Electronic Supplementary Information

A new open benzodipyrrole-based chemosensor for hydrogenpyrophosphate anion in aqueous environment

David Curiel,* Arturo Espinosa, Miriam Más-Montoya, Guzmán Sánchez, Alberto Tárraga and Pedro Molina

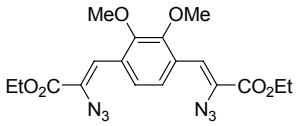
Universidad de Murcia, Facultad de Química, Departamento de Química Orgánica, Campus de Espinardo, Murcia 30100, España

Reagents used as starting materials were purchased from Sigma-Aldrich Co. and were used without further purification. Solvents were dried following the usual protocols (THF, Et_2O and Toluene were distilled from sodium wire with benzophenone indicator; CH_3CN and CH_2Cl_2 were distilled from $CaCl_2$; EtOH and MeOH were distilled from magnesium and stored with molecular sieves). Unless stated otherwise, all reactions were carried out under nitrogen atmosphere. Column chromatography was run with silica gel 60 A CC 70-200 μm as stationary phase, purchased from Carlo Erba-SDS, and using HPLC grade solvents purchased from either Panreac, Lab-Scan or Scharlab. Melting points were measured in a Reichert instrument and are not corrected. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on either a Bruker AV300 instrument, or a Bruker AV400 instrument, or Varian Unity-300 instrument. Chemical shifts are referred to tretamethylsilane (δ= 0 ppm). In the experimental data "bp" stands for broad peak and "Cq" for quaternary carbon atom. Mass spectrometry was recorded on HPLC-MS TOF 6220 instrument. Absorption spectra were recorded on a Cary 500 UV-vis-NIR spectrophotometer. Emission spectra were recorded on a Cary Eclipse spectrophotometer. Isothermal titration calorimetry experiments were run in a Microcal VP-ITC microcalorimeter and data were analysed using Origin software.

Titrations experiments protocol: A stock solution of the receptor was prepared in an acetone-water (5% v/v) mixture of solvents. The anion was then dissolved with the appropriate volume of the former solution to get the right concentration of the titrant. Aliquots of the latter solution are added to the solution which contains the receptor without having to consider any dilution effects on the titrated species.

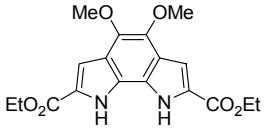
2-(Aminomethyl)pyrrole was synthesised according to reported methods.[1]

[1] Putochin, N., *Chem. Ber.* **1926,** 59, 1987.



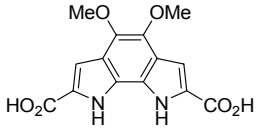
1,4-di[(Z)-2-azido-2-ethoxycarbonylvinyl]-2,3-dimethoxybenzene, **2**: A solution of sodium ethoxide (6 g, 88 mmol) in anhydrous ethanol (80 ml) was cooled to -20ºC under nitrogen atmosphere. At this temperature, a solution of ethyl azidoacetate (11.3 g, 88 mmol) and 2,3-dimethoxytherephthaldehyde (2.1 g, 11 mmol) in dry ethanol (100 ml) was added dropwise over three hours. The reaction mixture was stirred under these conditions for 18 h. A bright yellow precipitate appeared which was filtered while cold. The isolated solid (2.5 g, 55% yield) corresponded to the expected product without further purification.

mp: 129-132ºC; ^{1}H-NMR ($CDCl_3$), δ (ppm): 1.41 (t, J = 7.2 Hz, 6H), 3.87 (s, 6H), 4.38 (c, J = 7.2 Hz, 4H), 8.04 (s, 2H); ^{13}C-NMR ($CDCl_3$), δ (ppm): 14.17 (2xCH_3), 61.31 (2xCH_3), 62.34 (2xCH_2), 117.88 (2xCH), 125.07 (2xCH), 126.91 (2xCq), 128.91 (2xCq), 151.56 (2xCq), 163.43 (2xC=O); HRMS (m/z): ($C_{18}H_{20}N_2O_6$) Found: 361.1389 (M^+-2N_2+1); Calcd: 361.1399.



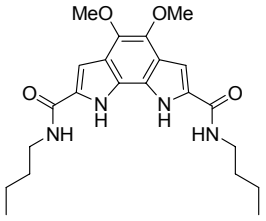
2,7-di(ethoxycarbonyl)-4,5-dimethoxypyrrolo[2,3-g]indole, **3**: Compound **2** (2.5 g, 6 mmol) was dissolved in toluene and refluxed for 6 h. The reaction is then allowed to cool to room temperature and the solvent is evaporated under reduced pressure. The crude is purified by column chromatography, using ethyl acetate:hexane (1:2) as eluent. The fractions which contain the desired product were combined and evaporated in the rotary evaporator to obtain a pure yellow solid (1.2 g, 55% yield).

mp: 242-245ºC; ^{1}H-NMR (DMSO-d_6), δ (ppm): 1.34 (t, J = 7.2 Hz, 6H), 3.91 (s, 6H), 4.33 (c, J = 7.2 Hz, 4H), 7.15 (s, 2H), 11.95 (s, 2H); ^{13}C-NMR (DMSO-d_6), δ (ppm): 14.3 (2xCH_3), 60.4 (2xCH_2), 61.0 (2xCH_3), 106.8 (2xCH pyrr), 120.05 (2xCq), 121.5 (2xCq), 124.9 (2xCq), 138.1 (2xCq), 160.8 (2xC=O); HRMS (m/z): ($C_{18}H_{20}N_2O_6$) Found: 361.1385 (M^++1) Calcd: 361.1399.



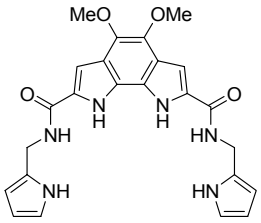
2,7-dicarboxy-4,5-dimethoxypyrrolo[2,3-g]indole, **4**: Compound **3** (1.1 g, 3 mmol) was dissolved in a mixture of ethanol:water (7:1) (80 ml) which contained potassium hydroxide (24 mmol). The reaction mixtured was refluxed for 6 h. Then, it was allowed to cool to room temperature and further cooled to 0ºC in an ice bath. Hydrocloric acid (15%) was added until acid pH was obtained. A white solid precipitated in situ, which was filtered and washed with water (3x30ml). This solid was dried in the air and identified as the pure dicarboxylic acid (0.84 g, 91% yield).

mp: dec > 220 ºC; ^{1}H-NMR (DMSO-d_6), δ (ppm): 3.91 (s, 6H), 7.12 (s, 2H), 11.46 (s, 2H); ^{13}C-NMR (DMSO-d_6), δ (ppm): 60.9 (2xCH_3), 106.5 (2xCH), 120.0 (2xCq), 121.2 (2xCq), 125.8 (2xCq), 138.2 (2xCq), 162.3 (2xC=O); HRMS (m/z): ($C_{14}H_{12}N_2O_6$) Found: 305.0759 (M^++1) Calcd: 305.0773.



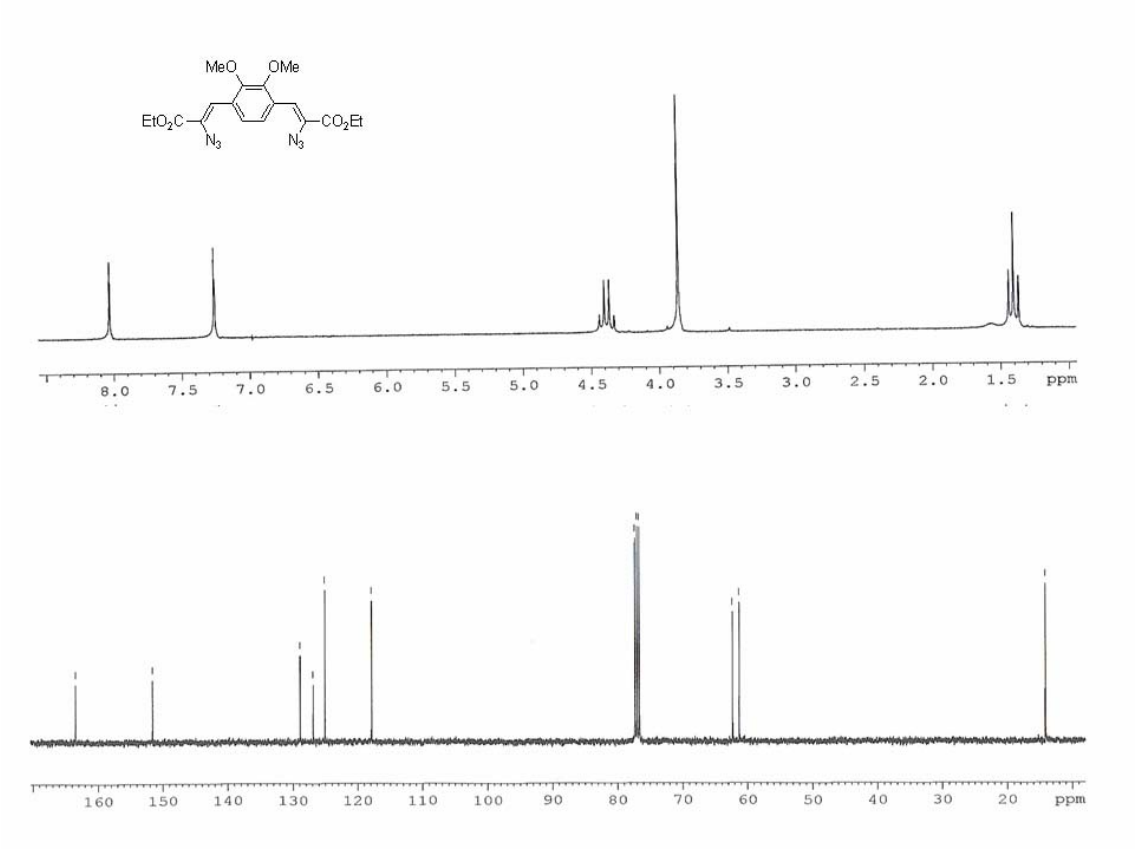
2,7-di(butylcarbamoyl)-4,5-dimethoxypyrrolo[2,3-g]indole, **5**: Compound **4** (0.31 g, 1mmol) and carbonyldiimidazole (0.65 g, 4 mmol) were stirred together in dimethylformamide (60 ml) for 4 h. Freshly distilled butylamine (0.44 g, 6 mmol) was then dissolved in DMF (5 ml) and added through a

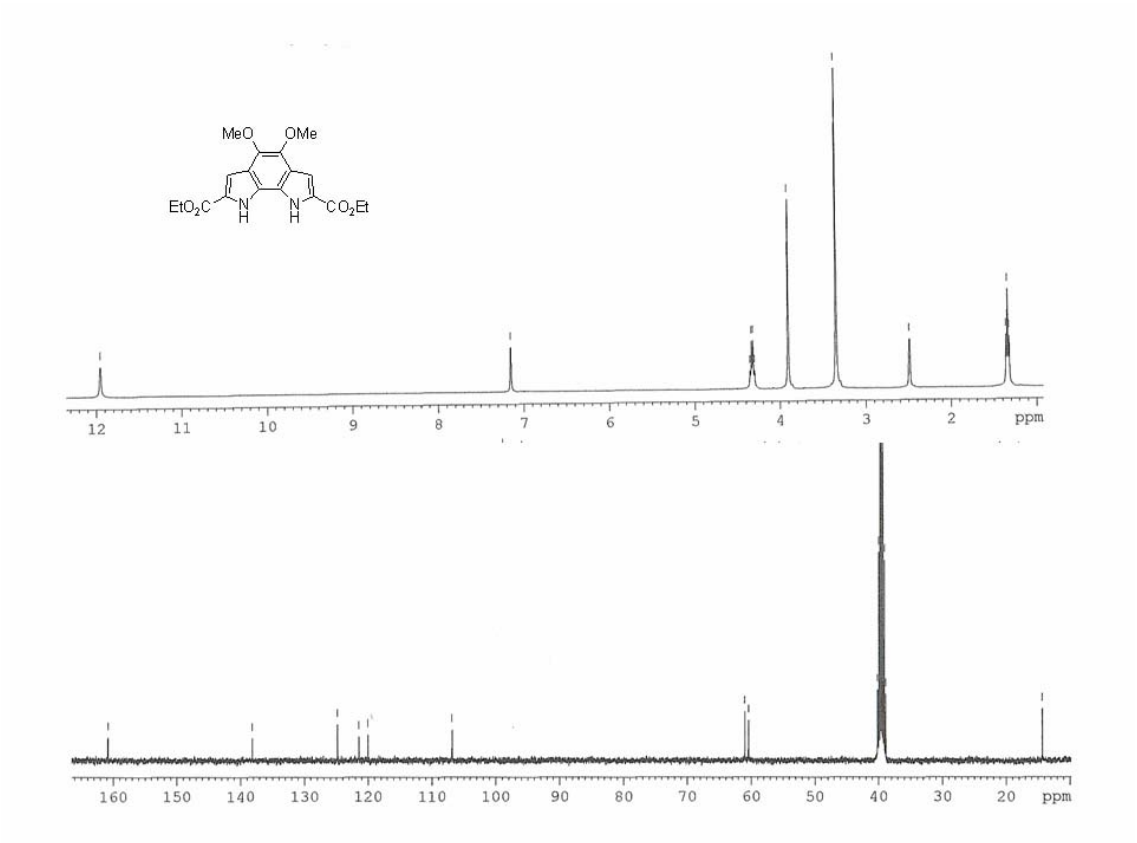
dropping funnel. The reaction mixture was stirred at room temperature overnight. The solvent was then evaporated under reduced pressure and the crude was purified by column chromatography, eluting sequentially with ethyl acetate:hexane (1:1), (2:1) and (4:1). The fractions which contained the main product were combined and evaporated under reduced pressure to obtain a white solid (0.34 g, 83% yield) which corresponded to the pure product.
mp:dec 218-221ºC; ^{1}H-NMR (DMSO-d_6), δ (ppm): 0.94 (bs, 6H), 1.35 (bs, 4H), 1.51 (bs, 4H), 3.30 approx included in the water peak (4H), 3.91 (s, 6H), 7.27 (bs, 2H), 8.39 (bs, 2H, NH), 11.31 (s, 2H, NH); ^{13}C-NMR (DMSO-d_6), δ (ppm): 13.7 (2xCH3), 19.7 (2xCH_2), 31.4 (2xCH_2), 38.4 (2xCH_2), 60.8 (2xCH_3), 101.6 (2xCH), 119.3 (2xCq), 120.2 (2xCq), 128.9 (2xCq), 137.9 (2xCq), 160.8 (2xC=O); HRMS (m/z): ($C_{22}H_{30}N_4O_4$) Found: 415.2340 (M^++1) Calcd: 415.2345.

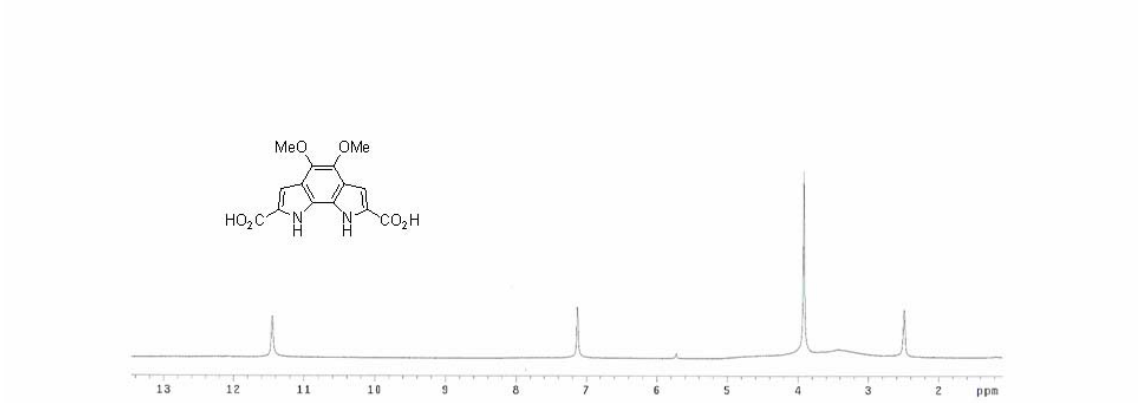


2,7-di(pyrrolyl-2-methylcarbamoyl)-4,5-dimethoxypyrrolo[2,3-g]indole, **6**: A procedure identical to the one described for compound **5** was followed to obtain the corresponding diamide (0.37 g, 81 % yield).

mp: dec > 240ºC; ^{1}H-NMR (DMSO-d_6), δ (ppm): 3.90 (s, 6H), 4.43 (d, *J* = 4.8 Hz, 4H), 5.94 (bs, 2H), 6.64 (bs, 2H), 7.34 (bs, 2H), 8.74 (t, *J* = 4.8 Hz, 2H, NH), 10.60 (bs, 2H, NH), 11.36 (s, 2H, NH); ^{13}C-NMR (DMSO-d_6), δ (ppm): 35.8 (2xCH_2), 60.7 (2xCH_3), 102.1 (2xCH), 105.9 (2xCH), 107.1 (2xCH), 117.1 (2xCH), 119.3 (2xCq), 120.3 (2xCq), 128.7 (2xCq), 128.9 (2xCq), 137.9 (2xCq), 160.7 (2xC=O); HRMS (m/z): ($C_{24}H_{24}N_6O_4$) Found: 461.1925 (M^++1) Calcd: 461.1937;


MeO
OMe
EtO2C
CO2Et
N3
N3
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


MeO
OMe
EtO2C
N
H
N
H
CO2Et
12 11 10 9 8 7 6 5 4 3 2 ppm
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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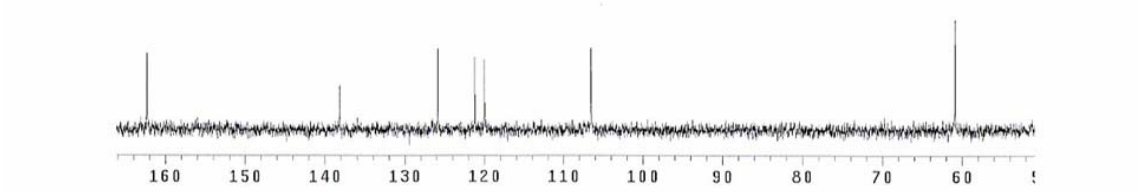
OMe
HO2C
CO2H
N
H
13 12 11 10 9 8 7 6 5 4 3 2 ppm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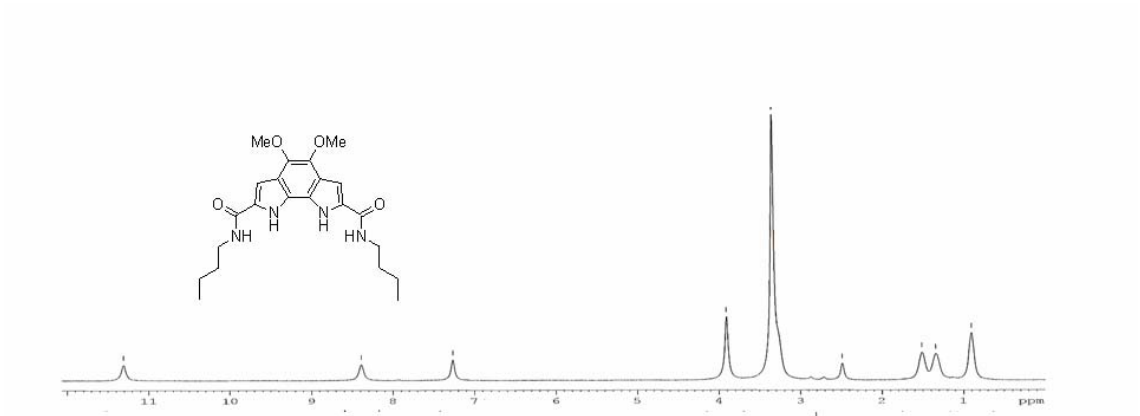
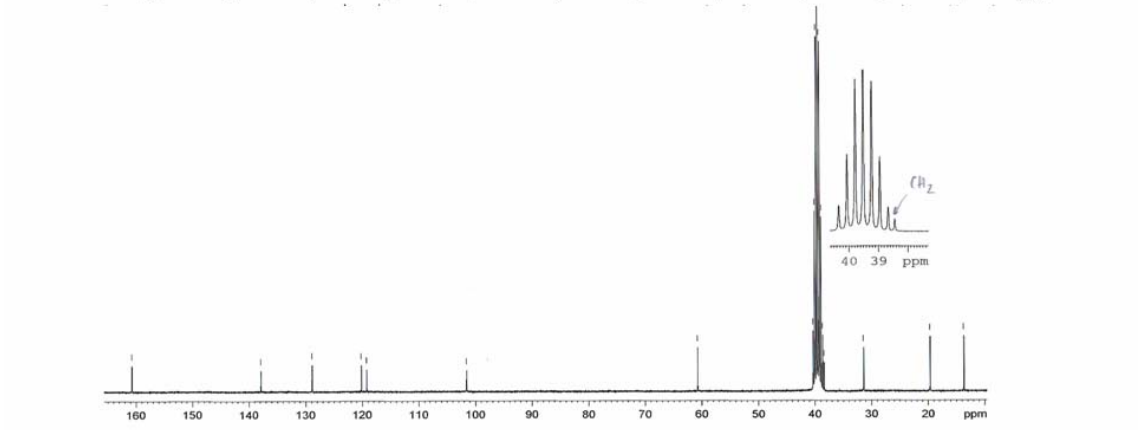
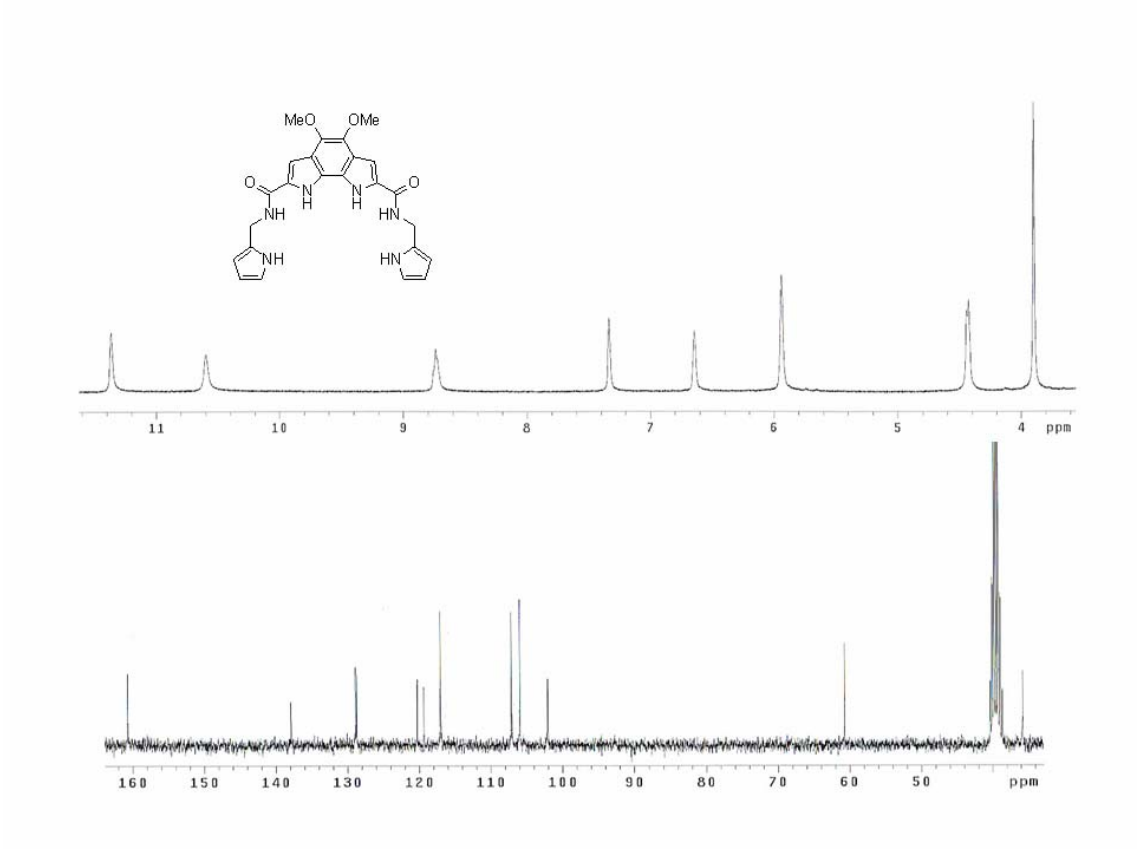
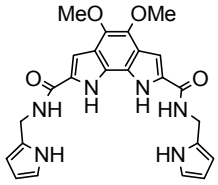

MeO
OMe
O
NH
HN
11 10 9 8 7 6 5 4 3 2 1 ppm

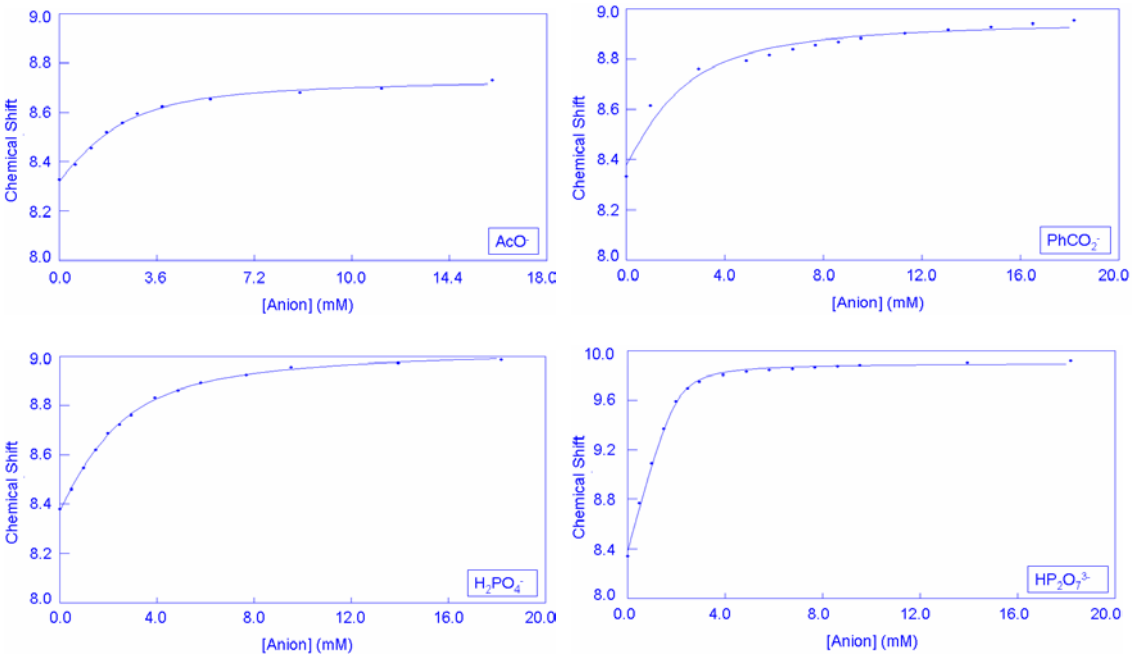

CH2
40 39 ppm
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

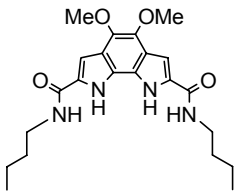

MeO
OMe
O
NH
N
H
N
H
O
HN
NH
HN
11
10
9
8
7
6
5
4
ppm
160
150
140
130
120
110
100
90
80
70
60
50
ppm

Non linear regression of ^{1}H-NMR titration data. [Host]=2x10^{-3} M in acetone-water (5% v/v), T=25ºC.

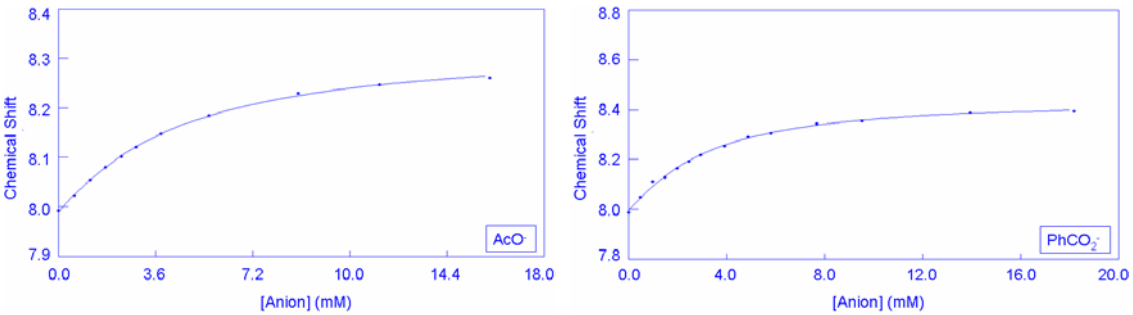


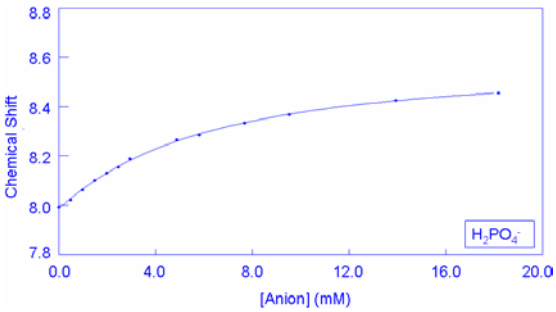
Compound **6**

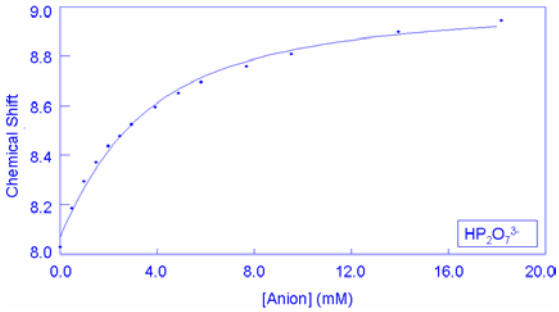


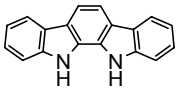


Compound **5**

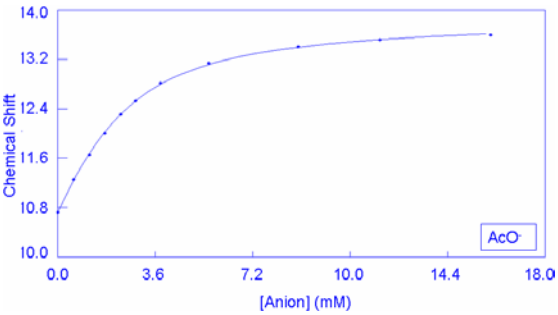


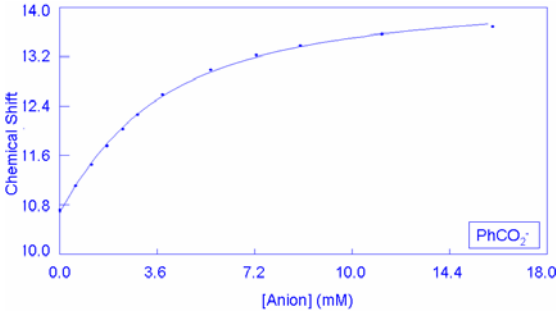


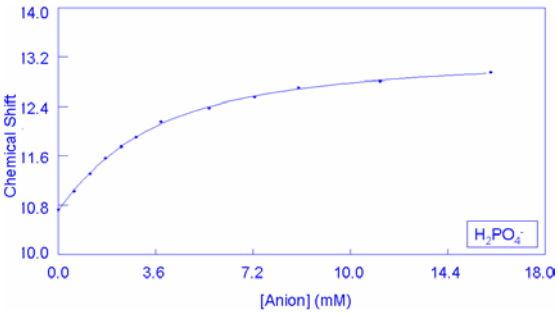




Compound **7**







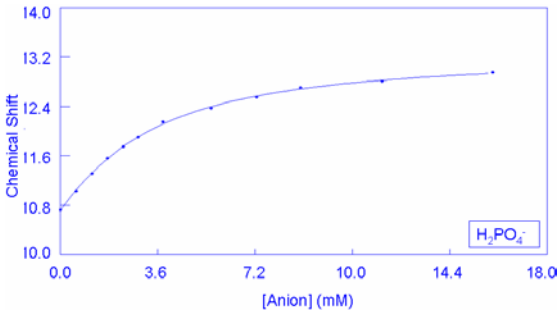


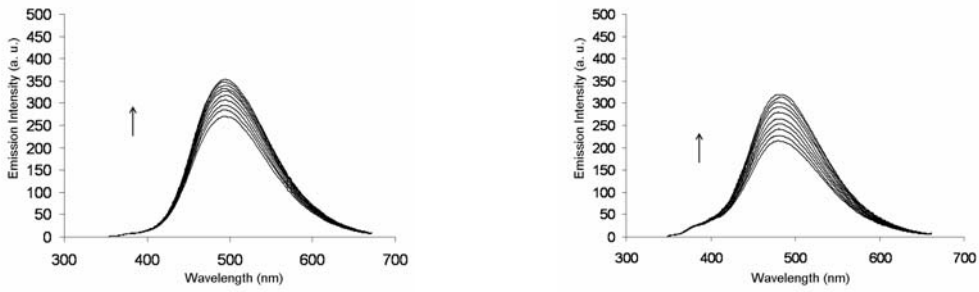
Table 1. Association constants [a] (M^{-1}) in acetone-water (5% v/v)

Receptor	AcO^-	BzO^-	$H_2PO_4^-$	$HP_2O_7^{3-}$
5	304	513	206	435
6	1036	889	831	9081
7	773 [b]	400 [b]	437 [b]	1746 [c]

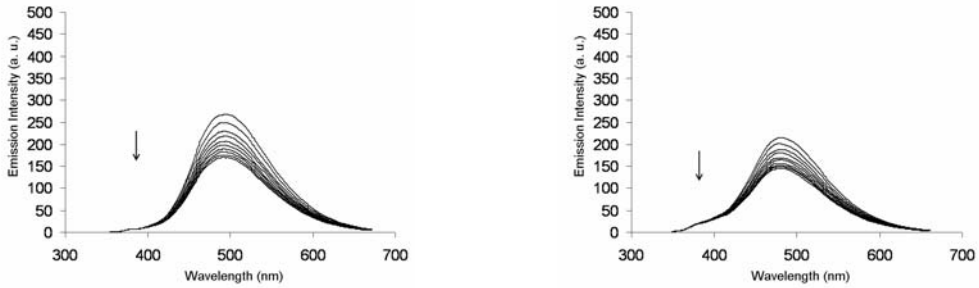
[Host]=2x10^{-3}M, T= 25ºC; error < 15% in all cases; [a] Calculated from the amide NH chemical shifts for comparative purposes. Benzodipyrrolic NHs disappeared upon titration with $TBA_3HP_2O_7$; [b] Calculated from the NH chemical shifts; [c] Calculated from the CH(1) chemical shifts.

Evolution of the emission spectra of **5** (right column) and **6** (left column), ($5x10^{-5}$ M) in acetone-water (5% v/v), upon titration with TBA-acetate, TBA-benzoate, $TBAH_2PO_4$ and $TBA_3HP_2O_7$.

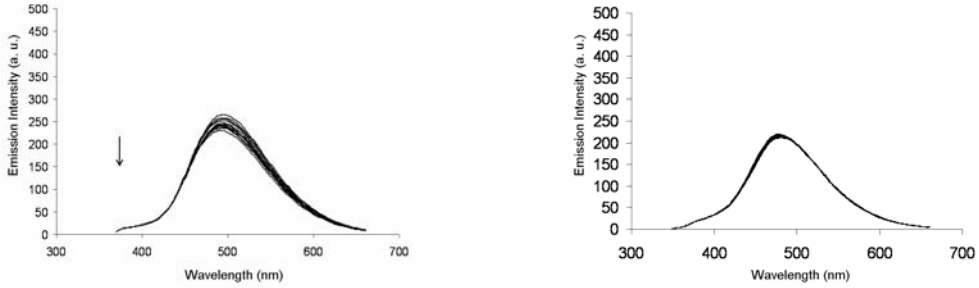
Acetate



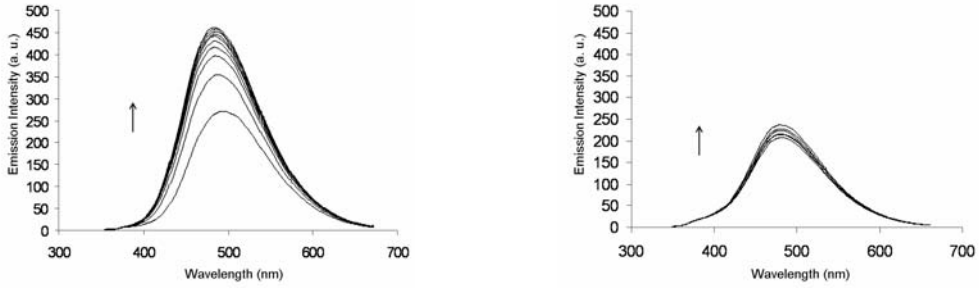
Benzoate

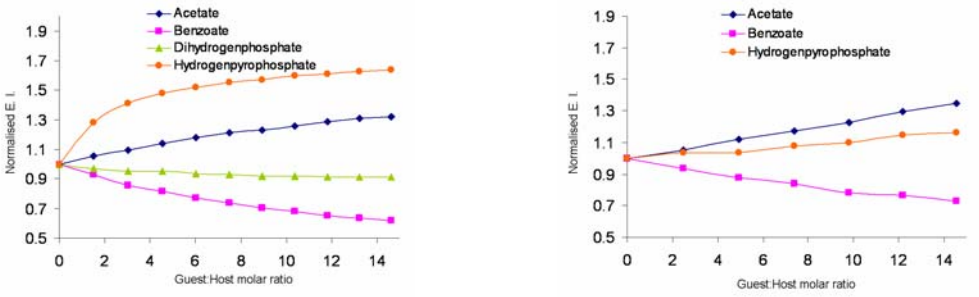


Dihydrogenphosphate



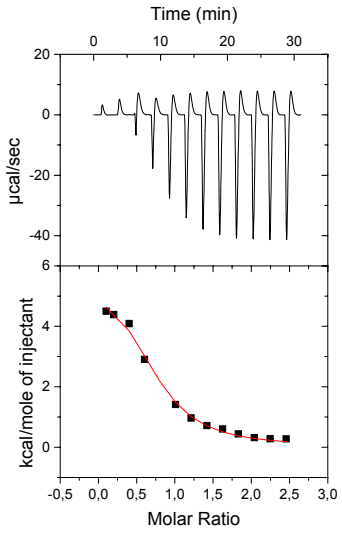
Hydrogenpyrophosphate



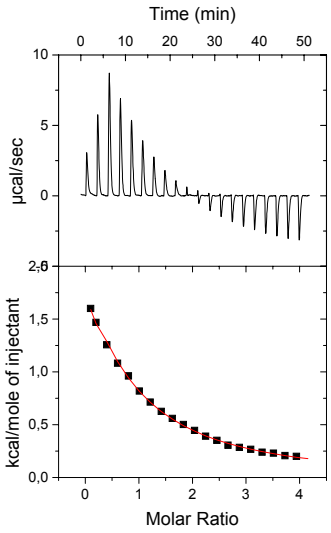


Isothermal titration calorimetry of **6** (10^{-3} M) in acetone-water (5% v/v) at 25ºC.

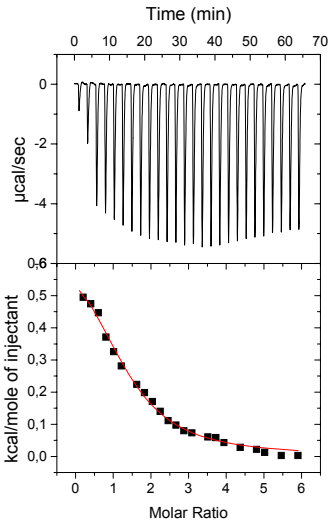
Data for the $TBA_3HP_2O_7$ titration: n= 0.69±0.03; K_a= 6028±1006; ΔH= 5902±322 cal/mole; ΔS= 37 cal/mole.
ITC results for $TBAH_2PO_4$ and $TBAPhCO_2$ showed a too weak interaction which could not be fitted accurately.
Calorimetric titrations with compound **5** also revealed very weak interactions with all the tested anions.



$TBA_3HP_2O_7$



$TBAH_2PO_4$



$TBAPhCO_2$

Computational details.

The reliably accurate description of weak interactions like hydrogen bonds and other found in supramolecular complexes generally requires a treatment of electron correlation. DFT has proved quite useful in this regard for studying supramolecular systems, offering a satisfactory compromise between electron-correlation correction and computational cost. Calculated geometries were fully optimised in the gas-phase with tight convergence criteria using the Gaussian 03 package[2] and the hybrid meta functional mPW1B95. The 6-31G** basis set was used in the optimizations for all atoms and adding diffuse functions on N and O atoms (denoted as aug6-31G**). Ultrafine grids (99 radial shells and 590 angular points per shell) were employed for numerical integrations. In order to take advantage of symmetry, and the corresponding speed up in the calculations, a C_2-symmetric form of the hydrogenpyrophosphate trianion was used and this symmetry constraint kept on the derived receptor-anion complexes. This form corresponds to a TS (transition state) between two degenerated no symmetric absolute minima. Nevertheless we assume that very similar changes (energy, WBI, ...) occur when considering the no symmetric minima and the C_2-symmetric TS. From these gas-phase optimised geometries all reported data were obtained by means of single-point (SP) calculations. Bond orders were characterised by the Wiberg's bond index (WBI) and calculated with the natural bond orbital (NBO) method as the sum of squares of the off-diagonal density matrix elements between atoms. The topological analysis of the electronic charge density was conducted by means of the Bader's AIM (Atoms-In-Molecules) methodology using the AIM2000 software.[3] Energy values were computed at the higher aug6-311G** level and considering solvent (acetone) effects by using the Cossi and Barone's CPCM (conductor-like polarizable continuum model) modification[4] of the Tomasi's PCM formalism.[5] Energy values include corrections for the basis set superposition error (BSSE) by means of the Bq-approach and thermal correction to Gibbs free energy, both of them computed at the lower (optimization) level. Complexation Gibbs free energies are computed relative to the **6**·acetone complex, *i.e.* for the reaction **6**·acetone + anion$^-$ → **6**·anion$^-$ + acetone. For both hydrogenpyrophosphate-containing monoanionic species $HP_2O_7TMA_2^-$ and **6**·$HP_2O_7TMA_2^-$ the frequency calculations - and hence the thermal correction to Gibbs free energy - were computed onto the fully optimised geometries after removing the TMA^+ counter-cations.

Strong hydrogen bonds with the anionic guests are evidenced by the high values of the corresponding Wiberg's bond index (WBI).[6] We have also used the Bader's Atoms-In-Molecules (AIM) methodology[7] to perform a topological analysis of the electronic density $\rho(r_c)$ for the non-covalent host-guest interactions. Every contact can be appropriately characterised by the $\rho(r_c)$ at its respective bond critical point (BCP). Also, the relatively large positive $\nabla^2\rho(r_c)$ values are usually diagnostic for ionic

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[2] Gaussian 03, Revision B.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

[3] AIM2000 v. 2.0, designed by F. W. Biegler-König and J. Schönbohm, 2002. Home page http://www.aim2000.de/. Biegler-König, F.; Schönbohm, J.; Bayles, D. *J. Comp. Chem.*, **2001**, *22*, 545-559. Biegler-König, F.; Schönbohm, J. *J. Comp. Chem.*, **2002**, *23*, 1489-1494.

[4] (a) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995-2001. (b) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comp. Chem.* **2003**, *24*, 669-681.

[5] (a) Miertus, S.; Scrocco, E.; Tomasi, J. *J. Chem. Phys.* **1981**, *55*, 117-129. (b) Cammi, R.; Mennucci, B.; Tomasi, J. *J. Phys. Chem. A* **2000**, *104*, 5631-5637.

[6] K. B. Wiberg, *Tetrahedron*, 1968, **24**, 1083-1096.

[7] Bader, R.F.W. Atoms in Molecules: A Quantum Theory, Oxford University Press, Oxford, 1990.

character of the bonds.[8] All three parameters WBI, $\rho(r_c)$ and $\nabla^2\rho(r_c)$ summed over all receptor-anion contacts reasonably correlate with the proposed order of binding strength (Table 2).

Table 2 Parameters related to the overall ligand-anion interaction in calculated complexes derived from receptor **6**.

	6·AcO^-	**6**·BzO^-	**6**·$H_2PO_4^-$	**6**·$HP_2O_7^{3-}$ [a]
Σ WBI	0.277	0.261	0.216	0.354
Σ ρ(r) [b]	0.133	0.128	0.120	0.193
Σ $\nabla^2\rho(r)$ [c]	0.385	0.374	0.355	0.545

[a] Calculated with two TMA^+ units[9]; [b] in $e{\cdot}a_0^{-3}$; [c] in $e{\cdot}a_0^{-5}$.

[8] Lixian Zhang, Fuming Ying, Wei Wu, Philippe C. Hiberty and Sason Shaik, *Chem. Eur. J.*, 2009, **15**, 2979-2989; Waro Nakanishi, Takashi Nakamoto, Satoko Hayashi, Takahiro Sasamori and Norihiro Tokitoh, *Chem. Eur. J.*, 2007, **13**, 255-268.

[9] In the case of hydrogenpyrophosphate trianion, the hypothetical naked species behaves as exceedengly polarizing. Therefore two explicit tetramethylammonium (TMA^+) units, as model for the experimentally used TBA^+ cations, were added in order to handle comparable overall monoanionic species.

Cartesian coordinates (Å) and energies for the computed most stable geometries of compound **6** and its complexes with acetate, benzoate, dihydrogenphosphate and hydrogenpyrophosphate anions**.**

Compound **6**: $E_{acetone}$ = -1558.466289 au
Thermal correction to G = 0.381786 au

C	0.00000000	0.00000000	0.00000000		H	2.41002156	-4.03928048	0.24708176
C	1.42697754	0.00000000	0.00000000		C	1.32769195	-5.89236398	0.05395021
C	2.17127853	1.22171202	0.00000000		H	0.56660423	-6.14207559	-0.70252294
C	1.49224554	2.43672051	0.04543165		H	2.27554275	-6.35200161	-0.25671009
C	0.06190599	2.44403463	0.02014307		C	-3.52036782	3.47444911	0.00098171
C	-0.68641003	1.22927204	-0.00515310		O	-4.50470868	2.69217952	0.02461165
O	3.55309826	1.11317102	-0.00841145		N	-3.66648009	4.83341231	-0.01247673
C	4.19479841	1.74047328	-1.13852683		H	-2.85677271	5.40238671	-0.24944790
H	4.08075486	2.83595108	-1.11485964		C	-5.00527645	5.45125605	-0.09388724
H	5.25651787	1.47229673	-1.06660238		H	-5.63038112	4.92686770	0.64646608
H	3.77754488	1.35326282	-2.08233040		H	-4.90500660	6.49620215	0.22896150
O	2.12433224	3.66989968	0.07726252		C	0.93728726	-6.40556144	1.40272193
C	2.97482231	3.87589040	1.22473037		N	-0.32098031	-6.15399326	1.91716356
H	3.84799899	3.20433998	1.20989103		C	-0.42395806	-6.68647651	3.18217726
H	3.30457540	4.92111553	1.16898715		C	0.77976059	-7.31012049	3.47973298
H	2.40965511	3.71448160	2.15710951		C	1.63942215	-7.12985778	2.36009967
N	-0.41552139	-1.30972311	-0.01140246		H	-0.99846107	-5.56560173	1.43087512
H	-1.35816633	-1.69319126	-0.02976796		H	-1.33748622	-6.58260357	3.76044182
C	0.69063575	-2.14456802	-0.02333408		H	1.01006476	-7.84095338	4.39981753
C	1.84249403	-1.36124484	-0.01904003		H	2.65757033	-7.49751757	2.25162279
H	2.87280932	-1.70711509	-0.03105080		C	-5.62297390	5.40149281	-1.45438203
N	-2.01946001	1.56252968	-0.01408452		N	-6.05954193	4.20346715	-1.98853266
H	-2.84055468	0.96106186	-0.01622929		C	-6.54441336	4.40767418	-3.26038237
C	-2.15028553	2.94203503	0.00918909		C	-6.43879879	5.76249716	-3.54271205
C	-0.87933747	3.51169452	0.03306951		C	-5.85438001	6.38866113	-2.40628574
H	-0.63368023	4.57011396	0.05991837		H	-5.92254954	3.31324738	-1.50852948
C	0.42524583	-3.59028892	-0.03414537		H	-6.92479700	3.58123410	-3.85369364
O	-0.75646312	-4.01761985	-0.08296399		H	-6.75360474	6.24614120	-4.46377925
N	1.50524814	-4.42773416	-0.00982686		H	-5.63536241	7.44719903	-2.28342204

Complex **6**·acetone: $E_{acetone}$ = -1751.601108 au
BSSE = 0.002037 au
Thermal correction to G = 0.453806 au

C	0.00000000	0.00000000	0.00000000		C	-2.17404355	2.91115008	0.00335966
C	1.42595114	0.00000000	0.00000000		C	-0.90708296	3.50046594	0.02970249
C	2.16362066	1.22751007	0.00000000		H	-0.67627570	4.56255581	0.05492223
C	1.48013730	2.44048121	0.04447086		C	0.42187237	-3.58775179	-0.01850167
C	0.04827182	2.44644858	0.01872342		O	-0.75043132	-4.04654616	-0.04564050
C	-0.69096933	1.22735100	-0.00697247		N	1.51867263	-4.40808847	-0.00479245
O	3.54804033	1.12811808	-0.00825264		H	2.41957949	-4.00043524	0.23488744
C	4.18280251	1.75452133	-1.14137776		C	1.37169942	-5.87348397	0.07228321
H	4.06671053	2.85002132	-1.11909092		H	0.59904504	-6.14383231	-0.66541646
H	5.24581811	1.48904815	-1.07493031		H	2.32065541	-6.31908523	-0.25543810
H	3.76206745	1.36571916	-2.08320249		C	-3.53989548	3.44856579	-0.01727440
O	2.11272518	3.67553631	0.07666078		O	-4.54036987	2.68399147	-0.01592149
C	2.95691424	3.88184702	1.22733768		N	-3.67238129	4.81185351	-0.01953940
H	3.83371433	3.21465883	1.21407871		H	-2.85249676	5.37308079	-0.23879742
H	3.28223715	4.92901526	1.17736664		C	-5.00000618	5.44698606	-0.11411518
H	2.38942391	3.71423525	2.15743442		H	-5.64498954	4.91914260	0.60676036
N	-0.42864968	-1.30105437	-0.00974037		H	-4.89491504	6.48606176	0.22611527
H	-1.40257321	-1.62026716	-0.02545573		C	1.01961090	-6.38565870	1.43286306
C	0.67087246	-2.14110404	-0.01997111		N	-0.21987560	-6.11995976	1.98378630
C	1.83199209	-1.36330498	-0.01749817		C	-0.29199579	-6.65113433	3.25176124
H	2.86012090	-1.71655900	-0.02777721		C	0.91205903	-7.29013279	3.51310236
N	-2.02568406	1.53555441	-0.01815922		C	1.74074484	-7.11921870	2.36845069
H	-2.80377503	0.86830671	-0.02323627		H	-0.89952206	-5.51945128	1.51472948

H	-1.18534659	-6.53391897	3.85839305	H	-5.63437225	7.49073698	-2.26364355
H	1.16352703	-7.82341495	4.42626551	O	-3.34632089	-1.07592600	-0.03909932
H	2.75137378	-7.49759387	2.23065669	C	-4.42604341	-1.68385681	-0.05191316
C	-5.59589474	5.42540840	-1.48594536	C	-4.46249668	-3.18854762	-0.16814020
N	-6.00138551	4.23351560	-2.05639072	H	-3.44562706	-3.60105864	-0.17101164
C	-6.47004539	4.46020743	-3.33078349	H	-5.04959837	-3.62116937	0.65755378
C	-6.38743331	5.82365541	-3.57685481	H	-4.98074816	-3.47355081	-1.09841801
C	-5.83233241	6.43187351	-2.41578075	C	-5.73345092	-0.93581815	0.04836531
H	-5.84878354	3.33625812	-1.59358873	H	-5.55900812	0.14745365	0.06537491
H	-6.82203275	3.64181246	-3.95219463	H	-6.39280094	-1.20500300	-0.79212120
H	-6.69653433	6.32448768	-4.49070193	H	-6.26254608	-1.24051673	0.96621350

Complex **6**·AcO^-:

$E_{acetone}$ = -1787.125212 au
BSSE = 0.003676 au
Thermal correction to G = 0.420168 au

C	0.00000000	0.00000000	0.00000000	C	-3.54508318	3.50535238	-0.01719663
C	1.42609060	0.00000000	0.00000000	O	-3.65415845	4.76232852	-0.04373342
C	2.13661230	1.24233590	0.00000000	N	-4.64919804	2.69500571	-0.00606798
C	1.44006434	2.44828800	0.01995041	H	-4.57000185	1.67412864	0.05413702
C	0.00896230	2.45384618	0.00661477	C	-5.99745545	3.26859555	-0.11384367
C	-0.70375692	1.21874098	-0.00675397	H	-5.97209309	4.01692352	-0.92565666
O	3.53234953	1.21341087	0.01735363	H	-6.67234054	2.45718472	-0.41825504
C	4.11120385	1.61140878	-1.23714464	C	-0.58247067	-6.36541869	-1.18993629
H	3.82574222	2.64440184	-1.49538739	N	0.69838918	-6.39797405	-1.70147975
H	5.20104262	1.54691141	-1.10900700	C	0.71836263	-7.12143077	-2.87176655
H	3.79773560	0.92834452	-2.04584573	C	-0.56885971	-7.58965671	-3.10294728
O	2.11265972	3.67173163	0.01541939	C	-1.39059920	-7.10950057	-2.04284925
C	2.73517227	3.96739147	1.27728069	H	1.43931419	-5.82752591	-1.27836885
H	3.48487210	3.20247868	1.53825426	H	1.63552468	-7.23743397	-3.44258038
H	3.22509297	4.94427087	1.15890813	H	-0.88056532	-8.20606774	-3.94317749
H	1.97950420	4.03288920	2.07947776	H	-2.45631256	-7.28315746	-1.90916170
N	-0.44697615	-1.29327554	-0.00203539	C	-6.51720531	3.89263802	1.14698474
H	-1.46100184	-1.57034267	0.00691524	N	-5.90907913	5.01562606	1.66897290
C	0.65760984	-2.13717506	-0.00527457	C	-6.53484295	5.38872877	2.83626462
C	1.82285219	-1.36698091	-0.00609308	C	-7.58567084	4.50688957	3.05474398
H	2.83110854	-1.76941284	-0.00216595	C	-7.57231057	3.56049867	1.98996583
N	-2.04735370	1.47810245	-0.01572620	H	-5.04119214	5.37409238	1.25468427
H	-2.79349776	0.73830353	-0.03675737	H	-6.18131536	6.23817331	3.41413443
C	-2.22618542	2.85669300	-0.00675749	H	-8.28195518	4.54090194	3.88969162
C	-0.97669424	3.48074568	0.00908652	H	-8.25435873	2.72499148	1.84678378
H	-0.82125915	4.55516396	0.01255787	C	-4.10436537	-1.55942724	-0.02531898
C	0.55941935	-3.60377367	-0.00319740	O	-3.02858148	-2.24838544	0.00126774
O	1.59301891	-4.32720625	0.02856838	O	-4.16581747	-0.28429215	-0.05003729
N	-0.69448787	-4.15399778	-0.02791513	C	-5.42069023	-2.33873453	-0.01118629
H	-1.53845795	-3.57420872	-0.09172316	H	-5.40096623	-3.12194390	-0.78258660
C	-0.87349642	-5.60875273	0.07183233	H	-5.53029993	-2.84404011	0.96065165
H	-0.21996663	-5.96507491	0.88771315	H	-6.28069129	-1.67662728	-0.17002053
H	-1.91637234	-5.78821943	0.36634508				

Complex **6**·BzO^-:

$E_{acetone}$ = -1978.852523 au
BSSE = 0.003754 au
Thermal correction to G = 0.467564 au

C	0.00000000	0.00000000	0.00000000	H	3.79745121	0.94712051	-2.05071320
C	1.42601154	0.00000000	0.00000000	O	2.11225983	3.67192895	0.01621394
C	2.13755746	1.24173054	0.00000000	C	2.74735940	3.96292116	1.27321879
C	1.44143485	2.44794235	0.02035609	H	3.50154426	3.19871336	1.52281042
C	0.01034379	2.45332644	0.00845087	H	3.23328749	4.94162653	1.15419010
C	-0.70322244	1.21874521	-0.00343735	H	1.99987688	4.02257864	2.08339512
O	3.53287554	1.20995181	0.01562235	N	-0.44598810	-1.29405943	-0.00581782
C	4.11308311	1.62021729	-1.23462984	H	-1.45673345	-1.57091513	-0.02496865
H	3.83093353	2.65679935	-1.48159868	C	0.65926296	-2.13775690	-0.01320126
H	5.20256806	1.55055827	-1.10684761	C	1.82340360	-1.36674602	-0.01018249

H	2.83193394	-1.76840506	-0.00582887
N	-2.04678288	1.48019761	-0.00756288
H	-2.79240257	0.74359388	0.00182898
C	-2.22422254	2.85926172	0.00497580
C	-0.97416050	3.48129640	0.01537116
H	-0.81720227	4.55546677	0.01749340
C	0.56256392	-3.60442778	-0.01486788
O	1.59569484	-4.32766785	0.01553037
N	-0.69164056	-4.15459982	-0.03952093
H	-1.53268437	-3.57390936	-0.11846357
C	-0.87129601	-5.61008588	0.04957765
H	-0.21511754	-5.97153640	0.86082448
H	-1.91303316	-5.79216478	0.34764433
C	-3.54240635	3.50951553	-0.00121915
O	-3.65133247	4.76604115	-0.02648220
N	-4.64652302	2.69888683	0.01033026
H	-4.56529605	1.67976612	0.08505110
C	-5.99577761	3.27215974	-0.08726347
H	-5.97359612	4.02503817	-0.89474110
H	-6.67220703	2.46282051	-0.39487687
C	-0.58481395	-6.35659254	-1.21896414
N	0.69511032	-6.38794595	-1.73310175
C	0.71054714	-7.10008922	-2.91049389
C	-0.57847966	-7.56198412	-3.14380897
C	-1.39675504	-7.08969683	-2.07759267
H	1.43931789	-5.82465520	-1.30686295
H	1.62631871	-7.21378214	-3.48396202
H	-0.89378777	-8.16896607	-3.98946713
H	-2.46282673	-7.26148976	-1.94402111
C	-6.50929372	3.88766299	1.18001684
N	-5.90025922	5.00898521	1.70465016
C	-6.51889420	5.37307050	2.87869071
C	-7.56574862	4.48711297	3.09902684
C	-7.55743258	3.54746215	2.02831013
H	-5.03663591	5.37344659	1.28734501
H	-6.16385991	6.22004505	3.45921988
H	-8.25607621	4.51382204	3.93909734
H	-8.23850502	2.71111630	1.88503084
C	-4.11476628	-1.56204675	-0.02262805
O	-3.04203269	-2.25122405	-0.10013802
O	-4.17528496	-0.28880023	0.06050612
C	-5.42897002	-2.32036986	-0.02993022
C	-5.44693625	-3.71126320	-0.22768196
C	-6.65818479	-4.41109136	-0.23771135
C	-7.86614011	-3.72666809	-0.04347197
C	-7.85585208	-2.33929287	0.15753638
C	-6.64378615	-1.64081778	0.16097176
H	-4.49379760	-4.22308916	-0.37705979
H	-6.66203604	-5.49285606	-0.39700812
H	-8.81326988	-4.27318183	-0.04873455
H	-8.79565392	-1.80203579	0.31158989
H	-6.61120508	-0.56021088	0.31582658

Complex **6**·$H_2PO_4^-$: $E_{acetone}$ = -2202.337262 au
BSSE = 0.005044 au
Thermal correction to G = 0.407939 au

C	0.00000000	0.00000000	0.00000000
C	1.42707104	0.00000000	0.00000000
C	2.14553963	1.23630479	0.00000000
C	1.45457096	2.44448095	0.02590754
C	0.02485907	2.45269962	0.00347993
C	-0.69899882	1.22304226	-0.01897638
O	3.53990693	1.19497053	0.01789002
C	4.12636699	1.61749300	-1.22569333
H	3.85152050	2.65882720	-1.46046864
H	5.21486039	1.53900294	-1.09543419
H	3.80866937	0.95657703	-2.05076798
O	2.12650565	3.66709248	0.02959030
C	2.76848162	3.94685049	1.28599887
H	3.52265730	3.17954240	1.52577851
H	3.25501927	4.92576479	1.17218350
H	2.02486324	4.00102628	2.09999308
N	-0.43639528	-1.30069899	0.00497711
H	-1.42468360	-1.60090371	0.10557413
C	0.67236033	-2.14084176	0.01285735
C	1.83053243	-1.36494029	0.00236965
H	2.84110295	-1.76109153	0.00176861
N	-2.04104168	1.50703190	-0.04252090
H	-2.79942732	0.80868642	-0.16135368
C	-2.20244169	2.88876523	-0.04051047
C	-0.94657607	3.49293690	-0.00481954
H	-0.77534027	4.56471104	0.00811990
C	0.58662785	-3.60996290	0.01833942
O	1.62974162	-4.31853970	0.05411854
N	-0.65975307	-4.17154918	-0.01573725
H	-1.51149225	-3.59748264	-0.04033167
C	-0.82542427	-5.62835276	0.09088000
H	-0.17844663	-5.97531334	0.91627290
H	-1.87030381	-5.81468231	0.37304977
C	-3.51173226	3.56037031	-0.06055698
O	-3.59262317	4.81903708	-0.08629022
N	-4.62837365	2.77104827	-0.05115093
H	-4.56613798	1.74563310	-0.03479915
C	-5.96600672	3.36843285	-0.17346310
H	-5.92381365	4.10938314	-0.99166087
H	-6.65211785	2.56517815	-0.47370491
C	-0.51410792	-6.38844993	-1.16356605
N	0.77432399	-6.42306590	-1.65625228
C	0.81083446	-7.15061112	-2.82365800
C	-0.47292751	-7.61999312	-3.07111439
C	-1.30981720	-7.13590587	-2.02495619
H	1.50784324	-5.84639466	-1.22978527
H	1.73591435	-7.26790976	-3.38130596
H	-0.77279838	-8.23947955	-3.91335274
H	-2.37765819	-7.30717587	-1.90683040
C	-6.48278584	4.01106970	1.07883785
N	-5.86683059	5.13439840	1.59140643
C	-6.49358184	5.52451083	2.75264987
C	-7.55309267	4.65427505	2.97564182
C	-7.54400755	3.69694297	1.92084111
H	-4.99115687	5.47768130	1.18173985
H	-6.13419783	6.37612035	3.32370799
H	-8.25224042	4.70263587	3.80745014
H	-8.23137058	2.86478626	1.78439049
O	-3.01346627	-2.38426605	0.34539040
O	-4.27653301	-0.16067869	-0.43317870
P	-4.28907807	-1.64068341	-0.05061851
O	-4.97574679	-2.48353333	-1.30308589
H	-5.48836860	-1.85191072	-1.84215663
O	-5.38334243	-1.81596916	1.18325542
H	-5.10759686	-2.58301075	1.71985310

Complex **6**·$HP_2O_7TMA_2^-$ (C_2): $E_{acetone}$ = -3197.595742 au
BSSE = 0.017226 au
Thermal correction to G = 0.404863 au

C	0.00000000	0.00000000	0.00000000	C	-8.09159123	0.59202290	-0.29030220
C	1.43087866	0.00000000	0.00000000	C	-8.74015576	1.50160555	-1.11537802
C	2.15759700	1.22992859	0.00000000	C	-8.02883637	2.73269011	-1.02400964
C	1.47318798	2.44236492	0.02902352	H	-6.29848600	0.78302517	0.87468762
C	0.04477554	2.45615110	0.01194407	H	-8.25726756	-0.46633269	-0.11097261
C	-0.69481285	1.23135443	-0.00525692	H	-9.61394753	1.29541556	-1.72968554
O	3.55288929	1.18018731	0.02382896	H	-8.25363805	3.66309340	-1.54239704
C	4.14971417	1.59546488	-1.21459896	O	-3.28198775	-1.04030990	-0.02588507
H	3.88186891	2.63718472	-1.45675235	P	-3.70638170	-1.80484328	-1.50688058
H	5.23700738	1.51177817	-1.07868632	O	-2.62770411	-2.91864204	-1.67349266
H	3.83708449	0.93138306	-2.04092835	O	-5.14162081	-2.37964547	-1.22759565
O	2.15209174	3.66257706	0.02163260	O	-3.59981944	-0.69966872	-2.56935535
C	2.80115667	3.95035632	1.26993422	P	-4.17357234	-1.01838449	1.44468130
H	3.55148896	3.18090439	1.51591133	O	-4.57141565	0.47960973	1.61668900
H	3.29315370	4.92523805	1.14653748	O	-5.40407361	-1.94786220	1.14427033
H	2.06119443	4.02045950	2.08792180	O	-3.18526301	-1.50572195	2.51583295
N	-0.42659535	-1.30686769	0.03633279	H	-5.37541207	-2.22163128	-0.04247549
H	-1.42551721	-1.56782656	0.08162672	N	-0.75975411	-0.26915114	-4.22046697
C	0.68377656	-2.14569551	0.04490179	C	-1.93126205	-0.72685617	-5.05806874
C	1.83675841	-1.36745846	0.02426387	H	-1.62337073	-1.61835260	-5.62024998
H	2.84710417	-1.76426697	0.03731414	H	-2.20078505	0.08746442	-5.74411887
N	-2.03351980	1.54206031	-0.05557976	H	-2.75780365	-0.94454930	-4.35319189
H	-2.77266945	0.82222372	-0.11464794	C	-1.19396245	0.91503063	-3.38473380
C	-2.17750682	2.92622006	-0.05649014	H	-0.35002395	1.22673865	-2.75667896
C	-0.91565340	3.51067691	-0.01671461	H	-2.05700938	0.58048661	-2.78183516
H	-0.73293020	4.58073540	-0.02030979	H	-1.48827125	1.72322572	-4.06776024
C	0.63330653	-3.63491128	0.03817274	C	-0.34216007	-1.40391693	-3.31141493
O	1.66007995	-4.29830607	0.31546427	H	0.02627551	-2.22269320	-3.94454172
N	-0.56734070	-4.17956732	-0.29271846	H	-1.22019866	-1.74586294	-2.73349168
H	-1.32230351	-3.58827284	-0.69946064	H	0.45594976	-1.04553754	-2.64681229
C	-0.76107123	-5.62982789	-0.38854425	C	0.38932756	0.12384994	-5.09607575
H	-0.57330181	-5.94465603	-1.43566952	H	1.22727643	0.43498360	-4.45910472
H	0.01127215	-6.10749127	0.22997098	H	0.07874999	0.95625402	-5.74071772
C	-3.47840631	3.65285669	-0.06047071	H	0.68281800	-0.73889553	-5.70823019
O	-3.51220677	4.87658710	-0.32989292	N	-1.36863444	0.69153740	4.20384894
N	-4.56918315	2.90445989	0.25226091	C	-0.56938995	-0.28665411	3.37100869
H	-4.45816226	1.94978835	0.65389984	H	0.14118688	0.27885238	2.75527341
C	-5.91185707	3.48772592	0.33591067	H	-1.29459290	-0.84836106	2.75552314
H	-6.09687624	3.80410603	1.38305773	H	-0.03792730	-0.96102306	4.05591458
H	-5.91408316	4.39996725	-0.27650137	C	-2.37601324	-0.08030549	5.02418300
C	-2.12485409	-6.05040902	0.06814923	H	-2.98672827	0.64030723	5.58396435
N	-3.26923826	-5.43212837	-0.39428167	H	-1.82653246	-0.73664563	5.71245179
C	-4.37390376	-6.00287590	0.19176242	H	-2.98110006	-0.67048167	4.30796046
C	-3.94047016	-7.03385715	1.01513333	C	-2.11319308	1.64179674	3.29220570
C	-2.51792923	-7.06080225	0.94067583	H	-1.38591515	2.14419516	2.63969179
H	-3.26959088	-4.55886231	-0.95026531	H	-2.63122037	2.37615827	3.92414697
H	-5.36330844	-5.59633366	0.00327880	H	-2.85278104	1.07091451	2.70146274
H	-4.57599138	-7.67937395	1.61747952	C	-0.44882721	1.46601234	5.09585371
H	-1.84395358	-7.73773623	1.46262294	H	0.25826926	2.02674929	4.47112719
C	-6.97128217	2.54088844	-0.13998678	H	0.09541021	0.76546275	5.74234743
N	-7.03911420	1.23855299	0.31283729	H	-1.04297635	2.15909582	5.70562542