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Confirmation of a 'cleft-mode' of binding in a 2,5-diamidopyrrole anion receptor in the solid state

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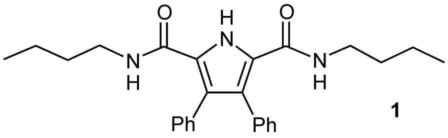
Abstract—The crystal structure of the tetrabutylammonium benzoate complex of 3,4-diphenyl-1*H*-pyrrole-2,5-dicarboxylic acid bis-butylamide has been elucidated confirming the formation of a cleft conformation in the solid state upon anion binding.

The synthesis of new receptors for carboxylate is of great importance in the design of hosts for amino-acids and polypeptides.[1] We have recently reported in this journal, the synthesis and anion binding properties of simple 2,5-diamidopyrroles such as compound **1**.[2] This molecule is selective for benzoate over other putative anionic guests, binding it with an association constant of 2500 M^{-1} in acetonitrile-d_3 (0.03% water). Comparison of the affinity of 2,5-diamidopyrroles for anions with 2-amido-5-methylpyrroles suggested that all three NH hydrogen bond donor groups in the former systems are utilised in the formation of an anion complex.[3] Whilst we have obtained the crystal structure of an unusual narcissistic dimer complex of a related anionic 3,4-dichloro-derivative[4] and Schmuck and Lex have obtained the crystal structure of acetate bound to a guanidinium functionalised pyrrole[5] we have up until now been unsuccessful at obtaining a crystal structure of an anion complex of any 2,5-diamidopyrrole. In this paper, we report the crystal structure of the benzoate complex of compound **1**[6] which reveals that all three NH hydrogen bond donors are indeed used in the formation of a carboxylate complex (as previously predicted).[3]



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Compound **1** was synthesised as previously described[2,3] and crystals of the tetrabutylammonium benzoate complex obtained by slow evaporation of a dichloromethane solution of the receptor in the presence of excess tetrabutylammonium benzoate. The benzoate anion is held within the cleft by three NH–O hydrogen bonds (Fig. 1) with the aromatic ring of the benzoate anion at an angle of 58.83(9)° to the pyrrole ring. One oxygen atom in the benzoate is in the plane of the pyrrole ring and one of the amide groups bound in a similar fashion to DMSO solvates previously observed.[3] The other amide groups twists out of plane by 38.03(10)° to accommodate a hydrogen bond to the other benzoate oxygen atom. The hydrogen bonds are in the range 2.771(3)–2.864(3) Å (Fig. 2).

In conclusion, we have shown that the 2,5-diamidopyrrole receptor **1** is capable of forming three hydrogen bonds to a benzoate anion in the solid state. This receptor is selective for benzoate in acetonitrile-d_3 solution and we are currently working to produce more complex functionalised systems for biomolecule recognition based upon this carboxylate binding site motif.

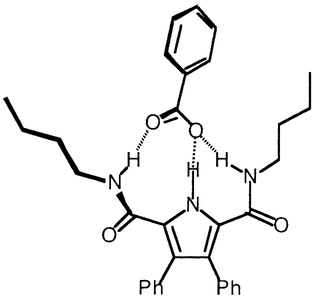

Figure 1. The three hydrogen bonds present in the benzoate complex of **1** in the solid state.

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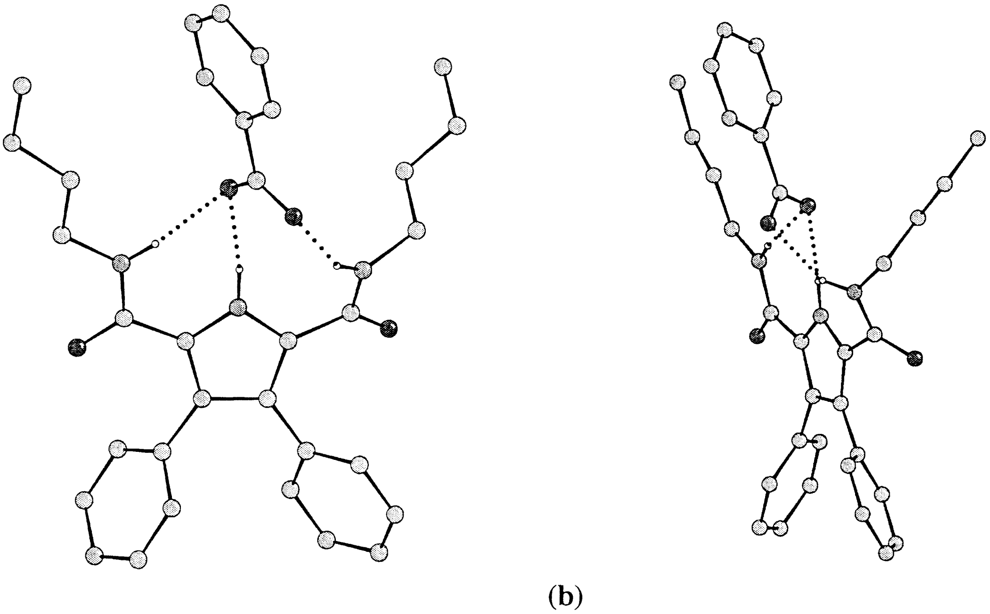

Figure 2. Front (a) and side (b) views of the crystal structure of the benzoate complex of **1** (tetrabutylammonium counter cation omitted for clarity).

Acknowledgements

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6. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number 187422 (compound **1**: tetrabutylammonium benzoate). Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk]. Crystal data: Colourless blocks, $C_{49}H_{72}N_4O_4$, Mr = 781.11, T = 120(2) K, monoclinic, space group $P2_1/n$, a = 10.0782(2), b = 26.9772(7), c = 17.7925(6) Å, β = 106.040(1), V = 4649.1(2) Å^3, ρ_{calcd} = 1.116 g cm^{-3}, μ = 0.07 mm^{-1}, Z = 4, reflections collected: 35158, independent reflections: 7892 (R_{int} = 0.1039), final R indices [I>2σ(I)]: R_1 = 0.0535, wR_2 = 0.0920, R indices (all data): R_1 = 0.1441. wR_2 = 0.1145.