Electronic Supplementary Material (ESI) for Chemical Communications

Discovery of anion-π interactions in the recognition mechanism of inorganic anions by 1,2,3-triazolium rings

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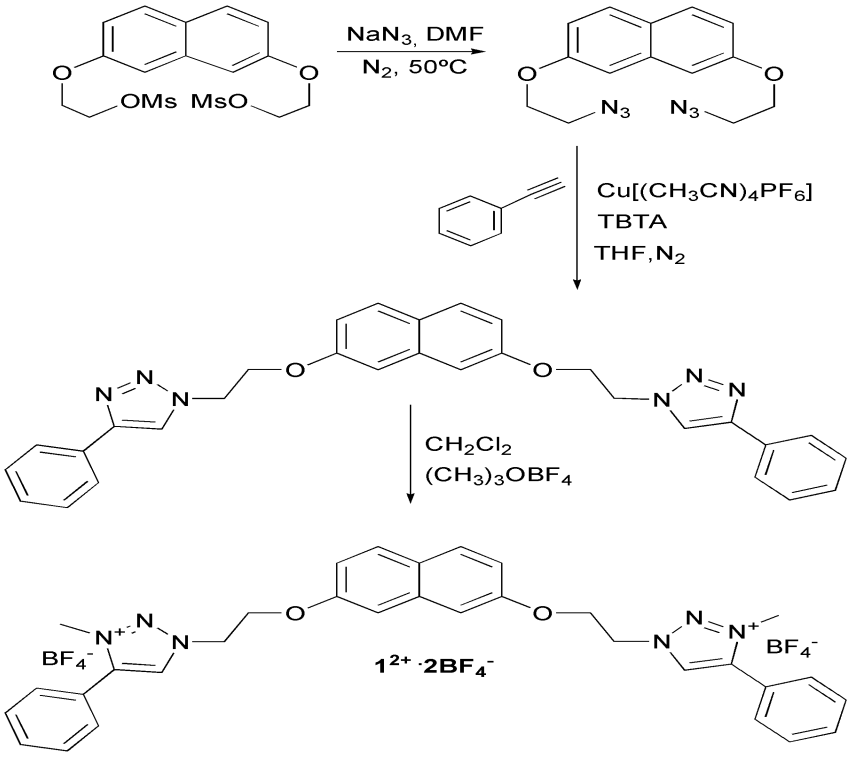
Contents

PART I: Synthesis

Experimental

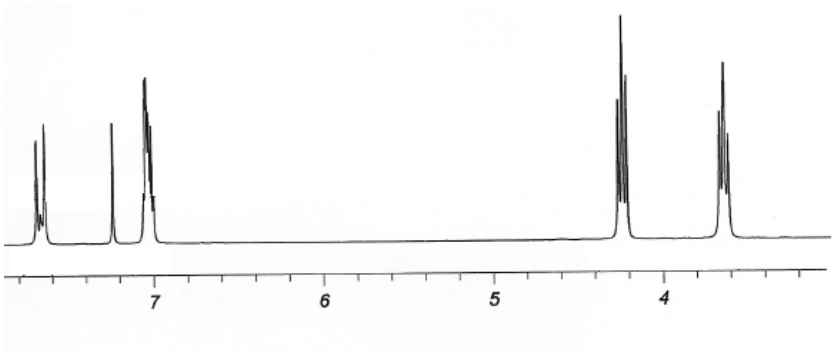
All reactions were carried out under N_2 and using solvents which were dried according to routine procedures. Column chromatography was performed with the use of a column of dimensions 60 cm 4.5 cm and of silica gel (60 A C.C. 70-200 μm, sds) as the stationary phase. NMR spectra were recorded at 200, 300, and 400 MHz. The following abbreviations for stating the multiplicity of the signals in the NMR spectra were used: s (singlet), d (doublet), dd (double doublet), t (triplet), m (multiplet). The ESI mass spectra were recorded on an AGILENT V spectrometer. Elemental analyses were carried out on a Carlo-Erba EA-1108 analyzer.



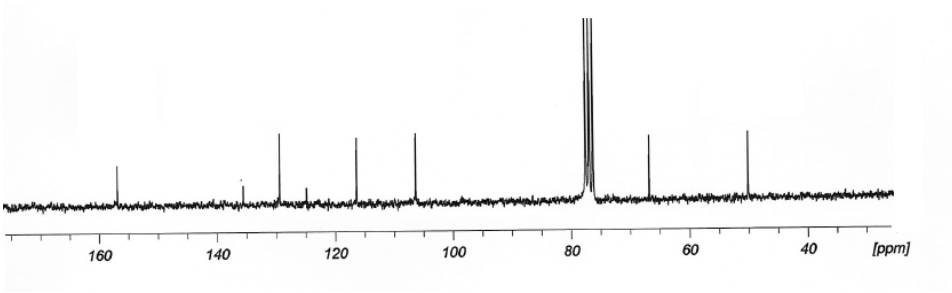
2,7-Bis(2´-azidoethoxy)naphthalene. Sodium azide (1.6 g, 24.7 mmol) was added to a solution of 2,7-bis(2´-hydroxyethoxy)naphthalene bis(methanesulfonate)ester (1g, 2.47 mmol) in 5 ml of anhydrous DMF and the suspension was heated at 50ºC for 18h. The reaction was cooled to room temperature and then added over cold water. The solid formed was filtered out and recrystallized from pentane giving a colorless solid (87%). ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.65 (4H, t, J = 5 Hz), 4.25 (4H, t, J = 5 Hz), 7.01-7.07 (4H, m), 7.69 (2H, d, J = 9 Hz); ^{13}C NMR ($CDCl_3$, 50

MHz) δ 156.7, 135.7, 129.6, 124.9, 116.6, 106.6, 67.1, 50.3; **MS (ESI)**: *m/z* calc. for $C_{14}H_{14}N_6O_2$ $[M+1]^+$ 298.3, found 299.3

^{1}H-NMR

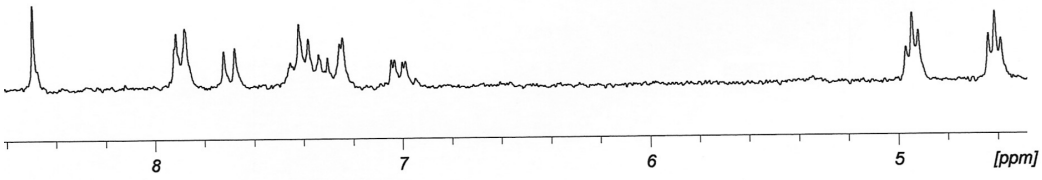


^{13}C-NMR

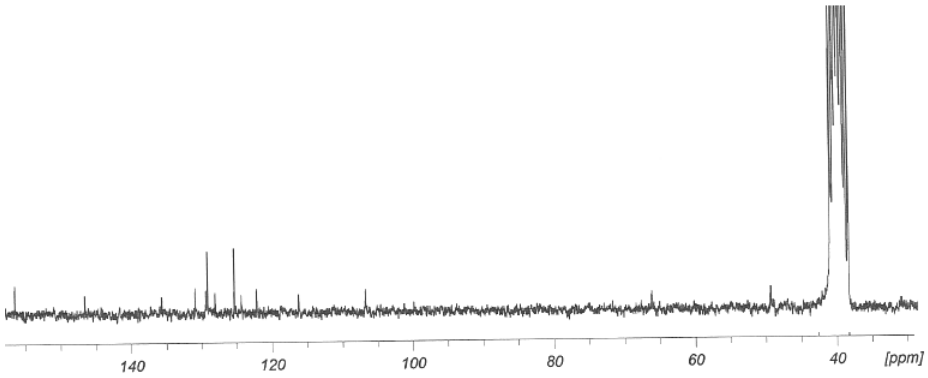


1-(2-(2-(2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethoxy)naphthalen-7-yloxy)ethyl)-4-phenyl-1H-1,2,3-triazole. Tetrakisacetonitrilecopper (I) hexafluorophosphate (0.15 g 0.4 mmol) and TBTA (0.21 g, 0.4 mmol) were added to a solution of 2,7-bis(2´-azidoethoxy)naphthalene (0.30 g, 1.0 mmol) and 1-ethynylbenzene (0.4 ml, 3.6 mmol) in dry THF (40 mL). *N*,*N*-Diisopropylethylamine (0.2 ml, 1.15 mmol) was added and the reaction left to stir in the dark for 48 h at r.t. The mixture was quenched with 10 % ammonium hydroxide solution (5 mL), volatile components removed in vacuo and the precipitated solid was filtered and washed with MeOH (3x50 ml) to give a yellow solid (90%). ^{1}H-NMR (acetone-d^6, 200 MHz) δ 4.60 (4H, t, *J* = 5 Hz), 4.94 (4H, t, *J* = 5 Hz), 7.01 (2H, dd, *J* = 9Hz, *J* = 3Hz), 7.24 (2H, d, *J*= 6 Hz), 7.30-7.45 (6H, m), 7.69 (2H, *J*= 8 Hz), 7.89 (4H, dd, *J*= 6 Hz, *J*= 8 Hz), 8.49 (2H); ^{13}C NMR (acetone-d^6, 50 MHz) δ 156.7, 146.7, 135.8, 131.1, 129.6, 129.3, 128.2, 125.5, 124.6, 122.4, 116.4, 106.4, 106.9, 66.46, 49.65. MS (ESI): *m/z* calc. for $C_{30}H_{26}N_6O_2$ $[M+1]^+$ 502.5, found 503.5

^{1}H-NMR

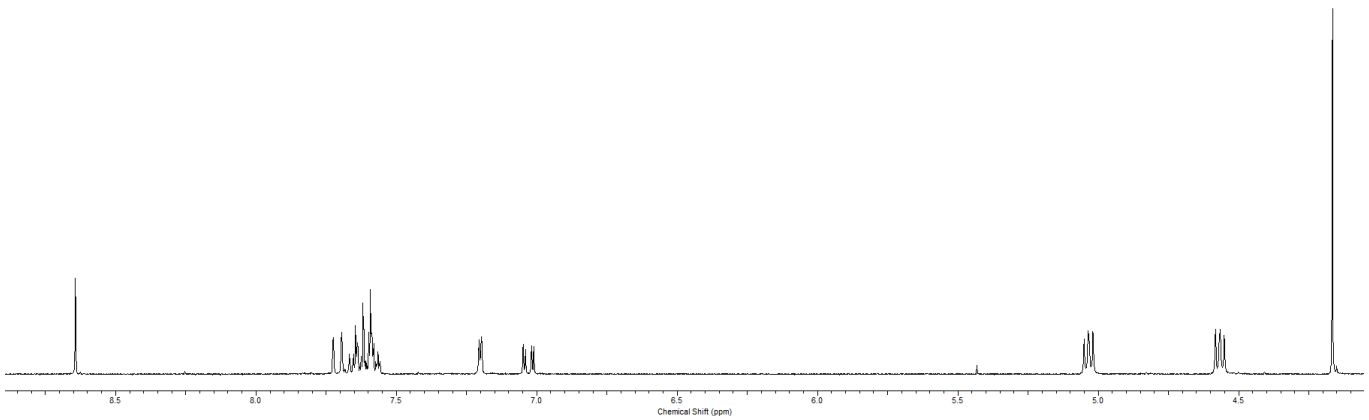


^{13}C-NMR

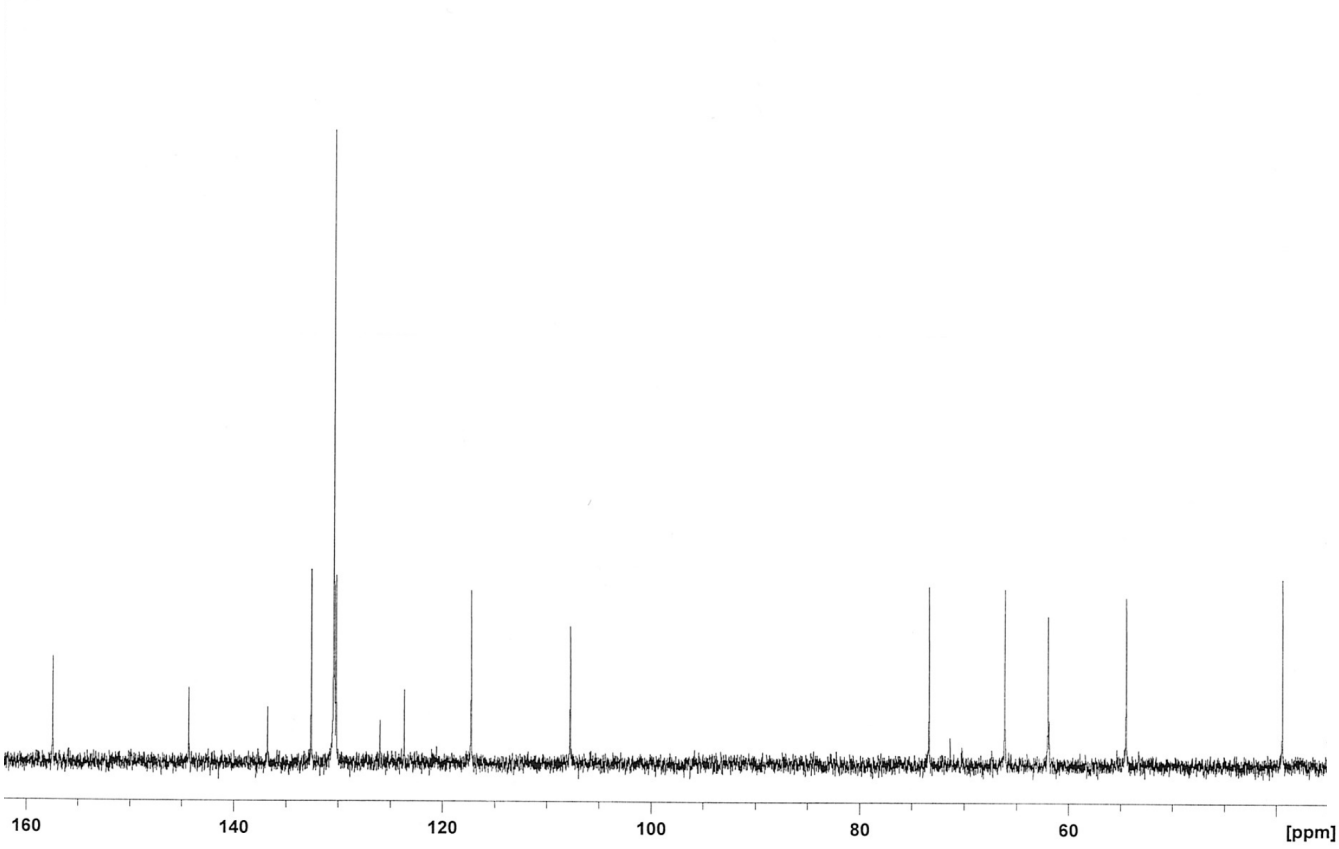


Receptor $\mathbf{1}^{2+}\cdot\mathbf{2BF_4^-}$. A suspension of bis-triazole (0.4 g, 0.79 mmol) in dry dichloromethane (20 mL) was treated with trimethyloxonium tetrafluoroborate (0.236 g, 1.59 mmol) and the reaction mixture left to stir under N_2 for 48 h at r.t. Methanol (2 mL) was added and all volatile components were removed in vacuo. The resulting residue was purified by silica gel column chromatography using $CHCl_3/CH_2OH$ 9:1 to give a white solid (40%). ^{1}H-NMR (CD_3CN/CD_3OD 9:1, 300 MHz) δ 4.17 (s,6H), 4.57 (4H, t, J = 5 Hz), 5.03 (4H, t, J = 5 Hz), 7.02 (2H, dd, J = 9Hz, J = 3Hz), 7.20 (2H, d, J= 6 Hz), 7.30-7.45 (10H, m), 7.71 (2H, J= 8 Hz), 8.65 (2H); ^{13}C NMR 38.4, 53.3, 65.0, 106.6, 116.2, 122.3, 124.9, 129.1, 129.3, 129.4, 131.7, 135.6, 143.3, 156.4 (CD_3OD, 75 MHz); MS (ESI): *m/z* calc. for $C_{32}H_{32}\ BF_4N_6O_2$ $[M^{2+}+BF_4^-]^+$ 619.26, found 619.26.

^{1}H-NMR



^{13}C-NMR



PART II: 31P NMR Anion Binding Studies

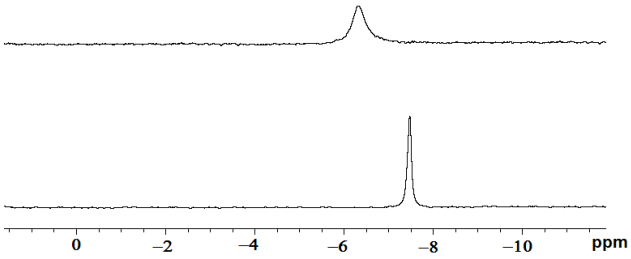


Figure SI1: ^{31}P NMR spectral changes observed in the free $HP_2O_7^{3-}$ (top) in CD_3CN/CD_3OD (9:1, v/v) after the addition of 1 equiv of the receptor $\mathbf{1}^{2+}\cdot 2BF_4^-$ in the same solvent (bottom).

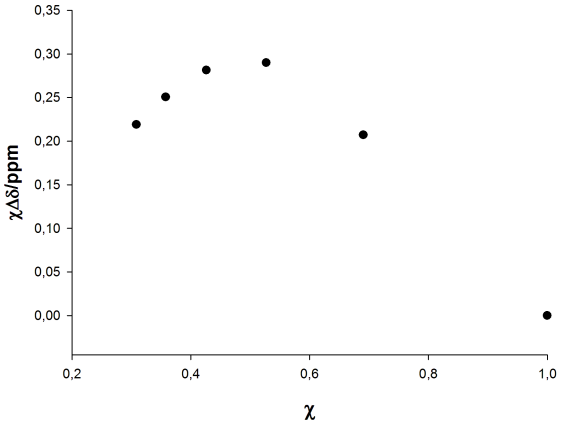


Figure SI2: Job Plot experiment indicating 1:1 stoichiometry for the receptor $\mathbf{1^{2+}\cdot 2BF_4^-}$ and $HP_2O_7^{3-}$.

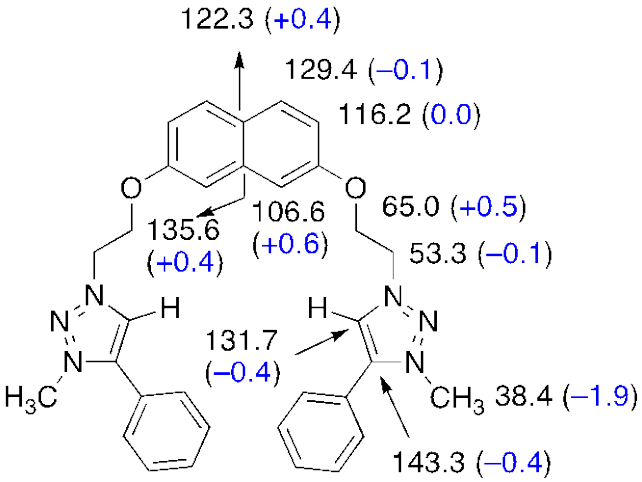


Figure SI3: Changes observed in the ^{13}C (CD_3CN/CD_3OD (9:1, v/v) in ppm of the receptor $\mathbf{1^{2+}\cdot 2BF_4^-}$ (number in black) after addition of $HP_2O_7^{3-}$ anions ($\Delta\delta$ values in blue).

Computational details

The geometry of the molecules has been fully optimized with the B97D functional of Grimme[1] and the 6-31+G(d) basis set.[2] Frequency calculations have been carried out at the same computational level to verify that the structures obtained correspond to energetic minima (0 imaginary frequencies). Solvent (CH_3CN) effects have been simulated by means of the PCM program.[3] All the calculations have been carried out with the Gaussian-09 package.[4]

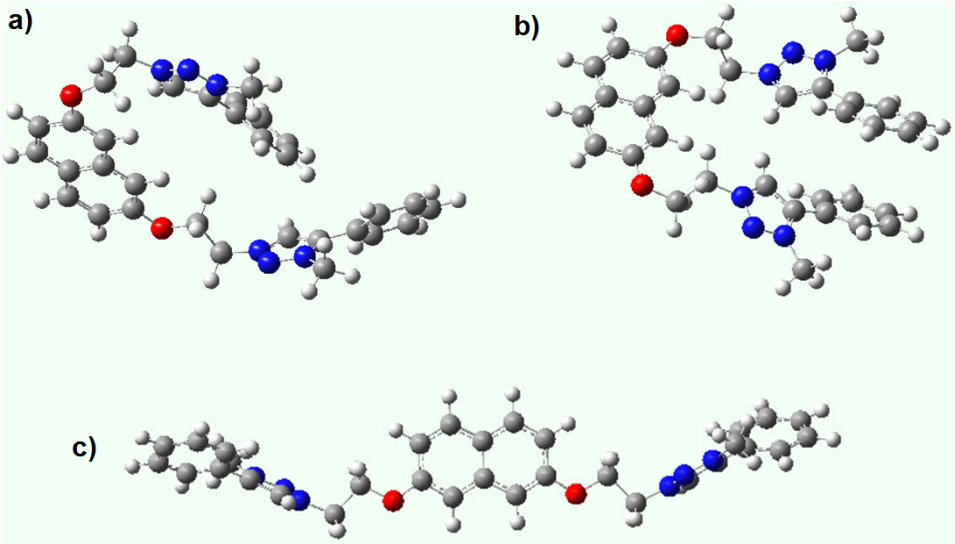


Figure SI4: The geometries of receptor $\mathbf{1}^{2+}$. a) Top left, folded minima; b) top right, folded C_2; c) bottom, extended conformation also of C_2 symmetry.

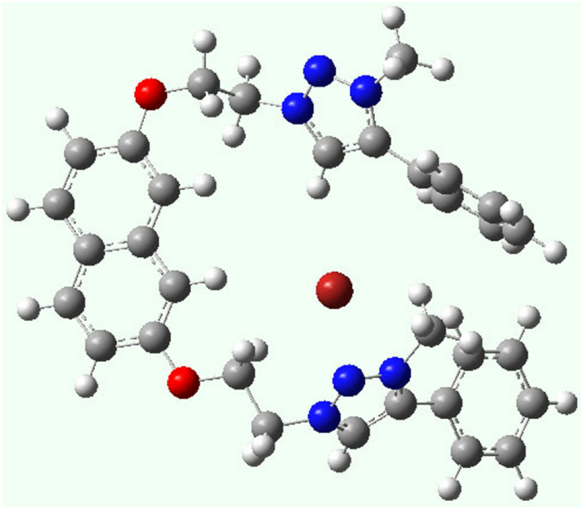


Figure SI5: The structure of the $\mathbf{1}^{2+}\cdot\mathbf{Br}^-$ complex.

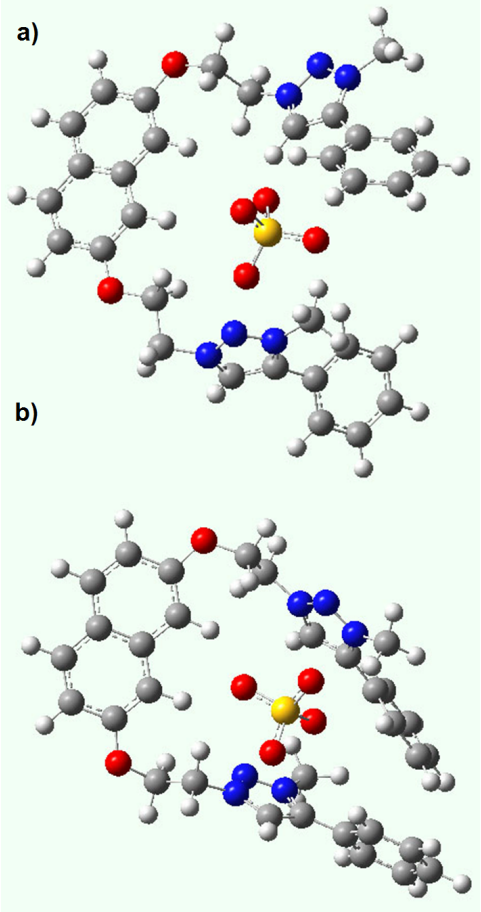


Figure SI6: The structure of the $\mathbf{1}^{2+}\cdot\mathbf{SO_4}^{2-}$ minima. a) left, H/π structure; b) right, π/π structure.

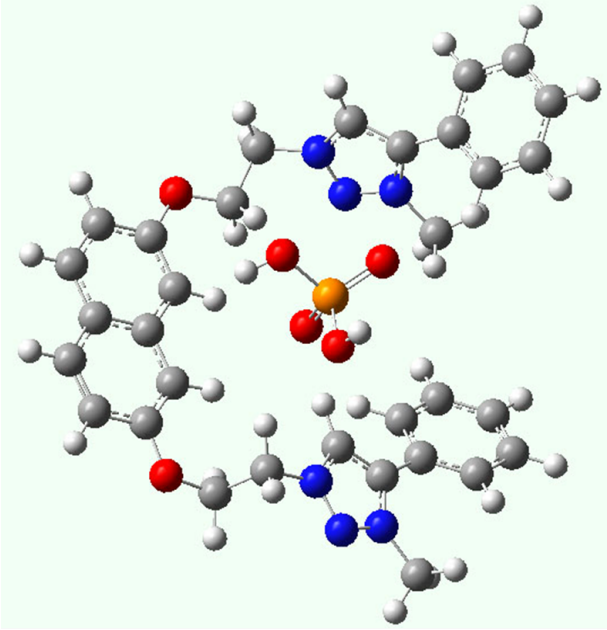


Figure SI7: Structure of $\mathbf{1}^{2+}\cdot\mathbf{PO_4H_2}^{2-}$.

Geometry and energy of the systems calculated at the PCM(CH_3CN)//B97D/6-31+G(d) computational level

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C,-0.2930427157,-5.9025709878,-1.6677781421
H,-1.1889989002,-5.740574528,-2.2778953974
H,0.5969049773,-5.9013935902,-2.3070668163
C,0.2930427157,5.9025709878,-1.6677781421
H,1.1889989002,5.740574528,-2.2778953974
H,-0.5969049773,5.9013935902,-2.3070668163
C,0.6006064919,-8.1308364879,-0.8161193316
C,-0.6006064919,8.1308364879,-0.8161193316
N,-1.3291576588,-8.8563916032,-0.1024758866
N,1.3291576588,8.8563916032,-0.1024758866
N,-1.579517049,-7.668511538,-0.6380230568
N,1.579517049,7.668511538,-0.6380230568
H,-1.6282065997,7.9553434669,-1.1095524381
H,1.6282065997,-7.9553434669,-1.1095524381
C,-0.5932333536,10.4549800003,0.3233112488
C,0.0527798137,11.7017732871,0.1652359771
C,-1.858289904,10.3936109681,0.9525203095
C,-0.5576590124,12.8701321784,0.6438976021
H,1.0102620255,11.7654794482,-0.3508125533
C,-2.4622010497,11.5666179166,1.4257105896
H,-2.3526603723,9.4296683521,1.0826685312
C,-1.8123714854,12.8055670752,1.2756751028
H,-0.0561338902,13.8304289714,0.5148809836
H,-3.435209195,11.5122195484,1.9164677061
H,-2.283551559,13.717265303,1.6470340339
C,0.5932333536,-10.4549800003,0.3233112488
C,-0.0527798137,-11.7017732871,0.1652359771
C,1.858289904,-10.3936109681,0.9525203095
C,0.5576590124,-12.8701321784,0.6438976021
H,-1.0102620255,-11.7654794482,-0.3508125533
C,2.4622010497,-11.5666179166,1.4257105896
H,2.3526603723,-9.4296683521,1.0826685312
C,1.8123714854,-12.8055670752,1.2756751028
H,0.0561338902,-13.8304289714,0.5148809836
H,3.435209195,-11.5122195484,1.9164677061
H,2.283551559,-13.717265303,1.6470340339

N,-0.3991937655,-7.2441107632,-1.0671788192
N,0.3991937655,7.2441107632,-1.0671788192
C,-0.0005254464,9.2126976126,-0.1821762847
C,0.0005254464,-9.2126976126,-0.1821762847
C,2.4437228726,9.605322454,0.5021493937
H,2.8889791281,10.2668570515,-0.2511623091
H,2.041834424,10.1899276405,1.3363038127
H,3.1809356935,8.8774933867,0.8565647888
C,-2.4437228726,-9.605322454,0.5021493937
H,-2.8889791281,-10.2668570515,-0.2511623091
H,-2.041834424,-10.1899276405,1.3363038127
H,-3.1809356935,-8.8774933867,0.8565647888

1^{2+}**.Br**$^{-}$, Total Energy= -4289.32330766 Hartree, NIMAG= 0
C,5.409119518,0.6170452883,0.5492820455
C,4.275288782,0.0143315177,0.0177806278
C,4.1623043803,-1.4060418337,-0.0007390413
C,5.2369758681,-2.2175335832,0.5074851855
C,6.3911695982,-1.5602222471,1.0320619791
C,6.4790958907,-0.1767971256,1.0629908394
H,2.1826097011,-1.3775497045,-0.8560111161
H,3.4446205934,0.5910310369,-0.3848588175
C,2.9809164769,-2.0244196004,-0.4976509237
C,5.086483996,-3.6379202193,0.4759435268
H,7.2138338379,-2.1648043093,1.4211583227
H,7.3575763327,0.3248449627,1.4715152261
C,3.9281538864,-4.2284271285,-0.0064011543
C,2.8585634416,-3.4105417095,-0.4814942463
H,5.8989149557,-4.2642298625,0.8519294403
H,3.8079196361,-5.312873039,-0.0148735868
O,5.6047197444,1.9838854228,0.6314728684
O,1.7266559695,-4.0825601508,-0.8957330364
C,4.5721132874,2.8398051636,0.1283138276
H,4.2323177698,2.5047051761,-0.8648309311
H,5.0364941722,3.826676901,0.028994989
C,0.6095456258,-3.2376248725,-1.2026608313
H,0.8301894585,-2.6234178216,-2.0897086454
H,0.3970113485,-2.5662492783,-0.3538494736
C,-0.6227353288,-4.1198872984,-1.4686848622
H,-0.6538295076,-4.519669351,-2.4893524817
H,-0.6922153058,-4.939535186,-0.7447900282
C,3.3845558819,2.8960507481,1.1279370035
H,3.1856899742,1.9091715365,1.5581157018
H,3.5813813157,3.6097194427,1.9371839414
C,-2.7373331102,-3.3593594118,-0.2722865964
C,0.9384304811,2.6683583276,0.4341597725
N,-2.891980619,-1.4704957513,-1.3488960607
N,0.890315465,4.5338554332,-0.703576716
N,-1.8820366729,-2.112796737,-1.9169979617
N,2.1284878819,4.4445132542,-0.2359749504
H,0.7446816262,1.7091128494,0.9131585275
H,-2.7960264418,-4.2092650381,0.3958822775

C,-1.3289314295,3.3310986453,-0.6438042877
C,-1.8155433319,3.5400139081,-1.9526069988
C,-2.2247912561,2.9949740033,0.3960659095
C,-3.1902914671,3.4358556464,-2.2130528615
H,-1.1234779706,3.766271438,-2.7641661972
C,-3.5978208933,2.9079544544,0.1293928033
H,-1.8439466231,2.8186214335,1.4018633564
C,-4.0836673923,3.1304775718,-1.1713217305
H,-3.5605610812,3.5911341158,-3.2275608726
H,-4.2887012647,2.6671838275,0.9376816991
H,-5.153591199,3.0559339885,-1.3734913762
C,-4.5654241248,-1.7156540605,0.5319860726
C,-5.6093230391,-2.6102513492,0.8564581999
C,-4.5759566975,-0.4006401812,1.0450576225
C,-6.6590109404,-2.1865406073,1.6848737278
H,-5.6010541079,-3.6234963147,0.4508833941
C,-5.6249619844,0.0114326672,1.8782465061
H,-3.7440154155,0.2673132654,0.8306801733
C,-6.6714671036,-0.874254974,2.1926373791
H,-7.4678622057,-2.877525276,1.9282654244
H,-5.6261541572,1.0242222211,2.2852045531
H,-7.4889415286,-0.5465556393,2.8375381643
N,2.1393907071,3.3095571897,0.4525743078
N,-1.8049495804,-3.2600081897,-1.2541007955
C,0.0981525832,3.4711182704,-0.3276107105
C,-3.4600166873,-2.1745946757,-0.3136179641
C,0.5172312488,5.7090779869,-1.508152073
H,0.6657695441,5.4840255987,-2.5715710686
H,-0.5366858006,5.9307529363,-1.3092365761
H,1.1558145981,6.5431495381,-1.1993321643
C,-3.1601520465,-0.0878558872,-1.7634498387
H,-4.2351872215,0.0970049624,-1.6732838647
H,-2.5943953861,0.5768931732,-1.0978351087
H,-2.8293309499,0.0250713859,-2.8009554976
Br,-0.8188767066,-0.4583318743,1.1852980525

$1^{2+}\cdot SO_4^{2-}$
h_diph_C2_so4_2_ch3cn, Total Energy= -2415.29032573 Hartree, NIMAG= 0
C,-4.0738922967,-2.6450503268,-0.7315696604
C,-3.5839242405,-1.3557152115,-0.5662772829
C,-4.4853954837,-0.2631316383,-0.4282098032
C,-5.9045309777,-0.4835514162,-0.5262723174
C,-6.3686158948,-1.8218145377,-0.7097483801
C,-5.4803771138,-2.8842461958,-0.7965898055
H,-2.9085026429,1.141269308,-0.0162109401
H,-2.5235578136,-1.1370616844,-0.4773778858
C,-3.9830124958,1.0429626435,-0.1582990881
C,-6.7728333982,0.6448323828,-0.4108555661
H,-7.4436244035,-2.0057325294,-0.7781647652
H,-5.8360934172,-3.9071996805,-0.9305269483
C,-6.2705358877,1.9150991127,-0.1706802635
C,-4.8638065293,2.1077473793,-0.0151269185

H,-7.8518478273,0.4954698418,-0.497569837
H,-6.9351112646,2.7740798657,-0.0647301059
O,-3.2763988206,-3.7713343132,-0.8394500096
O,-4.4817483596,3.4001685645,0.3028341641
C,-1.8928858676,-3.5727784236,-1.1700235968
H,-1.8046960664,-2.7702705324,-1.9166441401
H,-1.5584734373,-4.5187548246,-1.6153760324
C,-3.12112468,3.6025498943,0.7112630576
H,-2.7905366024,2.7863566074,1.3709015645
H,-3.1222481823,4.5407318315,1.2765694399
C,-2.2046717496,3.7156906234,-0.5331470133
H,-2.5323162307,3.0225437794,-1.3161727043
H,-2.2078756754,4.7369726084,-0.9358264218
C,-1.0464743631,-3.2491277143,0.0850131157
H,-1.4721489452,-2.4463340011,0.7015249584
H,-0.9041605271,-4.139813508,0.7069384978
C,0.1413729,2.9033349417,-1.0930556024
C,1.4718835804,-3.0518920489,0.3298582362
N,0.945594873,3.1582225089,0.9174804489
N,1.7508226602,-1.6958243736,-1.3529808595
N,-0.3260032085,3.5196433134,1.0008890921
N,0.4538971295,-1.9633376969,-1.3303714287
H,1.5302612114,-3.685691419,1.2029808161
H,-0.0728353932,2.6981822609,-2.1347646781
C,3.8833779166,-2.2098383237,-0.0990874146
C,4.3281903481,-2.0610117308,1.2334524825
C,4.8233173821,-2.2499563708,-1.1512698901
C,5.6991737271,-1.9464101738,1.5046906372
H,3.5975022175,-2.0105025896,2.0413627545
C,6.1925901967,-2.1300392307,-0.873569974
H,4.4880269534,-2.3869465045,-2.1793069607
C,6.6334601291,-1.9770080559,0.4527716522
H,6.036920903,-1.8216846614,2.5349767815
H,6.9134651758,-2.1586739531,-1.6923351718
H,7.6995316488,-1.8802149071,0.6662827429
C,2.647546521,2.3515435082,-0.7844784401
C,3.4825105564,1.5469554215,0.0221117574
C,3.0897362746,2.7566068583,-2.0655345796
C,4.7491559764,1.1684865183,-0.4449908001
H,3.1079490624,1.1665961017,0.9693363776
C,4.3540125532,2.3651820607,-2.5285294018
H,2.4494850692,3.3832569669,-2.688911561
C,5.18850146,1.5748110781,-1.7169410515
H,5.3773170161,0.5263026103,0.1725583528
H,4.6874482094,2.6798318555,-3.5189098084
H,6.1704164518,1.2653177336,-2.0797137084
N,-0.8024748066,3.3576503156,-0.2253688429
N,0.3036418418,-2.796163581,-0.3088037355
C,2.4441151678,-2.3341917572,-0.3524351039
C,1.3069646858,2.7613161919,-0.3499755393
C,2.2596570532,-0.7842233525,-2.3862915195
H,3.1303020655,-0.2629453812,-1.9794549073

H,2.5380808871,-1.3602701337,-3.2784863077
H,1.4637676546,-0.0722757143,-2.6255516854
C,1.7484475081,3.1524051093,2.1490195488
H,2.7906664404,3.3434392721,1.8730975925
H,1.3670209315,3.9492270693,2.7971917814
H,1.6230153302,2.1662611666,2.6179789405
S,0.0024251988,-0.3525549175,2.2487050592
O,-1.3745977776,-0.2426290189,1.5756580272
O,0.2286346424,-1.8027665825,2.7026491943
O,0.0597828634,0.5825443761,3.4684181789
O,1.0883800059,0.0501593352,1.2494812062

$1^{2+}\cdot SO_4^{2-}$
h_diph_so4_ch3cn, Total Energy= -2415.29179288 Hartree, NIMAG= 0
C,5.0691234286,-0.8517175926,0.6573647077
C,3.8249573304,-1.1842368385,0.1361389558
C,3.5063144651,-2.5503008086,-0.1226323275
C,4.478253031,-3.5796237294,0.1412733203
C,5.7435277371,-3.1942414583,0.6792085211
C,6.0366824521,-1.8640323837,0.938787908
H,1.5059814469,-2.084705037,-0.7728531209
H,3.0524561922,-0.4449525126,-0.0678437647
C,2.2181451752,-2.8963490466,-0.6213924201
C,4.1212583152,-4.934953715,-0.1357784135
H,6.4892855303,-3.9655097925,0.8873341506
H,7.0039846682,-1.5680549672,1.348086831
C,2.8647345763,-5.2615281218,-0.6240985955
C,1.9018162243,-4.2318747196,-0.8533454868
H,4.8530595284,-5.72438965,0.0529067664
H,2.5888927151,-6.298504933,-0.823719826
O,5.4837130922,0.4380584472,0.9411870872
O,0.6637324681,-4.6573125317,-1.2946134085
C,4.6757559826,1.5251482962,0.4803366687
H,4.2926681313,1.3211817423,-0.5330897556
H,5.3442242458,2.3950581886,0.4444417875
C,-0.3195924208,-3.615181585,-1.3906538982
H,-0.0490962338,-2.9167464328,-2.1980394779
H,-0.3759405394,-3.0486986645,-0.44853091
C,-1.6940728318,-4.244622954,-1.6745441481
H,-1.8465015695,-4.5007742114,-2.7299440981
H,-1.8698058867,-5.1263286746,-1.0477310386
C,3.5045395305,1.8108391501,1.452625828
H,2.8445361922,0.9462544639,1.5970083433
H,3.8758646976,2.1663932003,2.4205545765
C,-3.4926043746,-3.2405208787,-0.1804887728
C,1.6529986614,2.7007055371,-0.0147762961
N,-3.5086749856,-1.304914021,-1.1807783416
N,2.0221784425,4.8140500702,0.4216495209
N,-2.6936533559,-2.060209808,-1.9006461001
N,2.9127512172,4.1472782647,1.1498100719
H,1.2841860058,1.7109951146,-0.3190631471
H,-3.5870886525,-4.1027913726,0.4678284948

O,-1.0940003837,-1.3852771222,0.9208037327
S,-0.4219631451,-0.0247927785,0.7498850114
O,0.5526271214,0.2390203642,1.90588949
O,-1.4888913913,1.0799057923,0.7122103055
O,0.3745880632,0.0028987808,-0.5730026502
C,0.1146052165,4.3882970986,-1.2059211627
C,-0.112655023,3.6283674833,-2.3771928212
C,-0.7433023473,5.4677917326,-0.8979039538
C,-1.1770452946,3.9510671157,-3.229443509
H,0.547823844,2.7933103309,-2.6150725153
C,-1.8036983677,5.7882584464,-1.7587833084
H,-0.6082412617,6.0346156939,0.0225921728
C,-2.0226189263,5.0337814352,-2.9249485142
H,-1.3437338671,3.3601631258,-4.1317614546
H,-2.464778492,6.6201871613,-1.5104303491
H,-2.8503133297,5.285096043,-3.5907607603
C,-4.9334227335,-1.3732760857,0.8999505634
C,-6.0800923719,-2.0882126242,1.3111342188
C,-4.6354941205,-0.1153894044,1.4704670882
C,-6.9341869166,-1.5386353083,2.2788939179
H,-6.3041546594,-3.0585117768,0.8639530413
C,-5.4988277005,0.4257632128,2.4353375684
H,-3.7161559914,0.4018594559,1.1885221094
C,-6.6476971973,-0.2794870642,2.8381062834
H,-7.8231708691,-2.0893810519,2.5914661346
H,-5.2664779787,1.3944513505,2.881996946
H,-7.3150064893,0.1473098885,3.5895198412
N,2.6642634538,2.8712109593,0.8760967885
N,-2.6986298287,-3.2348497452,-1.2825213153
C,1.2069945583,3.9823979159,-0.31651292
C,-4.0329588259,-1.9654011984,-0.0958287018
C,2.0312858258,6.2842271546,0.4742546993
H,1.7282599203,6.6591478638,-0.5092717895
H,1.3315061816,6.6283214753,1.2463566247
H,3.0507397468,6.604948776,0.713220964
C,-3.689962067,0.1047928988,-1.5593022457
H,-4.716673104,0.3932189947,-1.3074611842
H,-2.9634154693,0.699114269,-0.9852838085
H,-3.5147780317,0.1865112832,-2.6374943977

$1^{2+}\cdot HP_2O_7^{3-}$ (a), Total Energy= -2926.31780225 Hartree, NIMAG= 0
C,0.7768216286,4.6490109904,-0.9740447502
C,0.4706043738,3.736832675,0.0298375047
C,-0.8685740001,3.6279536577,0.514773656
C,-1.8963345598,4.4779175434,-0.0305745697
C,-1.5314725875,5.4279351784,-1.0315228928
C,-0.2301846326,5.5137861476,-1.5011124451
H,-0.4084598148,1.9788806912,1.8251588092
H,1.2090416126,3.0482264908,0.4353507609
C,-1.202426018,2.6364429216,1.4798845214
C,-3.2358043356,4.3011194803,0.4310770495
H,-2.3022815366,6.0826947245,-1.4452756562

H,0.0439492244,6.2259508345,-2.2808911746
C,-3.5522739128,3.3096231223,1.3469302528
C,-2.5280353986,2.4539747324,1.8557334056
H,-4.023118485,4.9452271511,0.0319406757
H,-4.5815632772,3.1522961734,1.6740481535
O,2.0257062277,4.8023157444,-1.5447578759
O,-2.9667058064,1.4554592259,2.6944869266
C,3.0790604242,3.9285770696,-1.1168657275
H,3.1074989637,3.8555561059,-0.0176243776
H,4.0057055269,4.4012356236,-1.4633014894
C,-2.0011142805,0.4831819847,3.1458563684
H,-1.4302509987,0.8937424326,3.9950361099
H,-1.3234788023,0.2028734933,2.3269010468
C,-2.7743910327,-0.7535189118,3.6016237613
H,-2.1188604447,-1.4212967322,4.1724007378
H,-3.6539022125,-0.4935244473,4.2030070329
C,2.9188136646,2.5245324845,-1.7543838796
H,1.8988403697,2.1374787478,-1.648426522
H,3.1936057797,2.5410305864,-2.815590776
C,-4.3127680507,-1.2382409093,1.6360547611
C,3.4302327634,0.6362272332,-0.1529469099
N,-3.0664664457,-2.8196040221,0.7994788411
N,5.5976359909,0.6790292487,-0.4720314704
N,-2.4659202524,-2.4578365659,1.9221158851
N,5.1089808016,1.611589261,-1.2839070391
H,2.3822998201,0.4271482147,0.114298841
H,-5.049788523,-0.4864434616,1.8869295188
O,-1.8408290202,-0.3391371648,-0.13930184
O,-0.16823579,0.9837155054,-1.642562038
O,0.0288658004,-1.5279883685,-1.4096859719
O,0.6301250247,0.0125734249,0.6551568121
C,4.819659848,-1.0293662702,1.2393783847
C,3.9537906053,-1.078648004,2.357012319
C,5.8123817677,-2.0230690454,1.0857666189
C,4.0927163138,-2.0946570913,3.3116231789
H,3.1789897383,-0.3192130043,2.4710891548
C,5.948166642,-3.0355704195,2.0474134396
H,6.4560520088,-2.0283729031,0.2071740616
C,5.0934533461,-3.0727627098,3.1630066919
H,3.420776133,-2.1225518753,4.1712884906
H,6.7145733324,-3.8014383731,1.9165137195
H,5.2011274352,-3.8632172651,3.9081611671
C,-5.0873015877,-2.242151922,-0.6162857753
C,-5.4853077637,-1.0783500596,-1.3099916077
C,-5.5597807087,-3.5057468539,-1.0332195653
C,-6.3424439445,-1.1819638525,-2.4159184263
H,-5.1069669235,-0.1058408155,-0.9914209771
C,-6.412007911,-3.6023390633,-2.1435443242
H,-5.2789038442,-4.4027315453,-0.4792087592
C,-6.8031777208,-2.4425734248,-2.8369774611
H,-6.6417957882,-0.280332665,-2.9531495704
H,-6.7755808386,-4.5811914969,-2.4609293224

H,-7.4661163785,-2.5210373355,-3.7006786453
N,3.7957341546,1.5672189736,-1.0683748939
N,-3.2397049336,-1.5071985442,2.4227845099
C,4.6190643705,0.0385277827,0.255756497
C,-4.2128228168,-2.101987203,0.5555138884
C,7.0539518183,0.4801913512,-0.4361611734
H,7.3360729386,0.21336454,0.5882639498
H,7.3329932677,-0.32362376,-1.1292547794
H,7.5284510998,1.421079591,-0.7345112789
C,-2.3374486266,-3.72295567,-0.1058812044
H,-3.0155088633,-4.0222173574,-0.9087611533
H,-1.4841756301,-3.1607135645,-0.5102157945
H,-2.0078040308,-4.5984413053,0.4654152985
P,1.5658435374,-2.3630289874,-1.8108272845
O,1.0803166271,-3.2285923046,-3.0035893904
O,2.5592316332,-1.236100065,-2.1816942515
O,1.9159392258,-3.1599318003,-0.5295183792
H,-0.4900695836,1.8134256019,-1.2390583253
P,-0.3588867279,-0.2535116014,-0.4907150534

$1^{2+}\cdot HP_2O_7^{3-}$ (b) , Total Energy= -2926.31719313 Hartree, NIMAG= 0
C,5.3440602876,-1.5370229196,-0.3066008649
C,3.9774934935,-1.609369336,-0.5463698884
C,3.3378427768,-2.8823525079,-0.6382551936
C,4.1148540746,-4.0876955326,-0.5031253432
C,5.5176137075,-3.9673541826,-0.2674727037
C,6.1241672008,-2.7247628986,-0.1655677217
H,1.3692578376,-2.0276888193,-0.8730274303
H,3.3435471001,-0.7282419886,-0.6258177274
C,1.9271687204,-2.9623643343,-0.8330501759
C,3.4400699886,-5.3429161819,-0.598175846
H,6.1171638663,-4.8748835689,-0.1627259597
H,7.1955809779,-2.6322747713,0.0193295806
C,2.0701815475,-5.4090046557,-0.801777563
C,1.3070489757,-4.2060628055,-0.911602819
H,4.0204938317,-6.2638052969,-0.5017274516
H,1.5554895475,-6.3689705708,-0.8695998906
O,6.0608598089,-0.3597640224,-0.1861150666
O,-0.0450904593,-4.3771799481,-1.0969227618
C,5.3830394655,0.8784440867,-0.419980147
H,4.7244071206,0.8054940097,-1.3007670815
H,6.1732466319,1.6125519171,-0.6212647742
C,-0.8261094301,-3.1680656448,-1.1698760508
H,-0.4559698549,-2.5379159991,-1.9930637122
H,-0.7725106007,-2.6178909306,-0.2203993294
C,-2.2707563274,-3.6025289386,-1.438627099
H,-2.378489179,-4.0821127393,-2.4211745766
H,-2.623889485,-4.2724587711,-0.6480943767
C,4.5735457784,1.3133558341,0.8272592228
H,3.8317538082,0.5619953384,1.1239569827
H,5.2400756043,1.5310631489,1.6696484328
C,-4.2926995672,-2.2770394981,-0.6805776449

C,2.5558492556,2.6181386472,0.0415074746
N,-3.7187732885,-0.4269693011,-1.6742068992
N,3.5157745005,4.5829555382,0.1475987429
N,-2.7793944756,-1.2997067625,-1.9991334519
N,4.4360693134,3.722904341,0.5738053111
H,1.9127348222,1.7250457356,-0.028863882
H,-4.7080069212,-3.071500067,-0.0778063967
P,-2.1192741258,-1.0681994037,1.9682096466
O,-0.3374557328,-1.2944850554,1.8493979042
O,-2.4481406742,0.0442643828,0.9472204426
O,-2.5827716897,-2.4971418729,1.5877972478
O,-2.3577265431,-0.6899657438,3.4535179508
P,0.850535307,-0.2104250103,1.6261652856
O,2.1744058983,-1.1272578472,2.1406537507
H,2.3603679494,-1.8227474203,1.4797251535
O,0.8052860334,0.9767332396,2.583403411
O,1.0583131778,0.0739093913,0.1246814176
C,1.109129538,4.6181133626,-0.6864998852
C,0.3093729682,3.9084729905,-1.6137378823
C,0.6856632483,5.8862735618,-0.2290716711
C,-0.8893885852,4.4637428367,-2.0798861226
H,0.6337248791,2.9288653839,-1.9677520936
C,-0.5133528598,6.4381717121,-0.7049648878
H,1.2673276586,6.4265454891,0.5167467543
C,-1.3020201281,5.7315730778,-1.6300736548
H,-1.4984019091,3.9084643044,-2.7952602043
H,-0.8360176478,7.415342479,-0.3418135329
H,-2.2359212089,6.163671148,-1.9942266385
C,-5.8202978714,-0.2209467832,-0.2920251325
C,-7.1171346223,-0.7742807633,-0.3701073104
C,-5.6180808367,1.0177420567,0.3551721225
C,-8.2062850148,-0.0846668422,0.1845502705
H,-7.2672692087,-1.7321289025,-0.8719515059
C,-6.7133574903,1.703879604,0.9012449688
H,-4.6031926727,1.3983282964,0.4646306677
C,-8.007063079,1.1573441744,0.8152274099
H,-9.2080621084,-0.5134220283,0.1197476909
H,-6.5545199805,2.6582727339,1.4068725646
H,-8.8561494311,1.693747514,1.2436129297
N,3.8295066803,2.5422546334,0.5074077821
N,-3.1456311075,-2.4191510068,-1.3886263896
C,2.3277127063,3.9698302643,-0.1913139183
C,-4.6829321616,-0.9585968178,-0.8538567272
C,3.8688110731,6.0090509209,0.0753703423
H,3.3371632513,6.4458437759,-0.7767782181
H,3.5721196034,6.5080685402,1.006585547
H,4.9523312852,6.0798780133,-0.0667125082
C,-3.5529591531,0.9693229177,-2.0892720501
H,-4.5470071619,1.4166676862,-2.1944990313
H,-2.9754352558,1.4843292461,-1.3116582057
H,-3.0182264519,0.9796971574,-3.0453926086

References

1 . Grimme, *J. Comp. Chem.*, 2006, **27**,1787–1799.

2 . A. Hariharan and J. A. Pople, *Theor. Chim. Acta* 1973, **28**, 213–222.

3 Continuum Solvation Models in Chemical Physics: From Theory to Applications, B. Mennucci and R. Cammi, Eds., John Wiley & Sons, Chichester, 2007.

4 Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.