass = 377.1721. Δ = 0.06 ppm.

*Corresponding author. E-mail: philip.gale@soton.ac.uk

ISSN 1061-0278 print/ISSN 1029-0478 online © 2007 Taylor & Francis
DOI: 10.1080/10610270600879076



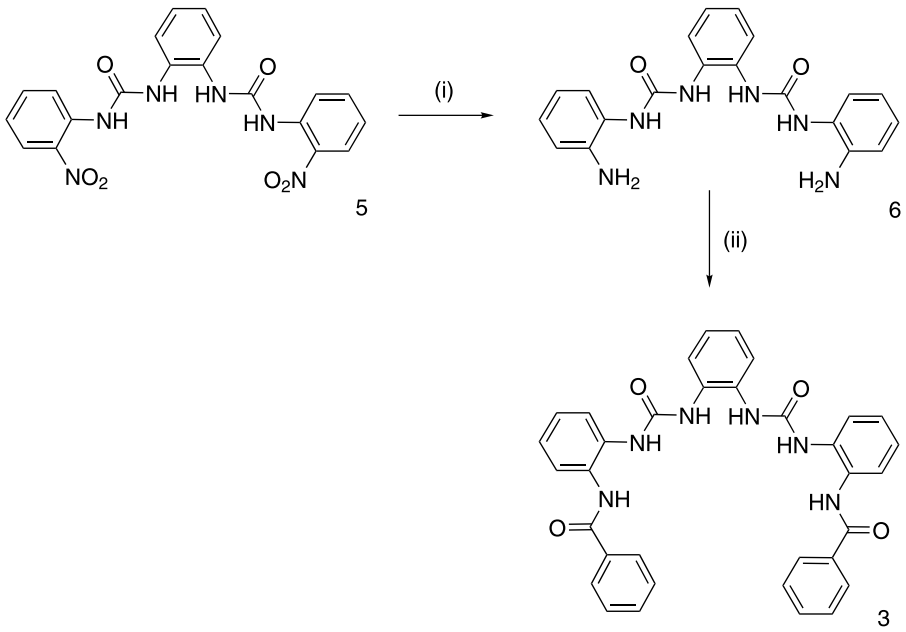
SCHEME 1 (i) Aniline, $AlMe_3/CH_2Cl_2$/hexane.

Compound 3: *N,N′*- (2,2′- (1,2-Phenylene bis (azanediyl))bis (oxomethylene) bis(azanediyl)bis(2,1-phenylene))dibenzamide

Benzoyl chloride (0.74 mL, 6.4 mmol) in DMF (dry) was added dropwise over a 15 minute period and to a stirred solution of compound **6** (1.20 g, 3.2 mmol), triethylamine (0.76 mL, 7.1 mmol) and DMAP (0.01 g, cat.) in anhydrous DMF (50 mL) under a nitrogen atmosphere. The reaction was stirred at room temperature for 18 hours before being filtered to remove precipitated triethylamine hydrochloride. The remaining DMF was removed *in vacuo* to give an oily brown residue that was redissolved in dichloromethane (50 mL). The solution was washed with water (3 × 50 mL) and the organic phase retained, dried over anhydrous $MgSO_4$ and filtered before the removal of solvent *in vacuo*. The resulting brown solid was washed with ethyl acetate (10 mL), and then hot ethyl acetate (3 × 10 mL), giving a white solid, dried under high vacuum. Mass of product = 0.55 g. Yield = 29%. ^{1}H NMR 300 MHz (DMSO-d_6) δ (ppm): 10.02 (s, 2H, NH), 8.58 (s, 2H, NH), 8.44 (s, 2H, NH), 8.00 (app d, 4H, $J = 7.0$ Hz, ArH), 7.77 (dd, 2H, $J = 8.0$ Hz and 1.0 Hz, ArH), 7.50 (m, 10H, ArH), 7.20 (td, 2H, $J = 7.9$ Hz and 1.1 Hz, ArH), 7.04 (m, 4H, ArH). ^{13}C NMR—75 MHz (DMSO-d_6) δ (ppm): 165.6 (CO), 153.8 (CO), 134.2 (C), 133.9 (C), 131.1 (CH), 128.6 (C), 128.4 (CH), 127.7 (CH), 126.9 (CH), 126.1 (CH), 124.0 (CH), 123.0 (CH), 122.5 (CH). IR (cm^{-1}): 3288, 3057, 1654, 1596, 1507, 1439, 1309, 1206, 757. LRMS (ES): 619.3 $[M + Cl]^-$, 697.2 $[M + TFA\text{-}H]^-$, 1203.6 $[2M + Cl]^-$, 1281.1 $[2M + TFA\text{-}H]^-$. Microanalysis for $C_{34}H_{28}N_6O_4$. Expected (%) C = 69.85; H = 4.83; N = 14.37. Found (%) C = 69.54; H = 4.81; N = 14.38.

Compound 4: Diethyl 3,3′- (1,2-phenylene bis (azanediyl))bis(oxomethylene) bis (azanediyl)dibenzoate

3-Ethylisocyanatobenzoate (2.16 mL, 13.1 mmol) was added dropwise to a stirring solution



SCHEME 2 (i) Pd/C, hydrazine (ii) benzoyl chloride, Et_3N, DMAP (cat), DMF.

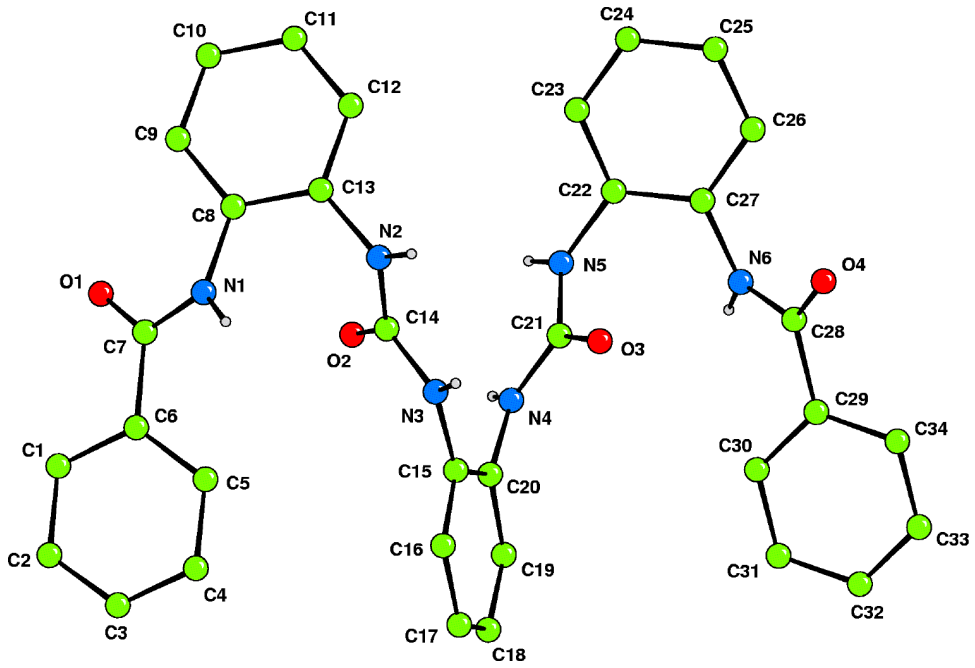


FIGURE 1 The X-ray crystal structure of compound **3**.

of *ortho*-phenylenediamine (0.71 g, 6.5 mmol) in dry dichloromethane (150 mL). Within 5 minutes of addition the reaction mixture formed a viscous gel. At this point MeOH (5 mL) was then added to dissolve the gel. The reaction was left at room temperature for 16 hours, after which solvent was removed from reaction *via* rotary evaporation. The product was recrystallized from boiling MeOH before washing with Et_2O (3 × 20 mL) and drying under high vacuum. The product was isolated as a white solid. Mass of product = 2.74 g. Yield = 86%. ^{1}H NMR 300 MHz (DMSO-d_6) δ (ppm): 9.35 (s, 2H, NH), 8.15 (s, 2H, ArH), 8.07 (s, 2H, NH), 7.70 (m, 2H, ArH), 7.60 (m, 2H, ArH), 7.55 (m, 2H, ArH), 7.41 (t, 2H, J = 7.9 Hz, ArH), 7.11 (dd, 2H, J = 6.0 Hz and 3.8 Hz, ArH), 4.30 (q, 4H, J = 7.1 Hz, CH_2), 1.31 (t, 6H, J = 7.1 Hz, CH_3). ^{13}C NMR—100 MHz (DMSO-d_6) δ (ppm): 166.2 (CO), 153.7 (CO), 140.7 (C), 131.8 (C), 130.9 (C), 129.6 (CH), 124.7 (CH), 124.7 (CH), 123.1 (CH), 122.9 (CH), 119.0 (CH), 61.2 (CH_2), 14.6 (CH_3). IR (cm^{-1}): 3351, 3245, 2980. 1724, 1652, 1559, 1458, 1280, 1251, 1217, 1103, 752. LRMS (ES): 491.3 $[M + H]^+$, 513.3 $[M + Na]^+$, 100.3 $[2M + Na]^+$. Microanalysis for $C_{26}H_{26}N_4O_6$. Expected (%) C = 63.66; H = 5.34; N = 11.42. Found (%) C = 63.46; H = 5.34; N = 11.34.

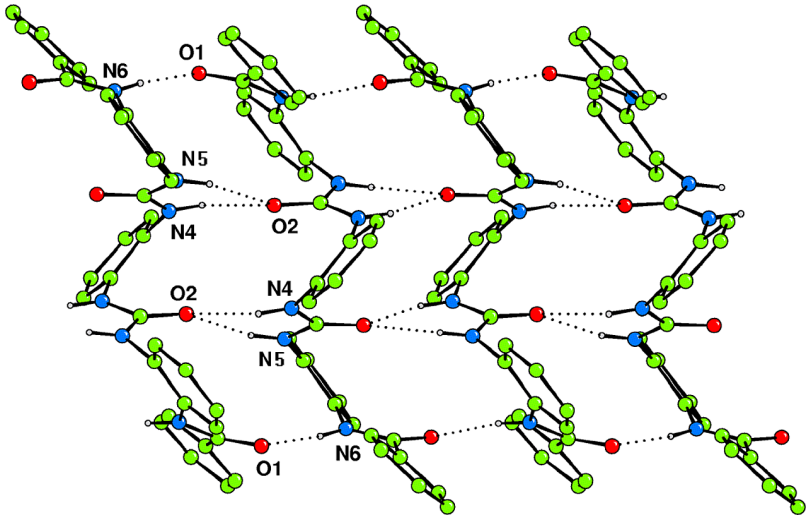


FIGURE 2 The hydrogen-bonded chain in crystals of compound **3** extending along the *a* axis in the solid-state.

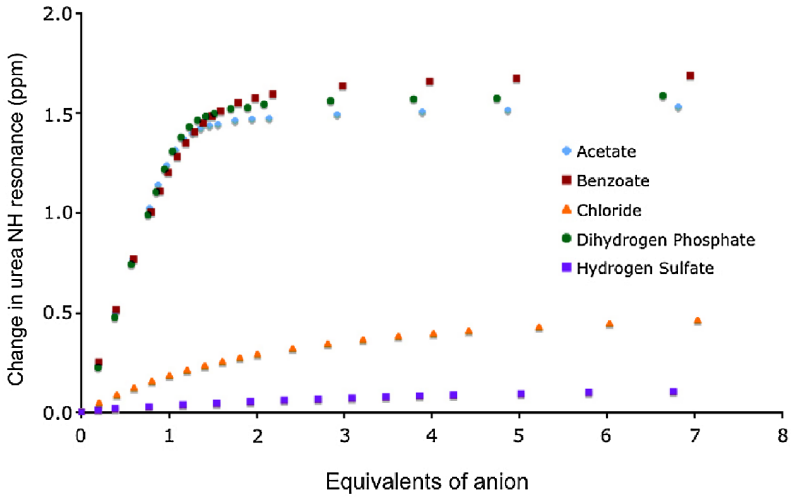


FIGURE 3 ^{1}H NMR titration curves of compound **2** (central urea NH) upon addition of anions as tetrabutylammonium salts in DMSO-d_6/0.5% water solution.

Compound 2: 3,3′-(1,2-Phenylenebis(azanediyl)) bis(oxomethylene)bis (azanediyl) bis(*N*-phenylbenzamide)

Aniline (0.40 mL, 4.1 mmol) was dissolved in dry dichloromethane (40 mL) and 2 M trimethylaluminium in hexanes (2.03 mL, 4.06 mmol) added dropwise under a nitrogen atmosphere. Reagents were left stirring under nitrogen for 30 minutes at which time compound **4** (1.00 g, 2.03 mmol) was added to the reaction mixture. The reaction was heated at reflux for 5 days under a nitrogen atmosphere. The reaction was allowed to cool and 2 M aqueous HCl solution was then added until reaction ceased bubbling resulting in the precipitation of the product. A further 20 mL of water was added and the mixture stirred for a further 15 minutes. The organic phase and precipitate were washed with water (3 × 50 mL). The organic phase containing the precipitate was then filtered and the white precipitate washed with Et_2O (3 × 20 mL) before drying under high vacuum. Mass of product = 0.94 g. Yield = 94%. ^{1}H NMR 300 MHz (DMSO-d_6) δ (ppm): 10.22 (s, 2H, NH), 9.33 (s, 2H, NH), 8.15 (s, 2H, NH), 8.00 (s, 2H, ArH), 7.76 (m, 6H, ArH), 7.63 (m, 2H, ArH), 7.56 (m, 2H, ArH), 7.43 (t, 2H, J = 7.7 Hz, ArH), 7.35 (t, 4H, J = 7.7 Hz, ArH), 7.11 (m, 4H, ArH). ^{13}C NMR — 75 MHz (DMSO-d_6) δ (ppm): 165.6 (CO), 153.2 (CO), 140.1 (C), 139.2 (C), 135.8 (C), 131.3 (C), 128.8 (CH), 128.6 (CH), 124.2 (CH), 124.1 (CH), 123.6 (CH), 121.1 (CH), 120.8 (CH), 120.3 (CH), 117.6 (CH). IR (cm^{-1}): 3351, 3250, 2980, 1724, 1648, 1555, 1462, 1280, 1217, 1103, 1026, 752. LRMS (ES): 619.1 $[M + Cl]^-$, 696.9 $[M + TFA - H]^-$, 1203.4 $[2M + Cl]^-$, 1281.3 $[2M + TFA - H]^-$, 1787.9 $[3M + Cl]^-$. Microanalysis for $C_{34}H_{28}N_6O_4$ +0.4 CH_2Cl_2. Expected (%) C = 66.79; H = 4.69; N = 13.59. Found (%) C = 66.60; H = 4.90; N = 13.58.

TABLE I Stability constants of compounds **1**, **2** and **3** with anionic guests added as tetrabutylammonium salts in DMSO-d_6/0.5% water solution at 298 K. Errors in fitting estimated <15%

	Stability constants K (M^{-1}) β (M^{-2})		
Anion	**1**	**2**[†]	**3**
Cl^-	43	54	17
HSO_4^{--}	10	12	–
$H_2PO_4^-$	732	2290	$K_1 = 7780$ $K_2 = 24$ $\beta_2 = 185000$
$CH_3CO_2^-$	3210	3200	$K_1 = 6010$ $K_2 = <10$ $\beta_2 = 55230$
$C_6H_5CO_2^-$	1330	974	$K_1 = 10110$ $K_2 = <10$ $\beta_2 = 16554$

[†] Non-random residual errors in the fitting of the data for oxo-anions with compound **2** is evidence that leads us to suggest that other stoichiometries may be present in solution. However it was found that the most satisfactory fit that could be obtained was to a 1:1 binding model.

X-ray Crystallography

Cell dimensions and intensity data were recorded at 120 K, using a Bruker Nonius KappaCCD area detector diffractometer mounted at the window of a rotating Mo anode (λ(Mo − Kα) = 0.71073 Å). The crystal-to-detector distance was 30 mm and ϕ and Ω scans were carried out to fill the asymmetric unit. Data collection and processing were carried out using the programs COLLECT [21], and DENZO [22] and an empirical absorption correction was applied using SADABS [23].

The structures were solved via direct methods [24] and refined by full matrix least squares on F^2. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated using a riding model.

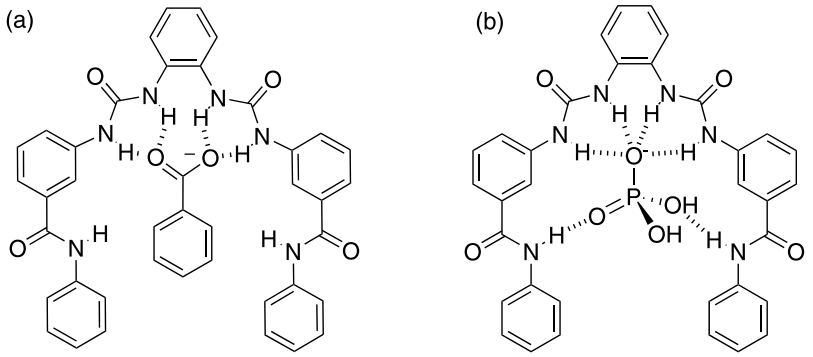


FIGURE 4 Proposed structures of the complexes of a) benzoate and b) dihydrogen phosphate with compound **2**.

The number of observed reflections was less than 50% and this is a contributing factor to the slightly high R-factors.

Crystal data for compound **3**: $C_{34}H_{28}N_6O_4$, Mr = 584.62, T = 120(2) K, monoclinic, space group $P2_1/c$, $a = 9.2368(5)$, $b = 27.4133(16)$, $c = 11.6115(7)$ Å, $\beta = 96.593(2)°$, $V = 2920.7(3)$ Å^3, $\rho_{calc} = 1.330\,g\,cm^{-3}$, $\mu = 0.090\,mm^{-1}$, Z = 4, reflections collected: 26187, independent reflections: 6645 ($R_{int} = 0.0420$), final R indices $[I > 2\sigma I]$: $R_1 = 0.0415$, $wR_2 = 0.0980$, R indices (all data): $R_1 = 0.0635$. $wR_2 = 0.1085$. CCDC 607431.

Compound **3** — tetrabutylammonium acetate complex: $C_{52}H_{67}N_7O_6$, Mr = 886.13, T = 120(2) K, triclinic, space group $P-1$, $a = 13.3008(4)$, $b = 14.9187(4)$, $c = 25.3629(7)$ Å, $\alpha = 97.297(2)$, $\beta = 96.686(1)$, $\gamma = 97.262(2)°$, $V = 4906.9(2)$ Å^3, $\rho_{calc} = 1.199\,g\,cm^{-3}$, $\mu = 0.079\,mm^{-1}$, Z = 4, reflections collected: 88632, independent reflections: 21661 ($R_{int} = 0.1139$), final R indices $[I > 2\sigma I]$: $R_1 = 0.0914$, $wR_2 = 0.1778$, R indices (all data): $R_1 = 0.1995$. $wR_2 = 0.2171$. CCDC 607429

Compound **3** — tetrabutylammonium benzoate complex: $C_{57}H_{69}N_7O_6$, Mr = 948.19, T = 120(2) K, triclinic, space group $P-1$, $a = 9.2831(3)$, $b = 10.9968(6)$, $c = 24.9522(13)$ Å, $\alpha = 91.299(2)$, $\beta = 92.310(3)$, $\gamma = 97.775(3)°$, $V = 2520.7(2)$ Å^3, $\rho_{calc} = 1.249\,g\,cm^{-3}$, $\mu = 0.082\,mm^{-1}$, Z = 2, reflections collected: 40028, independent reflections: 11395 ($R_{int} = 0.1568$), final R indices $[I > 2\sigma I]$: $R_1 = 0.0809$, $wR_2 = 0.1712$, R indices (all data): $R_1 = 0.2068$. $wR_2 = 0.2162$. CCDC 607430

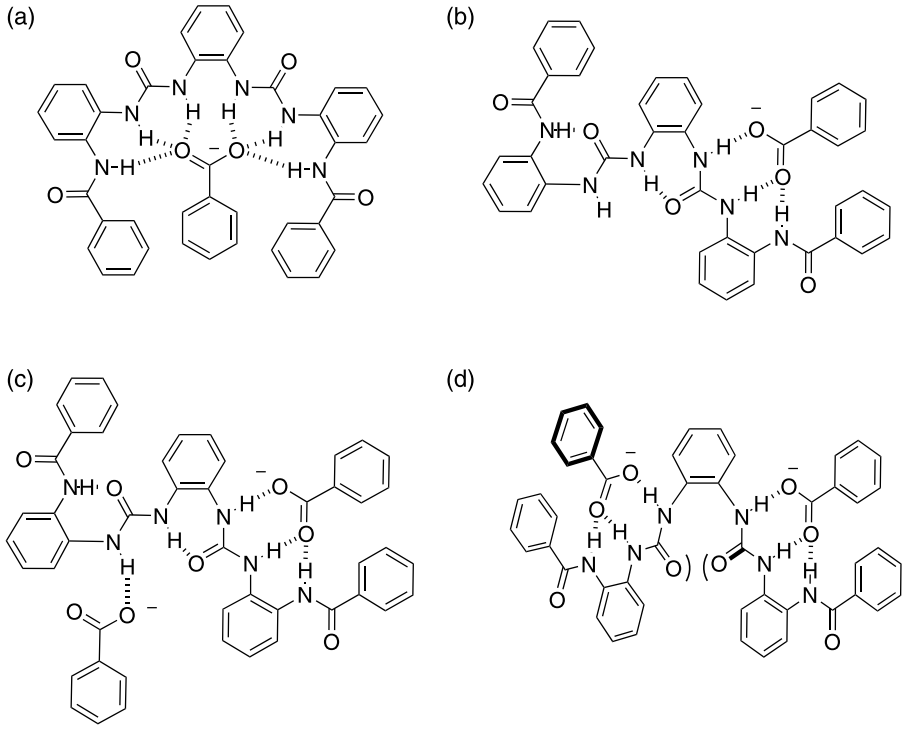


FIGURE 5 Possible binding modes of benzoate to compound **3** in a) and b) 1:1 stoichiometry and c) and d) 1:2 stoichiometry.

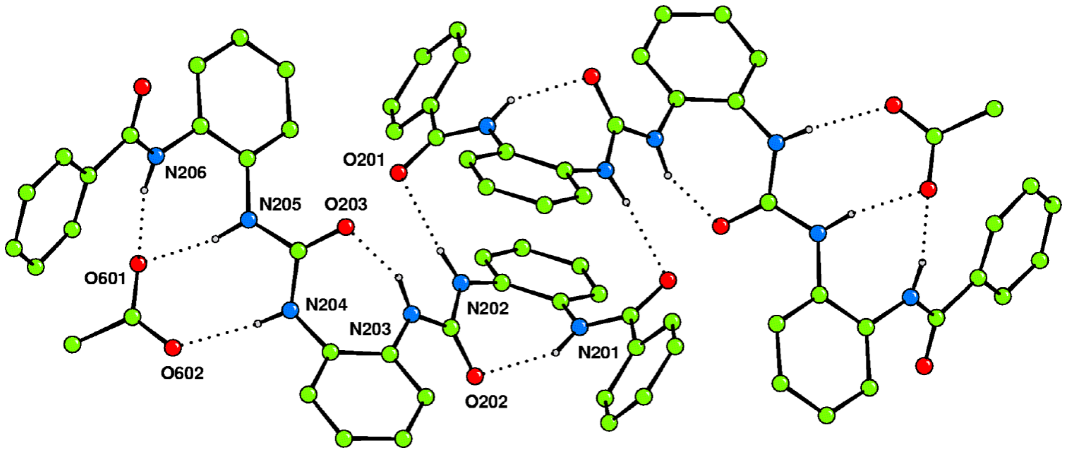


FIGURE 6 The X-ray crystal structure of the tetrabutylammonium acetate complex of receptor **3** (counter cation and non-acidic hydrogen atoms omitted for clarity) showing one of the dimers present in the unit cell binding two acetate anions.

RESULTS AND DISCUSSION

Compound **4** was synthesized by reaction of 3-ethylisocyanatobenzoate with *ortho*-phenylenediamine in dry dichloromethane. Reaction of this compound with the aluminium amide [20] species resulting from the reaction of aniline and trimethylaluminium afforded compound **2** (Scheme 1).

Compound **5** was synthesized according to literature methods [18]. This compound was reduced by addition of Pd/C and hydrazine monohydrate in ethanol affording compound **6**. This was coupled to benzoyl chloride to afford the bis-amide **3** (Scheme 2).

Crystals of compound **3** were grown from a DMSO solution of the receptor. The structure of the receptor was elucidated by single crystal X-ray diffraction and is shown in Fig. 1. The molecule forms chains along the *a*-axis via amide NH···amide O and urea NH···urea OC hydrogen bonds (Fig. 2).

^{1}H NMR titrations were performed with compounds **2** and **3** and a variety of putative anionic guests (as tetrabutylammonium salts) in DMSO-d_6/0.5% water at 298K. The NMR titration curves for compound **2** are shown in Fig. 3. Stability constants were determined using the EQNMR computer program (Table I) [25]. Compound **2** was found to have very similar affinities for anions as the parent compound **1** with the exception that dihydrogen phosphate is bound by compound **2** approximately three times more strongly than by compound **1**. This may be due to the participation of the terminal amide groups in dihydrogen phosphate complexation but not in benzoate complexation. Proposed structures for these complexes are shown in Fig. 4.

Compound **3** exhibits a higher affinity for oxo-anions than compound **2** and also a propensity to form 1:2 receptor:anion complexes albeit with low K_2 values. Unfortunately for solubility reasons studies were limited to DMSO-d_6/0.5% water solutions and so low variable temperature NMR experiments could not be performed to help elucidate the structure of the complex in solution. Fig. 5 shows possible structures for solution state complexes with benzoate. The high

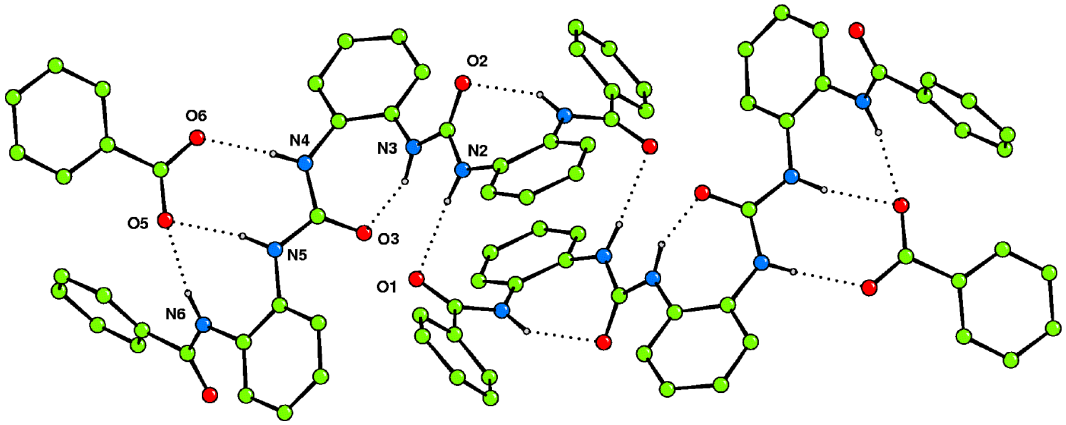


FIGURE 7 The X-ray crystal structure of the tetrabutylammonium benzoate complex of receptor **3** (counter cation and non-acidic hydrogen atoms omitted for clarity) the dimers present in the unit cell binding two benzoate anions.

TABLE II Hydrogen bonds lengths and angles in the acetate complex of compound **3** [Å and °]

D–H...*A*	*d*(D–H)	*d*(H...*A*)	*d*(*D*...*A*)	∠(*D*H*A*)
N101–H101...O102	0.88	1.92	2.683(3)	143.7
N203–H203...O203	0.88	2.01	2.738(4)	139.8
N103–H103...O103	0.88	2.01	2.737(4)	138.8
N104–H104...O502	0.88	2.05	2.780(3)	139.8
N105–H105...O501	0.88	1.97	2.837(4)	167.8
N106–H106...O501	0.88	2.13	2.954(4)	156.5
N201–H201...O202	0.88	1.92	2.682(3)	143.8
N102–H102...O101^{i}	0.88	2.06	2.897(3)	158.9
N202–H202...O201^{ii}	0.88	2.10	2.924(4)	155.0
N204–H204...O602^{iii}	0.88	2.05	2.803(4)	143.5
N205–H205...O601^{iii}	0.88	1.89	2.750(3)	165.1
N206–H206...O601^{iii}	0.88	2.12	2.953(4)	158.5

Symmetry transformations used to generate equivalent atoms: (i) −x, − y + 1, − z (ii) −x + 1, − y + 2, − z (iii) x,y + 1,z

TABLE III Hydrogen bonds lengths and angles in the benzoate complex of compound **3** [Å and °]

D–H...*A*	*d*(D–H)	*d*(H...*A*)	*d*(*D*...*A*)	∠(*D*H*A*)
N1–H91...O2	0.88	1.94	2.698(4)	142.6
N2–H92...O1^{i}	0.88	2.22	3.030(4)	152.4
N3–H93...O3	0.88	1.98	2.709(4)	139.8
N4–H94...O6	0.88	1.99	2.761(4)	145.4
N5–H95...O5	0.88	1.97	2.830(4)	165.3
N6–H96...O5	0.88	2.18	3.016(4)	159.1

Symmetry transformations used to generate equivalent atoms: (i) −x, − y, − z

K_1 values lead us to suggest that complex a predominates in solution at lower anion concentrations.

Crystals of the acetate and benzoate complexes of compound **3** were obtained by slow evaporation of an acetonitrile solution of the receptor in the presence of the excess tetrabutylammonium anion salt. The structures were elucidated by X-ray crystallography (Figs. 6 and 7) and reveal that both complexes adopt a similar arrangement in the solid-state which can be regarded as a dimer formed by complexes of type b in Fig. 5. The anions are bound at the ends of the dimer with the NH and OC group which are not involved in intramolecular hydrogen bonding in Fig. 5b forming a cyclic hydrogen bonding array with another receptor. Hydrogen bonding interactions in the two complexes are tabulated in Tables II (acetate) and III (benzoate).

CONCLUSION

Extending the hydrogen bond donor array has in the case of compound **3** resulted in a receptor with an enhanced affinity for anionic guests. X-ray crystallography has shown that in the solid-state carboxylate complexes of compound **3** dimerize with each anion bound by two urea and one amide hydrogen bond. We are continuing to investigate the anion binding properties of simple linear amidoureas and macrocyclic systems. These results will be published shortly.

Acknowledgements

We would like to thank the EPSRC for a DTA studentship (SJB) and for use of the crystallographic facilities at the University of Southampton.

References

[1] Sessler, J. L.; Gale, P. A.; Cho, W. S. In *Anion Receptor Chemistry (Monographs in Supramolecular Chemistry)*; Stoddart, J. F., Ed.; Royal Society of Chemistry: Cambridge, UK, 2006.
[2] Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609.
[3] Antonisse, M. M. G.; Reinhoudt, D. N. *Chem. Commun.* **1998**, 443.
[4] Pascal, R. A., Jr.; Spergel, J.; van Engen, D. *Tetrahedron Lett.* **1986**, *27*, 4099.
[5] Valiyaveetil, S.; Engbersen, J. F. J.; Verboom, W.; Reinhoudt, D. N. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 900.
[6] Beer, P. D. *Acc. Chem. Rec.* **1998**, *31*, 71.
[7] Kavallieratos, K.; Bertao, C. M.; Crabtree, R. H. *J. Org. Chem.* **1999**, *64*, 1675.
[8] Bondy, C. R.; Gale, P. A.; Loeb, S. J. *Chem. Commun.* **2001**, 729.
[9] Choi, K.; Hamilton, A. D. *J. Am. Chem. Soc.* **2001**, *123*, 2456.
[10] Hossain, Md. A.; Llinares, J. M.; Powell, D.; Bowman-James, K. *Inorg. Chem.* **2001**, *40*, 2936.
[11] Smith, P. J.; Reddington, M. V.; Wilcox, C. S. *Tetrahedron Lett.* **1992**, *33*, 6085.
[12] Hughes, M. P.; Smith, B. D. *J. Org. Chem.* **1997**, *62*, 4492.
[13] Pernía, G. J.; Kilburn, J. D.; Essex, J. W.; Mortishire-Smith, R. J.; Rowley, M. *J. Am. Chem. Soc.* **1996**, *118*, 10220.
[14] Gale, P. A. *Acc. Chem. Res.*, **2006**, *39*, 465.
[15] Gale, P. A. *Chem. Commun*. **2005**, 3761.
[16] Snellink-Ruël, B. H. M.; Antonisse, M. M. G.; Engbersen, J. F. J.; Timmerman, P.; Reinhoudt, D. N. *Eur. J. Org. Chem.* **2000**, 165.
[17] Brooks, S. J.; Gale, P. A.; Light, M. E. *Chem. Commun.* **2005**, 4696.
[18] Brooks, S. J.; Edwards, P. R.; Gale, P. A.; Light, M. E. *New. J. Chem.* **2006**, *30*, 65.
[19] Brooks, S. J.; Gale, P. A.; Light, M. E. *Cryst. Eng. Comm.* **2005**, *7*, 586.
[20] Basha, A.; Lipton, M.; Weinreb, S. M. *Tetrahedron Lett.* **1977**, *48*, 4171.
[21] COLLECT data collection software, Nonius B.V., 1998.
[22] Otwinowski, Z.; Minor, W. In *Methods in Enzymology: Macromolecular Crystallography, Part A*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: London, 1997; Vol. 276, p 307.
[23] Sheldrick, G. M. SADABS—Bruker Nonius area detector scaling and absorption correction—V2.10.
[24] Sheldrick, G. M. *SHELX97: Programs for Crystal Structure Analysis (Release 97-2)*; Institut für Anorganische Chemie der Universität Göttingen, Germany, 1998.
[25] Hynes, M. J. *J. Chem. Soc. Dalton Trans.* **1993**, 311.