Supplementary Material (ESI) for New Journal of Chemistry

Supporting Information for:

Acyclic pyrrole-based anion receptors: Design, synthesis, and anion binding properties

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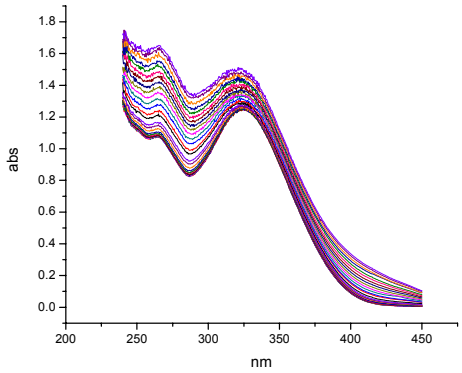
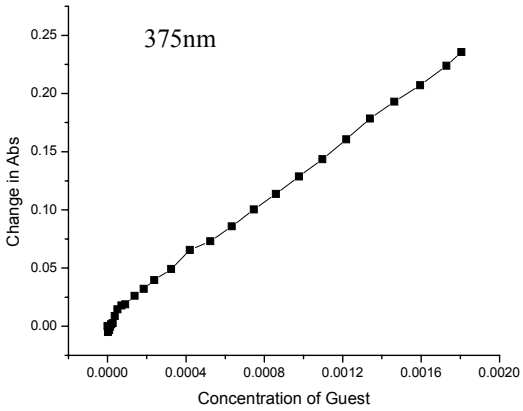
Anion Binding and Job plot titration data for the studied receptors.

All titrations were carried out in dichloroethane at 273K.

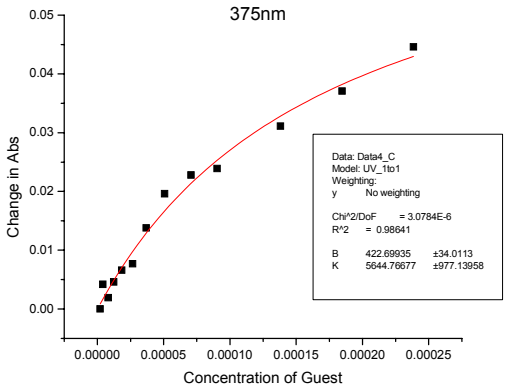
Fig. S1: TBA-CN titrated into Receptor **3**.
Guest Equiv. Range: 0 - 15

UV-Vis Spectra:





Binding isotherm:
Guest equiv. range: 0-1.5



Job Plot

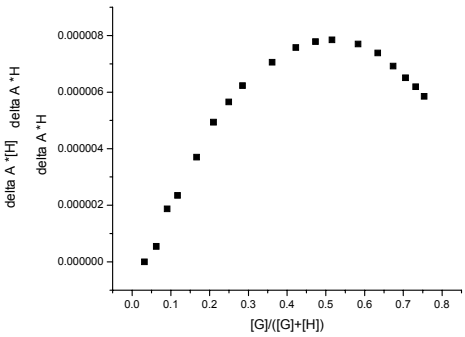
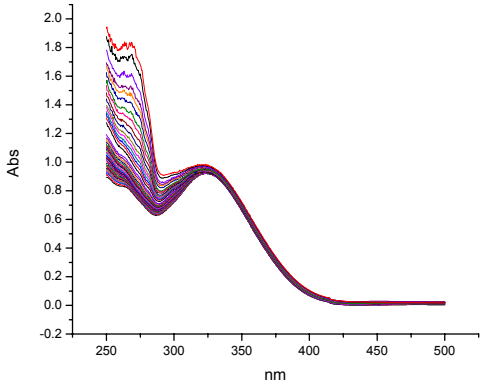
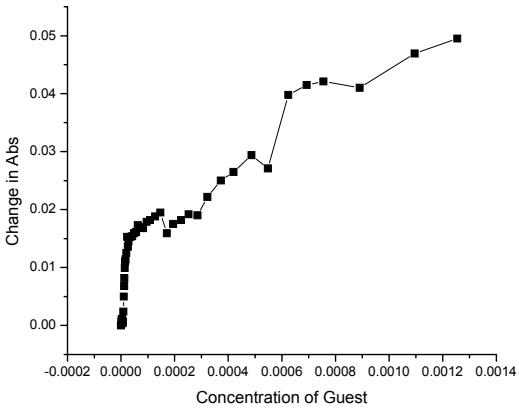


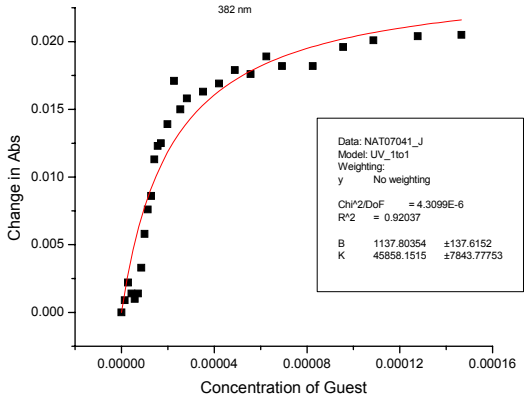
Fig. S2: TBA-Benzoate titrated into Receptor **3**.
Guest Equiv. Range: 0 – 14

UV-Vis Spectra:





Binding Isotherm:
Guest equiv. range: 0 – 1.7



Job plot

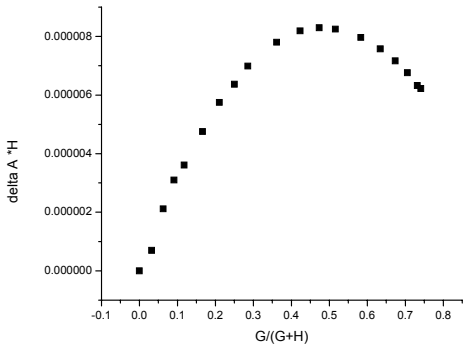
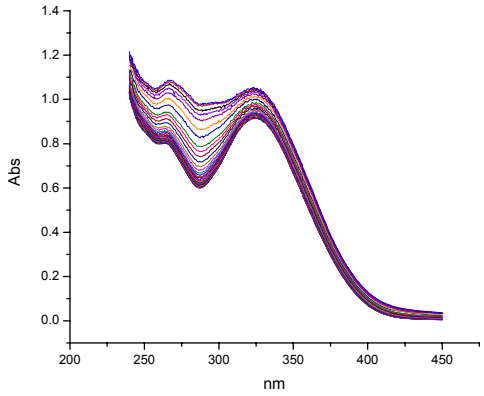
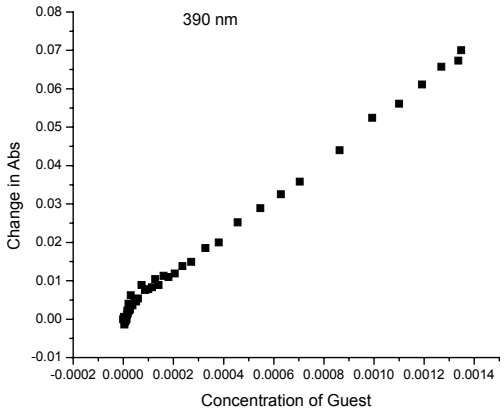


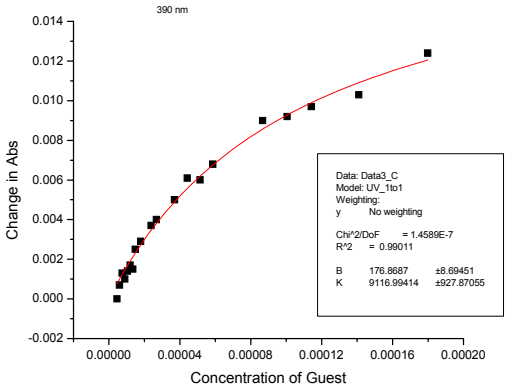
Fig. S3: TBA-Acetate titrated into Receptor **3**.
Guest Equiv. Range: 0 – 15.8

UV-Vis Spectra:





Binding Isotherm:
Guest equiv. range: 0 – 2.4



Job plot

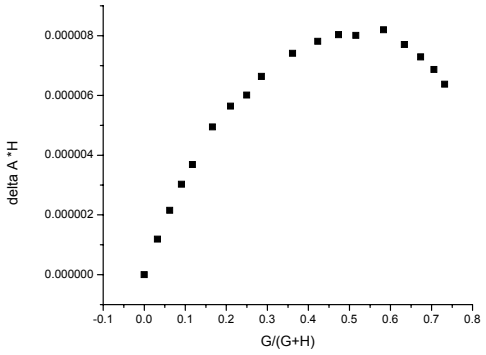
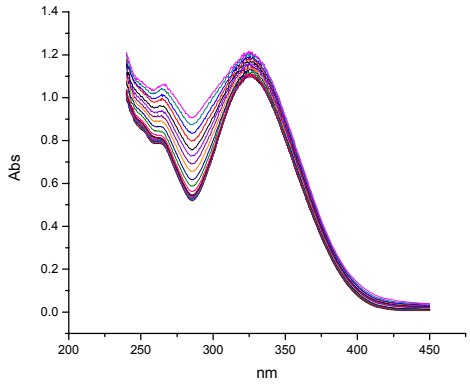
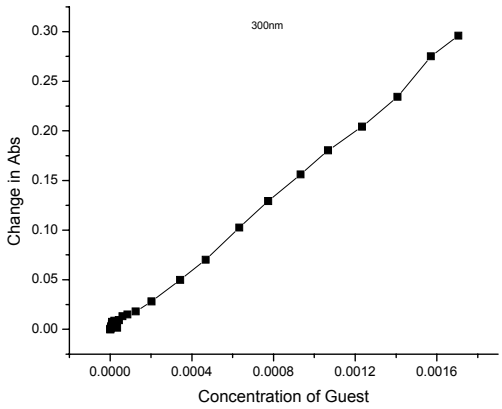


Fig. S4: TBA-Acetate titrated into Receptor **4**.
Guest Equiv. Range: 0 – 23

UV-Vis Spectra:





Binding Isotherm:
Guest equiv. range: 0 – 1.7

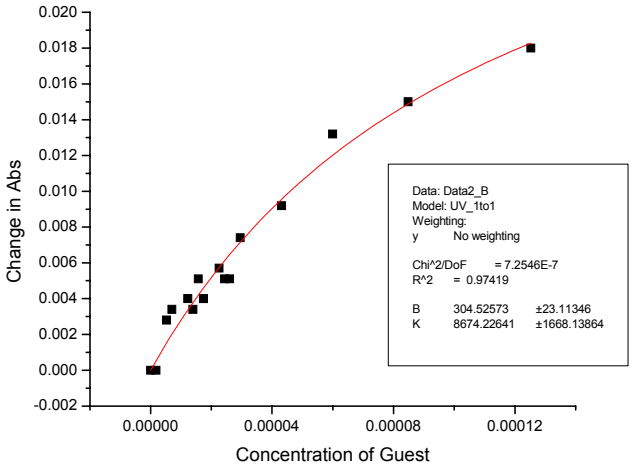
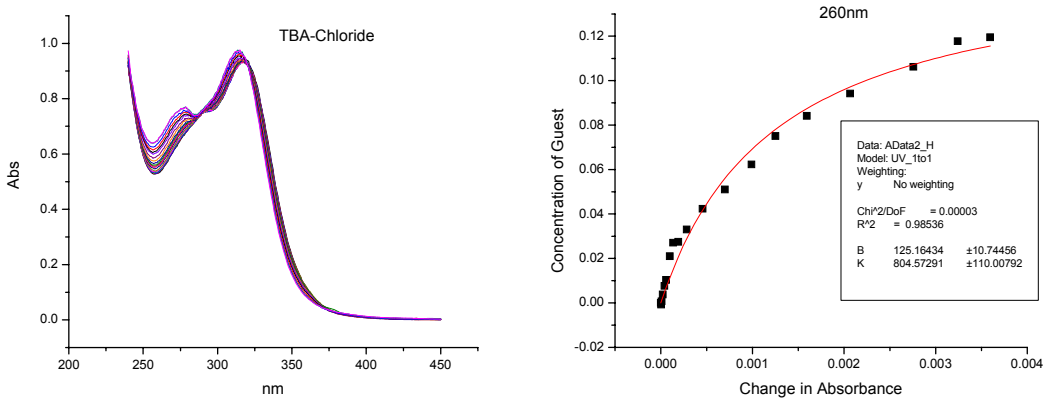


Fig. S5: TBA-Cl titrated into Receptor **6**.
Guest Equiv. Range: 0 – 88

UV-Vis Spectra:



NOE NMR data

Figure S6: Irradiation of the pyrrole α-hydrogen signal of receptor **4**.

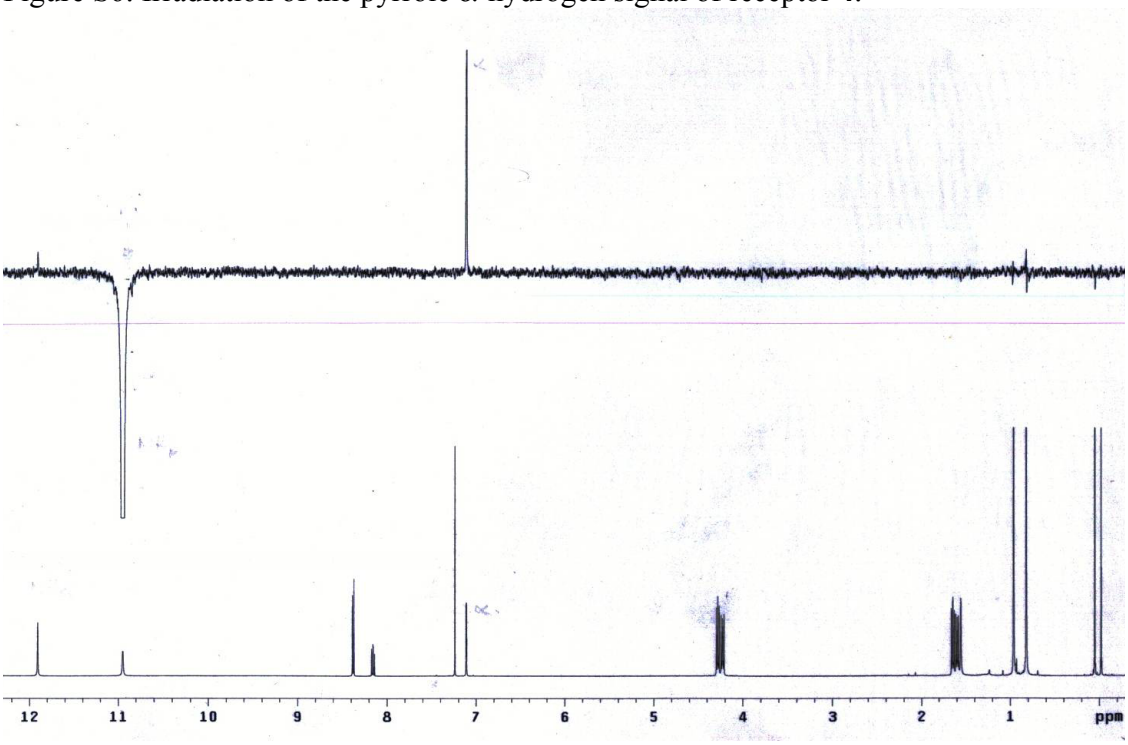
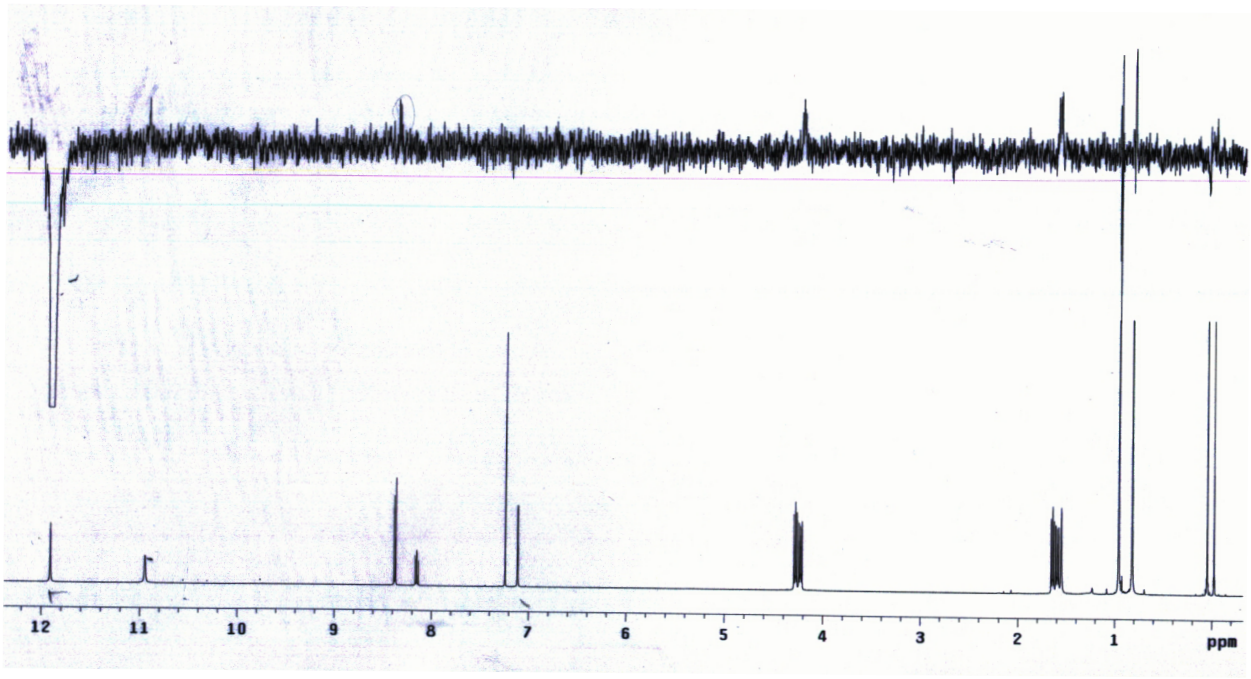


Figure S7: Irradiation of the amide N-H peak of receptor **4**.



Crystallographic data:

X-ray Experimental for $C_{27}H_{29}N_5O_{10}$ - CH_2Cl_2: Crystals grew as long, colorless laths by slow evaporation from methylene chloride. The data crystal was a long lathe that had approximate dimensions; 0.42 x 0.20 x 0.10 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073Å). A total of 504 frames of data were collected using ω-scans with a scan range of 1° and a counting time of 117 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.[1] The structure was solved by direct methods using SIR97[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[3] The hydrogen atoms on carbon were calculated in

ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

A cylindrical shaped region near 1/2, 0, z contained disordered solvent. The solvent appeared to be dichloromethane, which could not be modeled satisfactorily. The contribution to the scattering was removed by use of the utility, SQUEEZE, in PLATON98.[4] PLATON98 was used as incorporated in WinGX.[5]

One of the ethyl groups was found to be disordered about two principal orientations. The disorder was modeled by restraining the C-C bond lengths of the two orientations to be equivalent. The site occupancy factor of one component composed of atoms C26 and C27 was assigned the variable x. The site occupancy of the atoms of the alternate conformation was assigned to (1-x). A common isotropic displacement parameter was refined for the atom pairs, C26 and C26a, and C27 and C27a, while the site occupancy factor x was refined. The site occupancy factor for C26 and C27 refined to 80(2)%. C26 and C27 were refined anisotropically while C26a and C27a were refined isotropically.

The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.104*P)^2 + (0.0585*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.215, with R(F) equal to 0.0735 and a goodness of fit, S, = 1.16. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[6] The data were corrected for secondary extinction effects. The correction takes the form: $F_{corr} = kF_c/[1 + (2.2(5)x10^{-5})* F_c^2 \lambda^3/(\sin 2\theta)]^{0.25}$ where k is the overall scale factor. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[7] All figures were generated using SHELXTL/PC.[8] Tables of positional and thermal parameters, bond lengths and angles, torsion angles, H-bonding interactions, figures and lists of observed and calculated structure factors are located in tables 1 through 8.

Table 1. Crystal data and structure refinement for 1.

Empirical formula	C28 H31 Cl2 N5 O10	
Formula weight	668.48	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.6399(4) Å	α= 75.915(2)°.
	b = 12.1551(4) Å	β= 72.576(2)°.
	c = 12.5581(4) Å	γ = 76.920(2)°.
Volume	1621.52(9) $Å^3$	
Z	2	
Density (calculated)	1.369 Mg/m^3	
Absorption coefficient	0.262 mm^{-1}	
F(000)	696	
Crystal size	0.42 x 0.20 x 0.10 mm	
Theta range for data collection	3.34 to 25.00°.	
Index ranges	-13<=h<=13, -14<=k<=14, -14<=l<=14	
Reflections collected	10314	
Independent reflections	5681 [R(int) = 0.0363]	
Completeness to theta = 25.00°	99.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5681 / 2 / 388	
Goodness-of-fit on F^2	1.165	
Final R indices [I>2sigma(I)]	R1 = 0.0735, wR2 = 0.1973	
R indices (all data)	R1 = 0.1227, wR2 = 0.2147	
Extinction coefficient	$2.2(5)x10^{-5}$	
Largest diff. peak and hole	0.352 and -0.255 $e.Å^{-3}$	

Table S1. Hydrogen bonds for 1 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N1-H1N...O1	0.90	2.18	2.725(3)	118.7
N2-H2N...O5	0.90	2.12	2.734(3)	124.3
N4-H4N...O7	0.90	2.20	2.816(3)	125.5
N5-H5N...O2	0.90	2.15	2.702(3)	118.5
N1-H1N...O7#1	0.90	2.32	2.866(3)	119.2
N5-H5N...O5#2	0.90	2.15	2.846(3)	133.7

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1 #2 -x,-y+1,-z

Figure S8. View of **3** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

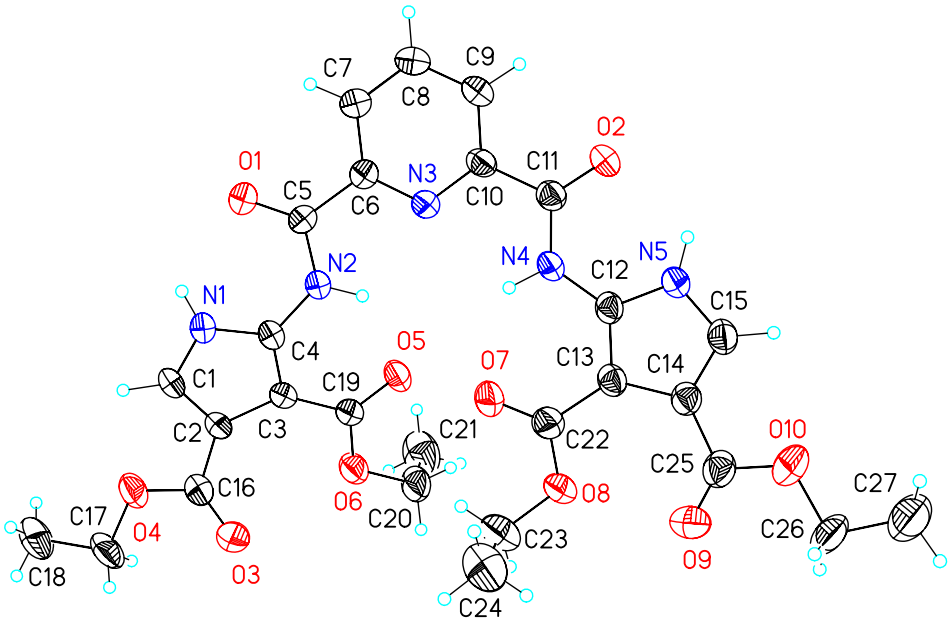
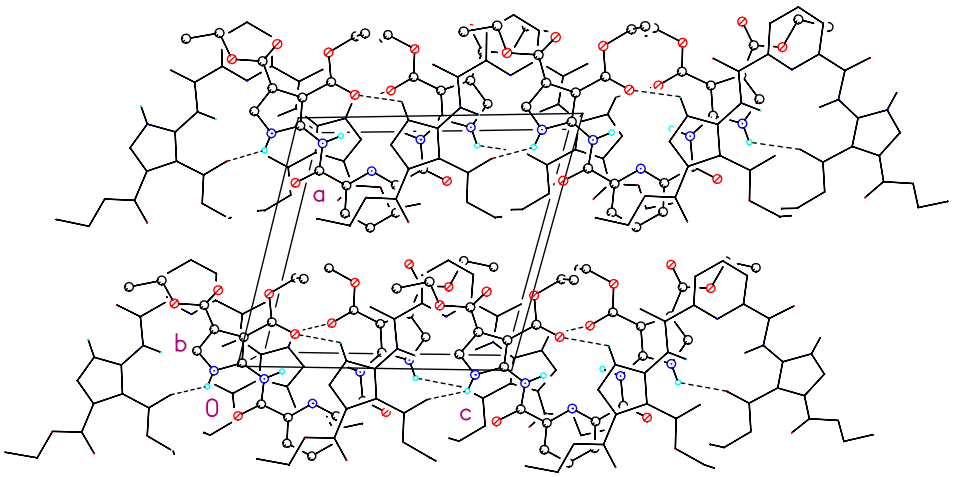


Figure S9. Unit cell packing diagram for **3**. The view is approximately down the **b** axis. Molecules pack in H-bound columns parallel to the **c** axis. Dashed lines are indicative of the H-bonding interactions.



References

1) Z. Otwinowski and W. Minor in *Methods in Enzymology*, **276**: Macromolecular Crystallography, part A, 307 – 326, C. W. Carter, Jr. and R. M. Sweets, Editors, Academic Press, 1997.

2) A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Cryst.* 1993, **26**, 343-350.

3) G. M. Sheldrick SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany, 1994.

4) R. I. Cooper, R. O. Gould, S. Parsons and D. J. Watkin, *J. Applied Cryst.* 2002, **35**, 168-174.

5) L. J. Farrugia, *J. Applied Cryst.* 1999, **32**, 837-838.

6) $R_w(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection. $R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$. $S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

7) International Tables for X-ray Crystallography. Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, Editor, Boston: Kluwer Academic Press, 1992.

8) G. M. Sheldrick, SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA, 1994.