Combined study of anion recognition by a carbazole-based neutral tripodal receptor in a competitive environment.

David Curiel, Guzmán Sánchez, Carmen Ramírez de Arellano, Alberto Tárraga and Pedro Molina

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Figure 1. Fitplots of 1 (A, B), 2 (C, D, E) and 3 (F, G), 2×10⁻³ M in DMSO-*d*₆.





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Figure 2. A) Evolution of the chemical shifts of the carbazole CH(1) proton of $1 (\blacktriangle)$, $2 (\blacksquare)$ and 3 (●), 2×10^{-3} M in DMSO-*d*₆, upon titration with TBAOH.

Evolution of the chemical shifts of different nuclei upon titration with various anioins: B) **1** + TBAF, C) 1 + TBAH₂PO₄, D) **1** + TBA₃HP2O₇, E) **2** + TBAF, F) **2** + TBAH₂PO₄, G) **2** + TBA₃HP₂O₇, H) **3** + TBAF, I) **3** + TBAH₂PO₄, J) **3** + TBA₃HP₂O₇.



Figure 3. ¹H-NMR spectra of 1, 2×10^{-3} M in DMSO-d₆, upon titration with TBAF.



Figure 4. ³¹P-NMR (120 MHz) titration isotherm of $H_2PO_4^- + 3$ (left) and $HP_2O_7^{3-} + 3$ (right), 2×10^{-3} M in DMSO-d₆,.

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Figure 5. NOESY spectra of **3** (top) and $\mathbf{3} + \text{HP}_2\text{O}_7^{3-}$ (bottom) in DMSO-d₆.



Figure 6. Mass spectrum of the 1:1 doubly charged complex $[\mathbf{3} \cdot \mathbf{H}_2 \mathbf{P}_2 \mathbf{O}_7^{2-}]$.



Figure 7. Diffusion NMR fitplots for (A) 3 (D= $0.16 \times 10^{-9} \text{ m}^2/\text{s}$), (B) 3 + 0.6 equivalents of HP₂O₇³⁻ (D= $0.14 \times 10^{-9} \text{ m}^2/\text{s}$), (C) 3 + 1.5 equivalents of HP₂O₇³⁻ (D= $0.13 \times 10^{-9} \text{ m}^2/\text{s}$) and (D) 3 + 3 equivalents of HP₂O₇³⁻ (D= $0.13 \times 10^{-9} \text{ m}^2/\text{s}$).

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Figure 8. Emission spectra of **3**, 2×10^{-5} M in DMSO, upon titration with (A) TBAAcO, (B) TBAH₂PO₄ and (C) TBAF (0-10 equivalents)



Figure 9. Evolution of the chemical shifts of different nuclei upon titration of **3**, 2×10^{-3} M in DMSO-d₆, with TBA₃HP₂O₇ in the presence of 5 equivalents of TBAAcO, TBABzO and TBAH₂PO₄.



Figure 10. Titration isotherm (λ_{em} = 390 nm) for 3 + HP₂O₇³⁻, 2×10⁻⁵ M in DMSO / water 5% (v/v).

A colourless lath of $0.20 \times 0.06 \times 0.05$ mm size, Triclinic, Pī, a = 14.183(3) Å, b = 14.993(3) Å, c = 15.927(3) Å, $\alpha = 1.000$ 64.96(3)°, $\beta = 71.58(3)°$, $\gamma = 68.87(3)°$, $V = 2808.2(13) Å^3$, $\rho = 1.311$ g cm⁻³, $2\theta_{max} = 50°$ 9, was measured at 120(2) K using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) and ω scan mode on a Oxford Diffraction SuperNova diffractometer. 33146 reflections collected of which 10672 were independent. The structure was solved by direct methods and all non hydrogen atoms refined anisotropically on F² (SHELXS-97 and SHELXL-97, G.M. Sheldrick, University of Göttingen, 1997). Two DMSO molecules are disordered over two sites with 80/20 and 66/34 % occupancy levels, respectively and were refined with appropriate similarity restraints (command SAME). Disordered atom U value components were restrained to be equal (commands DELU, SIMU, ISOR). Residual electron density about 1.6 Å from a disordered DMSO was tentatively identified as a water molecule with 50% occupancy level. The hydrogen atoms for this water molecule could not be located and were thus not included in the refinement. Other water molecule and carboxamide group hydrogen atoms were located in a difference Fourier synthesis and refined with restrained bond lengths and fixed atomic displacements. Other hydrogen atoms were included using a riding model. Disordered DMSO molecules with most of the scattering power (S atoms) could be the reason for very unequal components of the anisotropic parameters U and low bond precision on five C-C bonds. Final R(F) $[I > 2\sigma(I)] = 0.0619$ and wR2 (all data) = 0.1736 for 753 parameter. The programs use neutral atom scattering factors, $\Delta f'$ and $\Delta f''$ and absorption coefficients from International Tables for Crystallography (International Tables for Crystallography, Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C, Tables 6.1.1.4 (pp 500-502), 4.2.6.8 (pp 219-222), and 4.2.4.2 (pp 193-199)). CCDC 827347 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.



Figure 12. Asymmetric unit plot for compound 3.3 (DMSO)·2.5(H₂O) crystal structure showing the labelling scheme

(hydrogen and carbon labels have been omitted for clarity).



Figure 13. Packing view showing a linear chain along the a axis by dimmers assembly

The crystal structure of compound **3**, includes 3 DMSO and 2.5 water molecules in the asymmetric unit (Figure 1). In the crystal receptor **3** forms dimmers through N-H(carboxamide) \cdots O=C hydrogen bonds as it has been described in the paper. The dimmers assembly includes N-H(carboxamide) \cdots O=S(CH₃)₂ and N-H(carbazole) \cdots O=S(CH₃)₂ hydrogen bonds forming infinite chains along the a axis (Figure 1). These chains are assembled forming molecular layers through N-H(carbazole) \cdots OH₂, O-H(water) \cdots O=C, O-H(water) \cdots O=S(CH₃)₂, and O-H(water) \cdots OH₂ interactions. Layers are assembled through weak interactions involving C-H bonds and $\pi \cdots \pi$ stacking of the carbazole moieties with interplanar distance average of ca. 3.3-3.5 Å.

Table 1. Intermolecular hydrogen bonds (X-H···Y) lengths and angles for $3\cdot3(DMSO)\cdot2.5(H_2O)$ [Å and °].

D-H...A d(D-H) d(H...A) d(D...A) <(DHA)

Dimmers

N(1)-H(1)O(3)#1	0.82(2)	2.43(2)	3.221(4) 162(3)
N(5)-H(5)O(3)#1	0.83(2)	2.53(2)	3.339(4) 166(3)

(Chains							
ľ	N(3)-H(3)O(8)#1	0.82(2)	2.04(2)	2.855(3)176(3)				
ľ	N(19)-H(19)O(7)	0.88	2.05	2.831(4) 147.4				
ľ	N(39)-H(39)O(7)#2	0.88	2.10	2.962(4) 167.8				
Layers								
1	N(59)-H(59)O(9)#3	0.88	1.89	2.764(4) 173.6				
(D(9)-H(1W)O(1)#4	0.884(17	7) 1.862(18) 2.742(4) 173(5)				
(O(9)-H(2W)O(10)#5	0.91(2)	1.88(3)	2.757(5)159(5)				
(O(10)-H(4W)O(5)#6	0.91(2)	1.91(3)	2.797(4) 164(6)				
(D(10)-H(3W)O(6)	0.91(2)	2.05(3)	2.945(8) 169(6)				

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z+1 #2 x+1,y,z #3 x,y,z+1 #4 x,y-1,z

#5 -x+1,-y,-z #6 x-1,y,z-1