Electronic supplementary information for

Theoretical study of phenylbismuth anion as a blueprint for main-group single-molecule magnets

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CONTENTS

I. COMPUTATIONAL DETAILS

A. DFT calculations

All geometries were optimized using density functional theory (DFT) utilizing the hybrid PBE0 exchange-correlation functional.[1–4] All DFT calculations were carried out using the Gaussian16 code revision C.02.[5] Polarized triple-ζ quality def2-TZVP basis sets were used for all atoms.[6,7] The core electrons of the Bi atom were treated using a small-core pseudopotential.[8,9] The optimizations were carried out using the ground spin states (by fixing the projection of the spin) and test calculations were carried out to ensure that no lower-energy states with different spin existed. No restrictions were placed on the symmetry of the reference wave function or the geometry, and stability analyses[10,11] were carried out to ensure that the optimized states corresponded to minima in the molecular orbital coefficient space. Frequency calculations were carried out to ensure that the stationary structures correspond to minima on the potential energy surface and to produce the partition function for evaluation of thermal corrections to the enthalpies and free energies. The accuracy of the two-electron integrals was set to 10^{-12} atomic units and the integration grid was set to "UltraFine" accuracy.

Solvation energy was calculated using the integral equation formalism (IEF) variant of the polarizable continuum model (PCM).[12,13] The default parameters for acetonitrile were used, and the solvation energy was evaluated as a single point calculation.

B. Multireference calculations

The electronic structures of BiPh and $[BiPh]^-$ were calculated using multireference methods. All multireference calculations were carried out using the Orca code version 5.0.2.[14–16] At first, state-averaged (SA) complete active space self-consistent field (CASSCF) type calculations[17–21] were carried out. The active space consisted of the two $6p_\pi$ orbitals, the σ-bonding and anti-bonding combinations and all six phenyl π orbitals. In the case of BiPh this totals 10 electrons and 10 orbitals, and in the case of $[BiPh]^-$ 11 electrons and 10 orbitals. In case of BiPh, 3 pentet, 12 triplet and 11 singlet roots were solved, and in the case of $[BiPh]^-$, 8 quartet and 13 doublet roots were solved in a single SA-CASSCF calculation for each structure. This corresponds roughly to an energy cutoff of $50\,000\,\mathrm{cm}^{-1}$ based on

trial calculations. The weights of the roots in the orbital optimization were set so that only the states where the leading configuration included two electrons (BiPh) or three electrons ([BiPh]$^-$) in the $6p_\pi$ orbitals and had the lower-energy orbitals fully occupied had nonzero weights. Including the other roots in the orbital optimization would lead to a choice of orbitals that stabilized the higher-lying charge-transfer configurations but lead to too large splitting of the lower-energy states.

Electron correlation effects outside the active space were approximated using the N-electron valence state perturbation theory at second order (NEVPT2) in its strongly contracted form.[22–26] SOC was included using the quasi-degenerate perturbation theory (QDPT) approach, where the SOC operator is constructed in a basis of the SA-CASSCF eigenstates and diagonalized to yield the final spin-orbit coupled eigenvalues and eigenstates.[27,28] The SOC operator was constructed using the spin-orbit mean-field (SOMF) operator[29–31] and the NEVPT2 correction was included as shifts in the diagonal elements of the operator. The **g** and **D** tensors and the effective barrier for the relaxation of magnetization were calculated using the SINGLE_ANISO module[32–34] as interfaced to ORCA.

Scalar relativistic effects were introduced using the standard second-order Douglas–Kroll–Heß transformation[35,36] with picture change effects. Relativistically contracted basis sets specifically designed for DKH calculations were used in all multireference calculations. The Bi atom was treated using the polarized triple-ζ quality SARC-DKH-TZVP basis[37], and the C and H atoms were treated with the DKH-def2-TZVP basis sets[38]. The resolution of identity (RI) approximation[39,40] was used in the integral transformations. The necessary auxiliary basis sets were generated using the "AutoAux" feature[41] in ORCA.

C. Calculation of reduction potential

The free energy change for the reduction reaction was calculated as

$$\Delta G_r = G([\mathrm{BiPh}]^-) - G(\mathrm{BiPh}) + E_{\mathrm{sol}}([\mathrm{BiPh}]^-) - E_{\mathrm{sol}}(\mathrm{BiPh}) + E_{\mathrm{SOC}}([\mathrm{BiPh}]^-) - E_{\mathrm{SOC}}(\mathrm{BiPh}), \tag{1}$$

where G is the Gibbs free energy containing the zero-point energy, thermal correction to the energy, enthalpy correction and the entropy evaluated at DFT-level, E_{sol} is the solvation energy calculated at DFT-level using PCM and E_{SOC} is the stabilization of the ground-state energy due to SOC. The SOC contribution is calculated as the difference between

the ground-state energy before and after the inclusion of SOC using QDPT. The NEVPT2 or CASSCF energies cannot be used in the evaluation of the energy difference due to the size-consistency error. It should be noted that the contribution from SOC and the thermal corrections affect the final reduction potential by less than 0.1 V, and the main contribution comes from the DFT energy and the solvation energy. See Table S1 for the values of the energies.

The reduction potential versus SHE was calculated from the free energy difference as

$$E^0_{\mathrm{rel,SHE}} = -\Delta G_r/F - E^0_{\mathrm{SHE}}, \tag{2}$$

where F is the Faraday constant (assuming that the energies are given in units $\mathrm{kJ\,mol^{-1}}$) and $E^0_{\mathrm{SHE}} = 4.6\,\mathrm{V}$ is the experimentally determined absolute value of the SHE reduction potential in acetonitrile.[42]

D. Calculation of proton affinities

In order to evaluate the proton affinity the geometries, enthalpy corrections and solvation energies of the protonated specie $[\mathrm{HBiPh}]^+$ and HBiPh were calculated. Test calculations were carried out to ensure that specie were the proton was added to some other atom were higher in energy. The geometry of $[\mathrm{HBiPh}]^+$ was optimized in both the $M_S = 0$ state and the $M_S = 1$ state. The lowest-energy state is the singlet spin state, which does not display any symmetry-breaking. The energies of all calculated geometries are listed in Table S2. The proton affinity was calculated as the negative enthalpy change for the protonation reaction. The energies included the DFT energy, the enthalpy correction and the solvation energy. Since the effect of SOC on the reduction potential was negligible, it was not taken into account in the calculation of the proton affinities. The values of the energies are listed in Table S3.

II. COMPUTATIONAL DATA

TABLE S1. Ground state-energies (in Hartree atomic units) and corrections to energies calculated for BiPh and $[BiPh]^-$

	BiPh	$[BiPh]^-$
E(PBE0)	−446.061248	−446.098393
E(solvation)	−0.003006	−0.080514
G(PBE0) − E(PBE0)	0.055606	0.054319
E(CASSCF)	−21739.563844	−21739.564622
E(NEVPT2)	−21740.806340	−21740.837792
E(CASSCF + SOC)	−21739.579923	−21739.579821
E(NEVPT2 + SOC)	−21740.824148	−21740.852899

TABLE S2. Energies (in Hartree atomic units) of different structures obtained by protonation of BiPh and $[BiPh]^-$

	$[BiPh]^- + H^+$	$BiPh + H^+$	
Location of H^+	$M_S = 1/2$	$M_S = 0$	$M_S = 1$
Bi	−446.655829	−446.390297	−446.340331
ortho	−446.616970	−446.366855	−446.375861
meta	−446.603968	−446.355438	−446.366832
para	−446.622818	−446.369697	−446.378189

TABLE S3. Ground state-energies (in Hartree atomic units) and corrections to energies calculated for $[HBiPh]^+$ and HBiPh

	$[HBiPh]^+$	HBiPh
E(PBE0)	−446.390297	−446.655829
E(solvation)	−0.084655	−0.003353
H(PBE0) − E(PBE0)	0.104121	0.103339

TABLE S4. CASSCF eigenvalues calculated for BiPh

S	E / cm^{-1}
1	0.0
0	8143.3
0	8226.7
0	16332.0
0	30485.5
1	31326.7
2	35281.5
1	37545.1
0	37807.8
1	39018.8
1	40351.0
0	42377.6
1	43242.3
1	43363.9
1	44854.8
0	44950.5
2	45119.9
1	45130.1
2	45575.5
0	45595.5
1	45804.5
0	45828.9
1	46165.3
0	46334.1
1	49212.6
0	49982.3

TABLE S5. CASSCF eigenvalues calculated for $[BiPh]^-$

S	E / cm^{-1}
1/2	0.0
1/2	120.4
1/2	30182.5
3/2	32026.5
1/2	33186.1
3/2	35594.4
1/2	37539.3
3/2	38855.0
1/2	39656.6
3/2	40843.7
1/2	40902.5
1/2	42171.6
1/2	42656.9
1/2	42870.7
1/2	43616.3
3/2	44752.1
3/2	45627.0
1/2	46108.3
3/2	48319.8
1/2	48453.2
3/2	49803.1

TABLE S6. NEVPT2 eigenvalues calculated for BiPh

S	E / cm^{-1}
1	0.0
0	6240.6
0	6327.4
0	14012.1
0	31232.1
1	31972.6
0	33781.9
1	33907.8
1	34020.4
1	34215.7
1	35961.2
1	36400.4
0	36553.1
0	37012.0
2	37359.6
0	37818.3
0	38174.5
1	39165.8
0	39403.0
2	42207.2
0	42268.7
1	42322.6
2	42459.1
1	42718.3
1	43318.4
1	44518.8

TABLE S7. NEVPT2 eigenvalues calculated for $[BiPh]^-$

S	E / cm^{-1}
1/2	0.0
1/2	165.9
3/2	23125.8
1/2	25415.3
1/2	27451.0
3/2	27528.9
1/2	29801.4
1/2	30411.7
1/2	30947.8
1/2	32534.0
1/2	32798.1
1/2	33666.5
3/2	33805.8
1/2	34100.5
3/2	37838.6
3/2	38325.2
3/2	38387.2
1/2	39374.5
3/2	41816.1
3/2	42355.3
1/2	44704.3

TABLE S8. Eigenvalues (in cm^{-1}) of the SOC operator calculated for BiPh

CASSCF diagonal values			NEVPT2 diagonal values		
0.00	42792.17	48728.19	0.00	40088.58	46367.50
3121.20	43174.43	49104.43	3391.33	41305.76	46367.50
3123.29	43249.27	49104.43	3391.46	41310.38	46430.41
11178.44	43497.93	49495.01	9598.88	41369.54	46479.69
11346.49	43794.27	49495.64	9605.76	41439.57	46515.31
21974.00	43908.65	50416.69	19988.76	41494.22	46663.33
33017.71	44330.01	50513.77	33340.13	41778.21	46663.35
33605.50	44501.89	50649.90	33982.40	41843.49	46787.72
33605.83	45977.56	50852.90	33983.88	41859.43	47083.00
34630.75	47872.97	51029.58	34211.82	43111.36	47103.31
38145.69	47873.32	51030.46	34699.56	43236.12	47210.96
38345.01	47880.90	51160.20	35379.22	43247.43	48178.66
38348.14	47885.49	51227.05	35445.70	43354.52	48562.37
38745.52	47915.45	52004.81	35522.43	43487.33	48564.99
38746.12	47934.13	52020.48	35803.27	43752.22	48763.96
40129.51	48155.84	52290.52	36139.86	43878.87	48934.25
40129.51	48462.50	53304.47	36140.00	45407.64	48996.37
40152.37	48512.73	53383.80	36599.47	45514.28	49082.85
40331.18	48523.27	54241.75	39111.57	45527.31	41997.28
42618.23	48641.18	55080.81	39693.62	46144.86	43054.97
42761.35	48713.21		39707.60	46146.16	

TABLE S9. Eigenvalues (in cm^{-1}) of the SOC operator calculated for $[BiPh]^-$

CASSCF diagonal values			NEVPT2 diagonal values		
0.00	41967.57	48190.69	0.00	35231.84	41478.65
0.00	41967.57	48190.69	0.00	35231.84	41478.65
6494.48	42024.98	49370.15	6418.50	35749.98	42518.69
6494.48	42024.98	49370.15	6418.50	35749.98	42518.69
31106.80	43886.99	50038.50	25716.50	35979.34	42852.83
31106.80	43886.99	50038.50	25716.50	35979.34	42852.83
33818.29	43922.50	50762.11	26213.20	36115.92	44457.00
33818.29	43922.50	50762.11	26213.20	36115.92	44457.00
34383.26	44112.11	51574.40	28220.07	36171.52	46076.17
34383.26	44112.11	51574.40	28220.07	36171.52	46076.17
37799.38	44909.28	52613.17	28796.44	36992.86	46445.90
37799.38	44909.28	52613.17	28796.44	36992.86	46445.90
38418.01	45540.65	53196.31	30122.41	37717.72	46915.23
38418.01	45540.65	53196.31	30122.41	37717.72	46915.23
39493.92	46316.75	53764.37	30372.70	40141.29	47208.18
39493.92	46316.75	53764.37	30372.70	40141.29	47208.18
40266.53	47787.21	54551.19	32854.42	40332.20	48655.61
40266.53	47787.21	54551.19	32854.42	40332.20	48655.61
41551.13	47987.46		33003.31	41134.75	
41551.13	47987.46		33003.31	41134.75	

III. OPTIMIZED CARTESIAN COORDINATES

BiPh

	x / Å	y / Å	z / Å
Bi	0.00000002	−0.00000000	−1.19207092
C	−0.00000001	1.20015281	1.74936284
C	−0.00000001	−0.00000000	1.03739603
C	−0.00000002	−1.20015281	1.74936284
C	−0.00000000	−1.20018773	3.13700587
C	−0.00000001	0.00000000	3.83374263
C	−0.00000001	1.20018773	3.13700587
H	0.00000000	2.14933941	1.22236755
H	−0.00000001	−2.14933941	1.22236755
H	0.00000002	−2.14136265	3.67624287
H	0.00000001	−0.00000000	4.91791300
H	0.00000001	2.14136265	3.67624287

$[BiPh]^-$

	x / Å	y / Å	z / Å
Bi	0.00000000	0.00000000	−1.24190565
C	−0.00000000	1.19070440	1.75462389
C	0.00000000	0.00000000	1.01017918
C	−0.00000001	−1.19070440	1.75462389
C	0.00000000	−1.19444653	3.14133755
C	−0.00000000	−0.00000000	3.85486610
C	−0.00000000	1.19444653	3.14133755
H	0.00000000	2.14346168	1.23102819
H	−0.00000000	−2.14346168	1.23102819
H	0.00000001	−2.14219875	3.67483442
H	0.00000000	−0.00000000	4.94015127
H	0.00000000	2.14219875	3.67483442

$[HBiPh]^+$

	x / Å	y / Å	z / Å
Bi	−0.23267558	−0.18955763	1.09189122
C	−0.27935518	0.59492669	−3.20407631
C	−0.34854569	0.01385030	−1.95618821
C	−0.10420371	0.79229820	−0.80455431
C	0.20994726	2.16111138	−0.93295449
C	0.27584378	2.72947606	−2.18631454
C	0.03202877	1.94863162	−3.31612991
H	−0.46547295	0.00447096	−4.09285048
H	−0.59150781	−1.04083906	−1.87190666
H	0.39920576	2.76603504	−0.05394521
H	0.51625105	3.78006678	−2.29556674
H	0.08580021	2.40322938	−4.29895936
H	0.16422616	1.30299267	1.98710184

HBiPh

	x / Å	y / Å	z / Å
Bi	−0.22016294	−0.22108321	1.16976173
C	−0.27522218	0.61226200	−3.21366130
C	−0.33708505	0.03169187	−1.95533878
C	−0.09930911	0.78885655	−0.80719885
C	0.20250336	2.14365351	−0.94915416
C	0.26433425	2.72402909	−2.20769749
C	0.02581343	1.96073968	−3.34222506
H	−0.46258891	0.01010057	−4.09610303
H	−0.57430330	−1.02561284	−1.87689838
H	0.39144448	2.75313668	−0.07228145
H	0.50011668	3.77852172	−2.30273401
H	0.07449548	2.41616685	−4.32484283
H	0.17150591	1.29422992	2.04392042

IV. INPUT FILES

Final NEVPT2//CASSCF calculation on BiPh

```
! AllowRHF DKH
! SARC-DKH-TZVP AutoAux
! MORead

%MaxCore 3500
%MOInp "/path/to/guess/neutral.gbw"

%Pal
 NProcs 10
End

%Basis
 NewGTO    Bi "SARC-DKH-TZVP" End
 NewGTO    H  "DKH-def2-TZVP" End
 NewGTO    C  "DKH-def2-TZVP" End
 NewAuxGTO Bi "AutoAux" End
 NewAuxGTO H  "AutoAux" End
 NewAuxGTO C  "AutoAux" End
End

%Rel
 Method DKH
 PictureChange 2
End

%CASSCF
 NEl          10
 NOrb         10
 NRoots       3,12,11
```

```
 BWeight     0,1,1
 Weights[1]  = 1.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0
 Weights[2]  = 1.0,1.0,1.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0
 Mult      5,3,1
 TrafoStep   RI
 CI
  NGuessMat  1024
  MaxDim     20
  MaxIter    128
 End
 MaxIter     2048
 SwitchStep  NR
 SwitchConv  0.001
 SwitchIter  2048
 PTMethod    SC_NEVPT2
 Rel
  DoSOC      True
 End
 ANISO
  DoAniso    True
  MLTP       3
  UBar       True
 End
End

*xyzfile 0 1 /path/to/coordinates/neutral.xyz
```

Final NEVPT2//CASSCF calculation on $[BiPh]^-$

```
! AllowRHF DKH
! SARC-DKH-TZVP AutoAux
! MORead

%MaxCore 3500
%MOInp "/path/to/guess/anion.gbw"

%Pal
 NProcs 10
End

%Basis
 NewGTO    Bi "SARC-DKH-TZVP" End
 NewGTO    H  "DKH-def2-TZVP" End
 NewGTO    C  "DKH-def2-TZVP" End
 NewAuxGTO Bi "AutoAux" End
 NewAuxGTO H  "AutoAux" End
 NewAuxGTO C  "AutoAux" End
End

%Rel
 Method DKH
 PictureChange 2
End

%CASSCF
 NEl          11
 NOrb         10
 NRoots       8,13
 BWeight      0,1
 Weights[1]   = 1.0,1.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0
```

```
 Mult      4,2
 TrafoStep   RI
 CI
  NGuessMat  1024
  MaxDim     20
  MaxIter    128
 End
 MaxIter     2048
 SwitchStep  NR
 SwitchConv  0.001
 SwitchIter  2048
 PTMethod    SC_NEVPT2
 Rel
  DoSOC      True
 End
 ANISO
  DoAniso    True
  MLTP       2,2
  UBar       True
 End
End

*xyzfile -1 2 /path/to/coordinates/anion.xyz
```

Geometry optimization and frequency calculation of BiPh

```
%NProc=10
%Mem=30GB
%chk=neutral.chk
#P Opt Freq
#  Pseudo Gen UPBE1PBE
#  SCF=(XQC,MaxConventionalCycles=120)
#  Integral=(Grid=UltraFine,Acc2E=12) Symmetry=None

neutral

0 3
[initial coordinates]

H    0
S  3  1.00
    34.061341       .60251978E-02
    5.1235746       .45021094E-01
    1.1646626       .20189726
S  1  1.00
    .32723041       1.0000000
S  1  1.00
    .10307241       1.0000000
P  1  1.00
 .80   1.00
****
C    0
S  6  1.00
  13575.349682       .22245814352E-03
  2035.2333680       .17232738252E-02
  463.22562359       .89255715314E-02
  131.20019598       .35727984502E-01
```

```
  42.853015891       .11076259931
  15.584185766       .24295627626
S  2  1.00
  6.2067138508       .41440263448
  2.5764896527       .23744968655
S  1  1.00
  .57696339419       1.0000000000
S  1  1.00
  .22972831358       1.0000000000
S  1  1.00
  .95164440028E-01   1.0000000000
P  4  1.00
  34.697232244       .53333657805E-02
  7.9582622826       .35864109092E-01
  2.3780826883       .14215873329
  .81433208183       .34270471845
P  1  1.00
  .28887547253       .46445822433
P  1  1.00
  .10056823671       .24955789874
D  1  1.00
        1.0970000000         1.0000000000
D  1  1.00
        0.3180000000         1.0000000000
F  1  1.00
        0.7610000000         1.0000000000
****
Bi    0
S  4  1.00
  716.41435310       0.31254307133E-03
  83.806059047       0.17624768946E-02
  21.116962853      -0.21910983437
```

```
  15.491448187      0.40411224931
S  2  1.00
  23.239855029     -0.68255758685E-01
  6.6474255000      0.97888046471
S  1  1.00
  1.7617744005       1.0000000000
S  1  1.00
 0.87252866000       1.0000000000
S  1  1.00
 0.25618895997       1.0000000000
S  1  1.00
 0.97073913006E-01   1.0000000000
P  3  1.00
  15.249644669      0.74560356000
  14.846176053     -0.85578637338
  7.0636826784      0.40149159592
P  3  1.00
  2.5881255616      0.35542729633
  1.5020208499      0.63976991890
 0.76732724388      0.32332773839
P  1  1.00
 0.32797648982       1.0000000000
P  1  1.00
 0.13820335991       1.0000000000
P  1  1.00
 0.55137330969E-01   1.0000000000
D  6  1.00
  66.404481948      0.38102878348E-03
  13.858426961      0.10746152442E-01
  7.0654519000     -0.71947646845E-01
  2.5252144035      0.26195974989
  1.3419585000      0.42594750000
```

```
 0.68340941000       0.33680325627
D  1  1.00
 0.32934755420        1.0000000000
D  1  1.00
 0.14000000000        1.0000000000
F  1  1.00
   .31271             1.0000000
F  1  1.00
   1.05            1.0000000000
****

BI     0
BI-ECP     3     60
f POTENTIAL
  2
2      4.21454600           13.71338300
2      4.13340000           18.19430800
s-f POTENTIAL
  4
2     13.04309000          283.26422700
2      8.22168200           62.47195900
2      4.21454600          -13.71338300
2      4.13340000          -18.19430800
p-f POTENTIAL
  6
2     10.46777700           72.00149900
2      9.11890100          144.00227700
2      6.75479100            5.00794500
2      6.25259200            9.99155000
2      4.21454600          -13.71338300
2      4.13340000          -18.19430800
d-f POTENTIAL
```

```
 6
2       8.08147400          36.39625900
2       7.89059500          54.59766400
2       4.95555600           9.98429400
2       4.70455900          14.98148500
2       4.21454600         -13.71338300
2       4.13340000         -18.19430800
```

Geometry optimization and frequency calculation of $[BiPh]^-$

```
%NProc=10
%Mem=30GB
%chk=anion.chk
#P Opt Freq
#  Pseudo Gen UPBE1PBE
#  SCF=(XQC,MaxConventionalCycles=120)
#  Integral=(Grid=UltraFine,Acc2E=12) Symmetry=None

anion

-1 2
[initial coordinates]

H    0
S  3  1.00
    34.061341       .60251978E-02
    5.1235746       .45021094E-01
    1.1646626       .20189726
S  1  1.00
    .32723041       1.0000000
S  1  1.00
    .10307241       1.0000000
P  1  1.00
 .80   1.00
****
C    0
S  6  1.00
  13575.349682       .22245814352E-03
  2035.2333680       .17232738252E-02
  463.22562359       .89255715314E-02
  131.20019598       .35727984502E-01
```

```
  42.853015891       .11076259931
  15.584185766       .24295627626
S  2  1.00
  6.2067138508       .41440263448
  2.5764896527       .23744968655
S  1  1.00
  .57696339419       1.0000000000
S  1  1.00
  .22972831358       1.0000000000
S  1  1.00
  .95164440028E-01   1.0000000000
P  4  1.00
  34.697232244       .53333657805E-02
  7.9582622826       .35864109092E-01
  2.3780826883       .14215873329
  .81433208183       .34270471845
P  1  1.00
  .28887547253       .46445822433
P  1  1.00
  .10056823671       .24955789874
D  1  1.00
        1.0970000000         1.0000000000
D  1  1.00
        0.3180000000         1.0000000000
F  1  1.00
        0.7610000000         1.0000000000
****
Bi    0
S  4  1.00
  716.41435310       0.31254307133E-03
  83.806059047       0.17624768946E-02
  21.116962853      -0.21910983437
```

```
  15.491448187      0.40411224931
S  2  1.00
  23.239855029     -0.68255758685E-01
  6.6474255000      0.97888046471
S  1  1.00
  1.7617744005       1.0000000000
S  1  1.00
 0.87252866000       1.0000000000
S  1  1.00
 0.25618895997       1.0000000000
S  1  1.00
 0.97073913006E-01   1.0000000000
P  3  1.00
  15.249644669      0.74560356000
  14.846176053     -0.85578637338
  7.0636826784      0.40149159592
P  3  1.00
  2.5881255616      0.35542729633
  1.5020208499      0.63976991890
 0.76732724388      0.32332773839
P  1  1.00
 0.32797648982       1.0000000000
P  1  1.00
 0.13820335991       1.0000000000
P  1  1.00
 0.55137330969E-01   1.0000000000
D  6  1.00
  66.404481948      0.38102878348E-03
  13.858426961      0.10746152442E-01
  7.0654519000     -0.71947646845E-01
  2.5252144035      0.26195974989
  1.3419585000      0.42594750000
```

```
 0.68340941000      0.33680325627
D  1  1.00
 0.32934755420       1.0000000000
D  1  1.00
 0.14000000000       1.0000000000
F  1  1.00
   .31271            1.0000000
F  1  1.00
   1.05           1.0000000000
****

BI     0
BI-ECP     3     60
f POTENTIAL
  2
2      4.21454600           13.71338300
2      4.13340000           18.19430800
s-f POTENTIAL
  4
2     13.04309000          283.26422700
2      8.22168200           62.47195900
2      4.21454600          -13.71338300
2      4.13340000          -18.19430800
p-f POTENTIAL
  6
2     10.46777700           72.00149900
2      9.11890100          144.00227700
2      6.75479100            5.00794500
2      6.25259200            9.99155000
2      4.21454600          -13.71338300
2      4.13340000          -18.19430800
d-f POTENTIAL
```

```
  6
2       8.08147400           36.39625900
2       7.89059500           54.59766400
2       4.95555600            9.98429400
2       4.70455900           14.98148500
2       4.21454600          -13.71338300
2       4.13340000          -18.19430800
```

Stability analysis of BiPh

```
%NProc=10
%Mem=30GB
%chk=neutral.chk
#P Stable=Opt
#  Pseudo Gen UPBE1PBE
#  SCF=(XQC,MaxConventionalCycles=120)
#  Integral=(Grid=UltraFine,Acc2E=12) Symmetry=None
#  Geom=Checkpoint Guess=Read

neutral

0 3

H    0
S  3  1.00
    34.061341       .60251978E-02
    5.1235746       .45021094E-01
    1.1646626       .20189726
S  1  1.00
    .32723041       1.0000000
S  1  1.00
    .10307241       1.0000000
P  1  1.00
 .80   1.00
****
C    0
S  6  1.00
  13575.349682       .22245814352E-03
  2035.2333680       .17232738252E-02
  463.22562359       .89255715314E-02
  131.20019598       .35727984502E-01
```

```
  42.853015891       .11076259931
  15.584185766       .24295627626
S  2  1.00
  6.2067138508       .41440263448
  2.5764896527       .23744968655
S  1  1.00
  .57696339419       1.0000000000
S  1  1.00
  .22972831358       1.0000000000
S  1  1.00
  .95164440028E-01   1.0000000000
P  4  1.00
  34.697232244       .53333657805E-02
  7.9582622826       .35864109092E-01
  2.3780826883       .14215873329
  .81433208183       .34270471845
P  1  1.00
  .28887547253       .46445822433
P  1  1.00
  .10056823671       .24955789874
D  1  1.00
        1.0970000000         1.0000000000
D  1  1.00
        0.3180000000         1.0000000000
F  1  1.00
        0.7610000000         1.0000000000
****
Bi    0
S  4  1.00
  716.41435310       0.31254307133E-03
  83.806059047       0.17624768946E-02
  21.116962853      -0.21910983437
```

```
  15.491448187      0.40411224931
S  2  1.00
  23.239855029     -0.68255758685E-01
  6.6474255000      0.97888046471
S  1  1.00
  1.7617744005       1.0000000000
S  1  1.00
 0.87252866000       1.0000000000
S  1  1.00
 0.25618895997       1.0000000000
S  1  1.00
 0.97073913006E-01   1.0000000000
P  3  1.00
  15.249644669      0.74560356000
  14.846176053     -0.85578637338
  7.0636826784      0.40149159592
P  3  1.00
  2.5881255616      0.35542729633
  1.5020208499      0.63976991890
 0.76732724388      0.32332773839
P  1  1.00
 0.32797648982       1.0000000000
P  1  1.00
 0.13820335991       1.0000000000
P  1  1.00
 0.55137330969E-01   1.0000000000
D  6  1.00
  66.404481948      0.38102878348E-03
  13.858426961      0.10746152442E-01
  7.0654519000     -0.71947646845E-01
  2.5252144035      0.26195974989
  1.3419585000      0.42594750000
```

```
 0.68340941000      0.33680325627
D  1  1.00
 0.32934755420       1.0000000000
D  1  1.00
 0.14000000000       1.0000000000
F  1  1.00
   .31271            1.0000000
F  1  1.00
   1.05           1.0000000000
****

BI     0
BI-ECP     3     60
f POTENTIAL
  2
2      4.21454600           13.71338300
2      4.13340000           18.19430800
s-f POTENTIAL
  4
2     13.04309000          283.26422700
2      8.22168200           62.47195900
2      4.21454600          -13.71338300
2      4.13340000          -18.19430800
p-f POTENTIAL
  6
2     10.46777700           72.00149900
2      9.11890100          144.00227700
2      6.75479100            5.00794500
2      6.25259200            9.99155000
2      4.21454600          -13.71338300
2      4.13340000          -18.19430800
d-f POTENTIAL
```

```
 6
2       8.08147400          36.39625900
2       7.89059500          54.59766400
2       4.95555600           9.98429400
2       4.70455900          14.98148500
2       4.21454600         -13.71338300
2       4.13340000         -18.19430800
```

Stability analysis of $[BiPh]^-$

```
%NProc=10
%Mem=30GB
%chk=anion.chk
#P Stable=Opt
#  Pseudo Gen UPBE1PBE
#  SCF=(XQC,MaxConventionalCycles=120)
#  Integral=(Grid=UltraFine,Acc2E=12) Symmetry=None
#  Geom=Checkpoint Guess=Read

anion

-1 2

H    0
S  3  1.00
    34.061341       .60251978E-02
    5.1235746       .45021094E-01
    1.1646626       .20189726
S  1  1.00
    .32723041       1.0000000
S  1  1.00
    .10307241       1.0000000
P  1  1.00
 .80   1.00
****
C    0
S  6  1.00
  13575.349682       .22245814352E-03
  2035.2333680       .17232738252E-02
  463.22562359       .89255715314E-02
  131.20019598       .35727984502E-01
```

```
  42.853015891       .11076259931
  15.584185766       .24295627626
S  2  1.00
  6.2067138508       .41440263448
  2.5764896527       .23744968655
S  1  1.00
  .57696339419       1.0000000000
S  1  1.00
  .22972831358       1.0000000000
S  1  1.00
  .95164440028E-01   1.0000000000
P  4  1.00
  34.697232244       .53333657805E-02
  7.9582622826       .35864109092E-01
  2.3780826883       .14215873329
  .81433208183       .34270471845
P  1  1.00
  .28887547253       .46445822433
P  1  1.00
  .10056823671       .24955789874
D  1  1.00
        1.0970000000         1.0000000000
D  1  1.00
        0.3180000000         1.0000000000
F  1  1.00
        0.7610000000         1.0000000000
****
Bi    0
S  4  1.00
  716.41435310       0.31254307133E-03
  83.806059047       0.17624768946E-02
  21.116962853      -0.21910983437
```

```
  15.491448187      0.40411224931
S  2  1.00
  23.239855029     -0.68255758685E-01
  6.6474255000      0.97888046471
S  1  1.00
  1.7617744005       1.0000000000
S  1  1.00
 0.87252866000       1.0000000000
S  1  1.00
 0.25618895997       1.0000000000
S  1  1.00
 0.97073913006E-01   1.0000000000
P  3  1.00
  15.249644669      0.74560356000
  14.846176053     -0.85578637338
  7.0636826784      0.40149159592
P  3  1.00
  2.5881255616      0.35542729633
  1.5020208499      0.63976991890
 0.76732724388      0.32332773839
P  1  1.00
 0.32797648982       1.0000000000
P  1  1.00
 0.13820335991       1.0000000000
P  1  1.00
 0.55137330969E-01   1.0000000000
D  6  1.00
  66.404481948      0.38102878348E-03
  13.858426961      0.10746152442E-01
  7.0654519000     -0.71947646845E-01
  2.5252144035      0.26195974989
  1.3419585000      0.42594750000
```

```
 0.68340941000       0.33680325627
D  1  1.00
 0.32934755420        1.0000000000
D  1  1.00
 0.14000000000        1.0000000000
F  1  1.00
   .31271             1.0000000
F  1  1.00
   1.05            1.0000000000
****

BI     0
BI-ECP     3     60
f POTENTIAL
  2
2      4.21454600           13.71338300
2      4.13340000           18.19430800
s-f POTENTIAL
  4
2     13.04309000          283.26422700
2      8.22168200           62.47195900
2      4.21454600          -13.71338300
2      4.13340000          -18.19430800
p-f POTENTIAL
  6
2     10.46777700           72.00149900
2      9.11890100          144.00227700
2      6.75479100            5.00794500
2      6.25259200            9.99155000
2      4.21454600          -13.71338300
2      4.13340000          -18.19430800
d-f POTENTIAL
```

```
  6
2       8.08147400            36.39625900
2       7.89059500            54.59766400
2       4.95555600             9.98429400
2       4.70455900            14.98148500
2       4.21454600           -13.71338300
2       4.13340000           -18.19430800
```

Solvation calculation of BiPh

```
%NProc=10
%Mem=30GB
%chk=neutral.chk
#P Stable=Opt SCRF=(Solvent=Acetonitrile)
#  Pseudo Gen UPBE1PBE
#  SCF=(XQC,MaxConventionalCycles=120)
#  Integral=(Grid=UltraFine,Acc2E=12) Symmetry=None
#  Geom=Checkpoint Guess=Read

neutral

0 3

H    0
S  3  1.00
    34.061341       .60251978E-02
    5.1235746       .45021094E-01
    1.1646626       .20189726
S  1  1.00
    .32723041       1.0000000
S  1  1.00
    .10307241       1.0000000
P  1  1.00
 .80   1.00
****
C    0
S  6  1.00
  13575.349682       .22245814352E-03
  2035.2333680       .17232738252E-02
  463.22562359       .89255715314E-02
  131.20019598       .35727984502E-01
```

```
  42.853015891       .11076259931
  15.584185766       .24295627626
S  2  1.00
  6.2067138508       .41440263448
  2.5764896527       .23744968655
S  1  1.00
  .57696339419       1.0000000000
S  1  1.00
  .22972831358       1.0000000000
S  1  1.00
  .95164440028E-01   1.0000000000
P  4  1.00
  34.697232244       .53333657805E-02
  7.9582622826       .35864109092E-01
  2.3780826883       .14215873329
  .81433208183       .34270471845
P  1  1.00
  .28887547253       .46445822433
P  1  1.00
  .10056823671       .24955789874
D  1  1.00
        1.0970000000         1.0000000000
D  1  1.00
        0.3180000000         1.0000000000
F  1  1.00
        0.7610000000         1.0000000000
****
Bi    0
S  4  1.00
  716.41435310       0.31254307133E-03
  83.806059047       0.17624768946E-02
  21.116962853      -0.21910983437
```

```
  15.491448187      0.40411224931
S  2  1.00
  23.239855029     -0.68255758685E-01
  6.6474255000      0.97888046471
S  1  1.00
  1.7617744005       1.0000000000
S  1  1.00
 0.87252866000       1.0000000000
S  1  1.00
 0.25618895997       1.0000000000
S  1  1.00
 0.97073913006E-01   1.0000000000
P  3  1.00
  15.249644669      0.74560356000
  14.846176053     -0.85578637338
  7.0636826784      0.40149159592
P  3  1.00
  2.5881255616      0.35542729633
  1.5020208499      0.63976991890
 0.76732724388      0.32332773839
P  1  1.00
 0.32797648982       1.0000000000
P  1  1.00
 0.13820335991       1.0000000000
P  1  1.00
 0.55137330969E-01   1.0000000000
D  6  1.00
  66.404481948      0.38102878348E-03
  13.858426961      0.10746152442E-01
  7.0654519000     -0.71947646845E-01
  2.5252144035      0.26195974989
  1.3419585000      0.42594750000
```

```
 0.68340941000      0.33680325627
D  1  1.00
 0.32934755420       1.0000000000
D  1  1.00
 0.14000000000       1.0000000000
F  1  1.00
   .31271            1.0000000
F  1  1.00
   1.05           1.0000000000
****

BI     0
BI-ECP     3     60
f POTENTIAL
  2
2      4.21454600           13.71338300
2      4.13340000           18.19430800
s-f POTENTIAL
  4
2     13.04309000          283.26422700
2      8.22168200           62.47195900
2      4.21454600          -13.71338300
2      4.13340000          -18.19430800
p-f POTENTIAL
  6
2     10.46777700           72.00149900
2      9.11890100          144.00227700
2      6.75479100            5.00794500
2      6.25259200            9.99155000
2      4.21454600          -13.71338300
2      4.13340000          -18.19430800
d-f POTENTIAL
```

```
  6
2       8.08147400           36.39625900
2       7.89059500           54.59766400
2       4.95555600            9.98429400
2       4.70455900           14.98148500
2       4.21454600          -13.71338300
2       4.13340000          -18.19430800
```

Solvation calculation of $[BiPh]^-$

```
%NProc=10
%Mem=30GB
%chk=anion.chk
#P Stable=Opt SCRF=(Solvent=Acetonitrile)
#  Pseudo Gen UPBE1PBE
#  SCF=(XQC,MaxConventionalCycles=120)
#  Integral=(Grid=UltraFine,Acc2E=12) Symmetry=None
#  Geom=Checkpoint Guess=Read

anion

-1 2

H    0
S  3  1.00
    34.061341       .60251978E-02
    5.1235746       .45021094E-01
    1.1646626       .20189726
S  1  1.00
    .32723041       1.0000000
S  1  1.00
    .10307241       1.0000000
P  1  1.00
 .80   1.00
****
C    0
S  6  1.00
  13575.349682       .22245814352E-03
  2035.2333680       .17232738252E-02
  463.22562359       .89255715314E-02
  131.20019598       .35727984502E-01
```

```
  42.853015891       .11076259931
  15.584185766       .24295627626
S  2  1.00
  6.2067138508       .41440263448
  2.5764896527       .23744968655
S  1  1.00
  .57696339419       1.0000000000
S  1  1.00
  .22972831358       1.0000000000
S  1  1.00
  .95164440028E-01   1.0000000000
P  4  1.00
  34.697232244       .53333657805E-02
  7.9582622826       .35864109092E-01
  2.3780826883       .14215873329
  .81433208183       .34270471845
P  1  1.00
  .28887547253       .46445822433
P  1  1.00
  .10056823671       .24955789874
D  1  1.00
        1.0970000000         1.0000000000
D  1  1.00
        0.3180000000         1.0000000000
F  1  1.00
        0.7610000000         1.0000000000
****
Bi    0
S  4  1.00
  716.41435310       0.31254307133E-03
  83.806059047       0.17624768946E-02
  21.116962853      -0.21910983437
```

```
  15.491448187      0.40411224931
S  2  1.00
  23.239855029     -0.68255758685E-01
  6.6474255000      0.97888046471
S  1  1.00
  1.7617744005       1.0000000000
S  1  1.00
 0.87252866000       1.0000000000
S  1  1.00
 0.25618895997       1.0000000000
S  1  1.00
 0.97073913006E-01   1.0000000000
P  3  1.00
  15.249644669      0.74560356000
  14.846176053     -0.85578637338
  7.0636826784      0.40149159592
P  3  1.00
  2.5881255616      0.35542729633
  1.5020208499      0.63976991890
 0.76732724388      0.32332773839
P  1  1.00
 0.32797648982       1.0000000000
P  1  1.00
 0.13820335991       1.0000000000
P  1  1.00
 0.55137330969E-01   1.0000000000
D  6  1.00
  66.404481948      0.38102878348E-03
  13.858426961      0.10746152442E-01
  7.0654519000     -0.71947646845E-01
  2.5252144035      0.26195974989
  1.3419585000      0.42594750000
```

```
 0.68340941000      0.33680325627
D  1  1.00
 0.32934755420       1.0000000000
D  1  1.00
 0.14000000000       1.0000000000
F  1  1.00
   .31271            1.0000000
F  1  1.00
   1.05           1.0000000000
****

BI     0
BI-ECP     3     60
f POTENTIAL
  2
2      4.21454600           13.71338300
2      4.13340000           18.19430800
s-f POTENTIAL
  4
2     13.04309000          283.26422700
2      8.22168200           62.47195900
2      4.21454600          -13.71338300
2      4.13340000          -18.19430800
p-f POTENTIAL
  6
2     10.46777700           72.00149900
2      9.11890100          144.00227700
2      6.75479100            5.00794500
2      6.25259200            9.99155000
2      4.21454600          -13.71338300
2      4.13340000          -18.19430800
d-f POTENTIAL
```

```
 6
2       8.08147400           36.39625900
2       7.89059500           54.59766400
2       4.95555600            9.98429400
2       4.70455900           14.98148500
2       4.21454600          -13.71338300
2       4.13340000          -18.19430800
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