Chlorine-Benzene Complexes – The Reliability of Density Functionals for Non-Covalent Radical Complexes

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Supplementary information

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Key η_1-π Complex geometries (G03 archive entries)

η_1-σ Complex geometries (G03 archive entries)

Calculation of ZPE correction terms

Scale factors were determined from a least squares fit to a series of 20 small molecules for which the ZPE has already been experimentally determined (listed below). This procedure was based on those already in the literature.

Molecule	Experimental kcal mol^{-1}	Experimental (hartrees)
C_2H_2	16.46	0.026231
C_2H_4	31.47	0.050151
$CH_2(^1A_1)$	10.33	0.016462
$CH_2(^3B_1)$	10.55	0.016812
CH_2O	16.53	0.026342
CH_3Cl	23.45	0.037370
CH_4	27.71	0.044159
CHN	9.95	0.015856
CO	3.11	0.004956
CO_2	7.24	0.011538
F_2	1.30	0.002072
H_2	6.21	0.009896
H_2O	13.25	0.021115
H_2S	9.40	0.014980
NH_3	21.20	0.033784
HF	5.85	0.009323
LiF	1.30	0.002072
N_2	3.36	0.005355
O_2	2.25	0.003586
NO_2	6.77	0.010789

Calculation of ZPE correction term for BH&HLYP/6-31G(d)

BH&HLYP/6-31G(d) ZPE scale factor

$y = 0.9472x - 8E\text{-}05$

$R^2 = 0.9995$
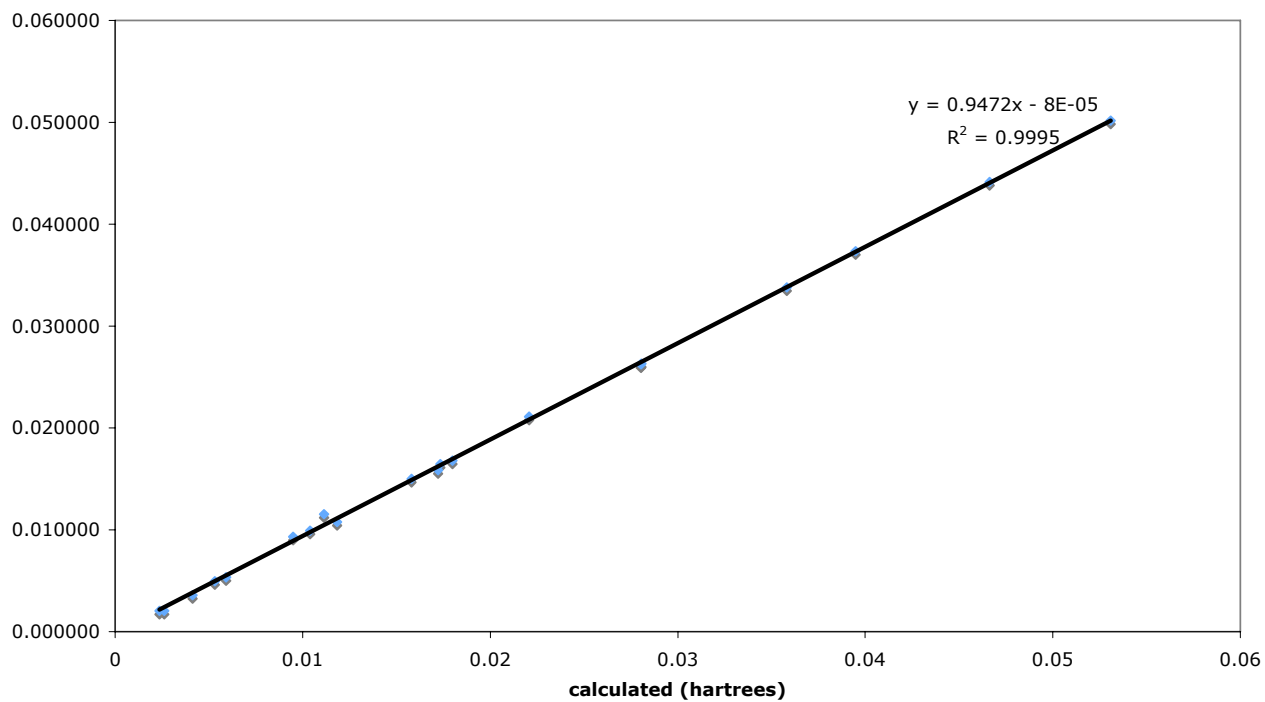
Calculation of ZPE correction term for BH&HLYP/6-311+G(d, p)

BH&HLYP/6-311+G(d,p) ZPE scale factor

$y = 0.9585x - 0.0001$

$R^2 = 0.9994$
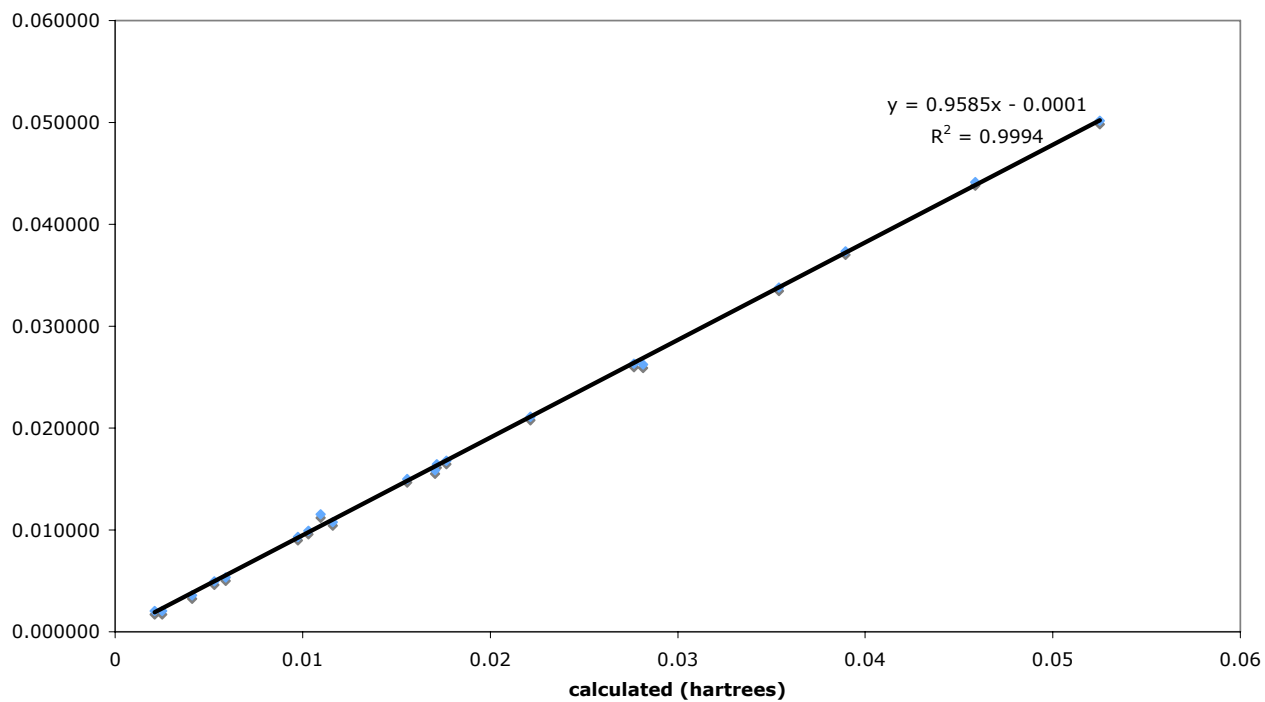
Calculation of ZPE correction term for B3PW91/6-311+G(d, p)

B3PW91/6-311+G(d,p) ZPE scale factor

$y = 0.9873x - 4E\text{-}05$

$R^2 = 0.9997$

calculated (hartrees)
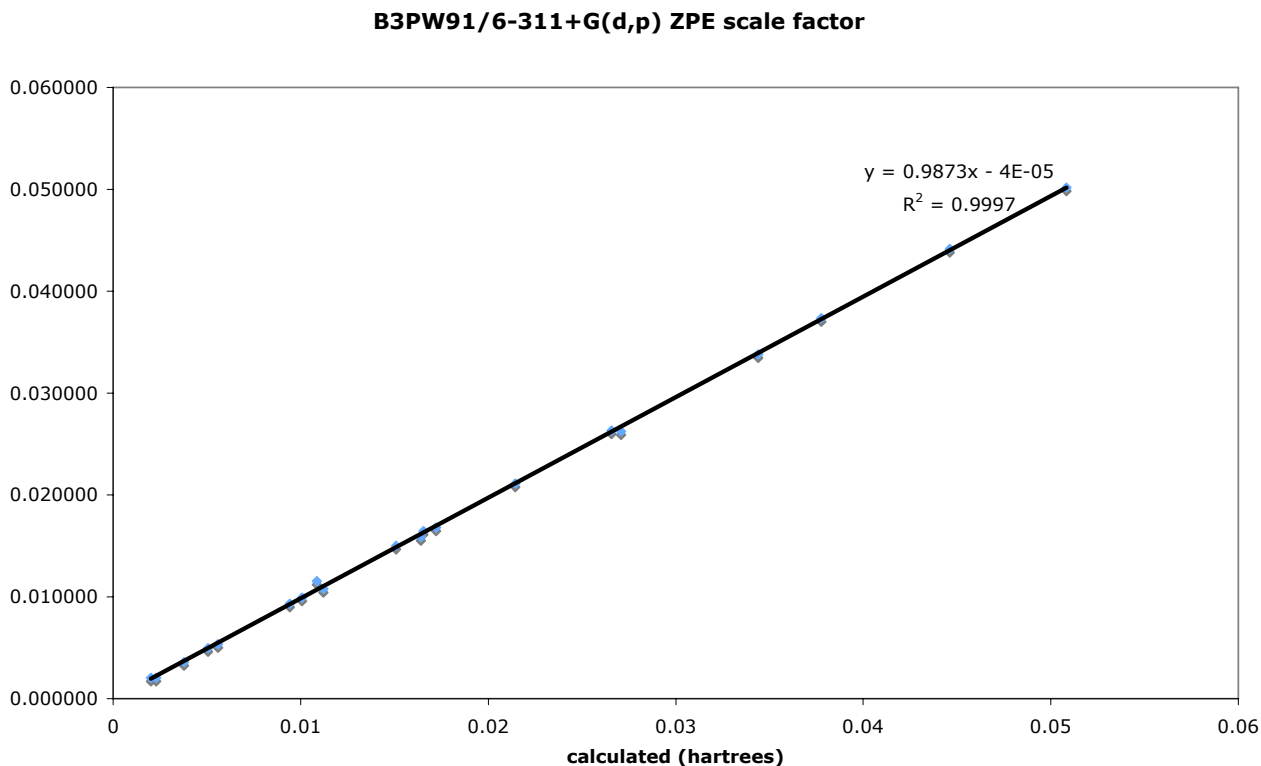
Calculation of ZPE correction term for MPW1K/6-311+G(3df, 2p)

MPW1K/6-311+G(3df,2p) ZPE scale factor

$y = 0.9653x - 0.0002$

$R^2 = 0.9994$

calculated (hartrees)
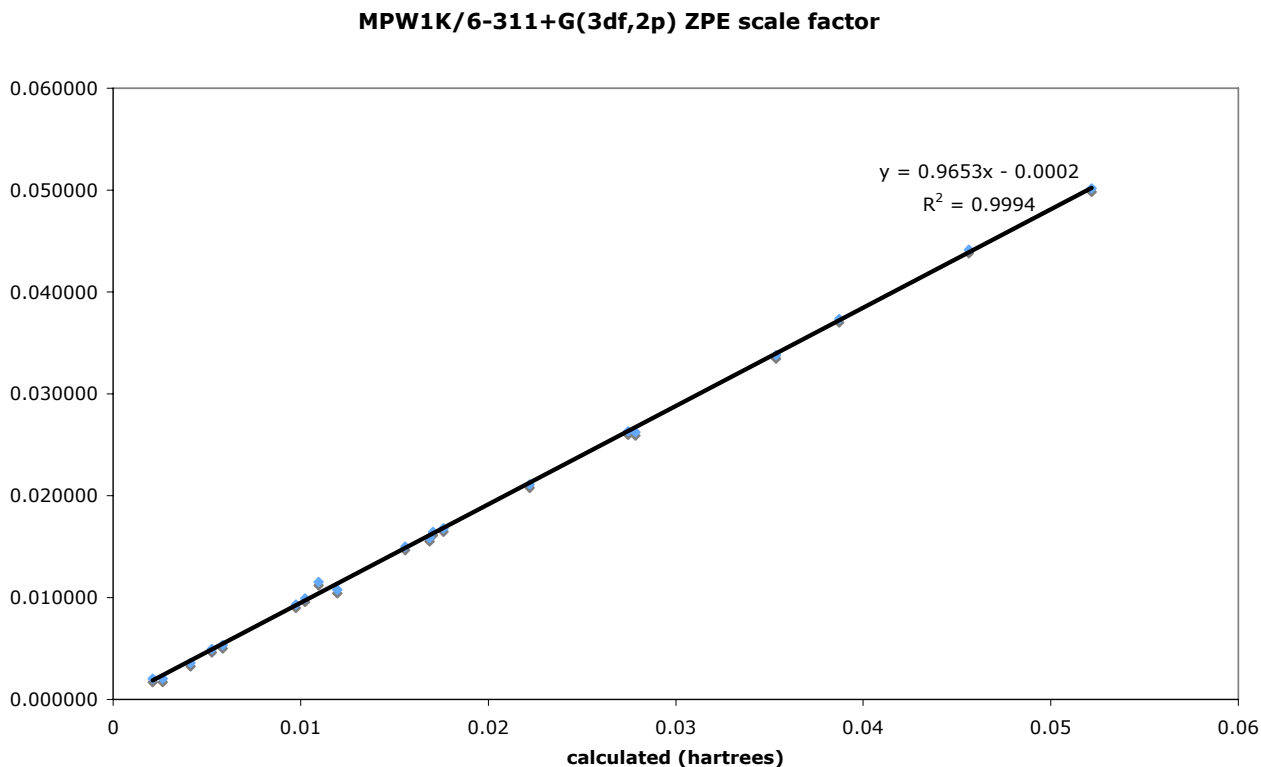
Calculation of ZPE correction term for MPWB1K/6-311+G(3df, 2p)

MPWB1K/6-311+G(3df,2p) ZPE scale factor

$$y = 0.967x - 0.0002$$
$$R^2 = 0.9994$$

calculated (hartrees)
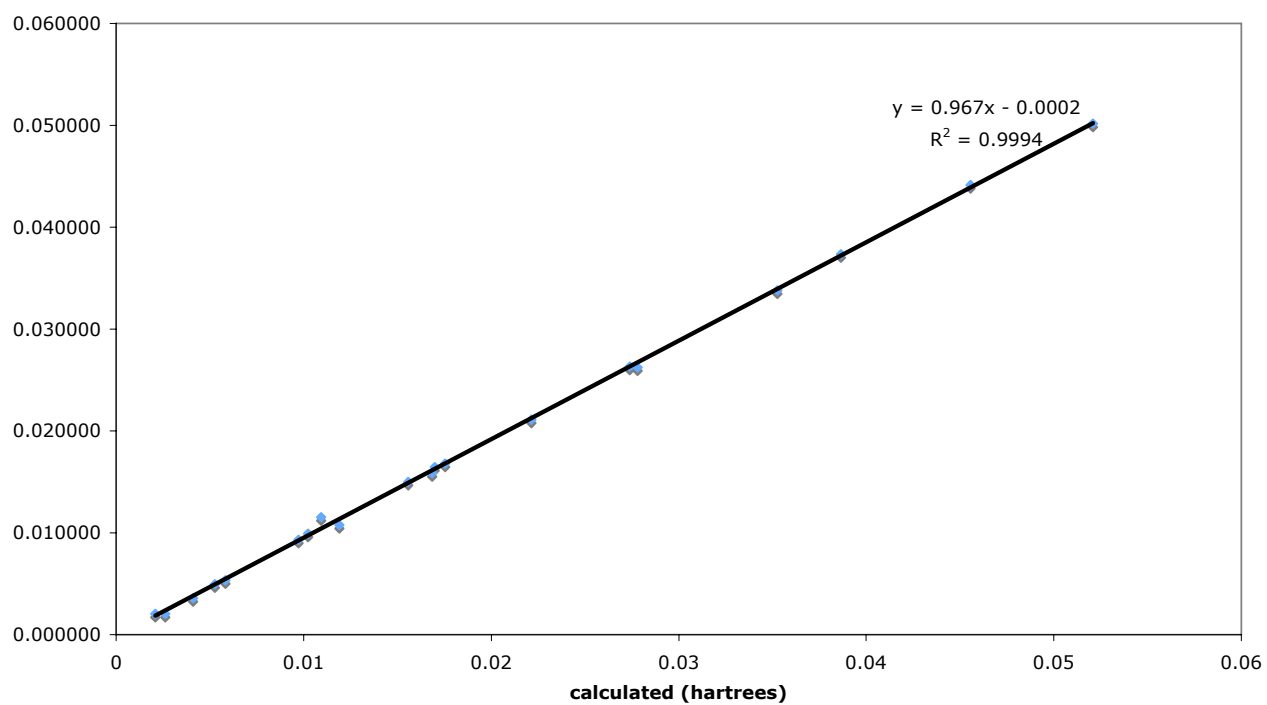
Key η₁-π Complex geometries

B3LYP/6-31G(d)

1\1\GINC-NODE13\FOpt\UB3LYP\6-31G(d)\C6H6Cl1(2)\CHS60A\11-Jan-2006\0\\
#P B3LYP/6-31G(D) OPT\\Cmplx\\0,2\C,0.,0.,0.\C,0.0030750793,-1.0827565
014,-0.8685209492\C,0.0081568466,-0.8667859538,-2.2538908637\C,0.00995
73362,0.4349647741,-2.7748137969\C,0.0069102752,1.5240371158,-1.914226
982\C,0.0148025945,1.3179725481,-0.514441476\H,-0.117029517,2.15979415
38,0.1553097937\H,0.010490012,2.5376583805,-2.3025141157\H,0.014677640
9,0.5884198723,-3.850039565\H,0.0124958705,-1.7170232976,-2.930802587\
H,0.002504134,-2.0962594488,-0.478018432\H,-0.0017021348,-0.1512807175
,1.074858688\Cl,2.5116563464,1.8183920484,-0.1070154679\\Version=x86-L
inux-G03RevB.04\State=2-A\HF=-692.4018954\S2=0.759809\S2-1=0.\S2A=0.75
007\RMSD=1.725e-09\RMSF=9.026e-05\Dipole=-0.0033028,-1.3354626,0.87057
64\PG =C01 [X(C6H6Cl1)]\\@

BH&HLYP/6-31G(d)

1\1\GINC-NODE01\FOpt\UBHandHLYP\6-31G(d)\C6H6Cl1(2)\CHS60A\10-Jan-2007
\0\\#P BHANDHLYP/6-31G(D) OPT FREQ\\C6H6---Cl\\0,2\C,-1.2128776211,-0.
7287305917,-0.1210653571\C,-1.2134088238,-0.7182653024,1.2584255313\C,
-0.0077232078,-0.7132014784,1.9518619786\C,1.2030650774,-0.7199039407,
1.2673882453\C,1.2127526223,-0.7303754064,-0.1120686559\C,0.0025565588
,-0.7205748281,-0.8210563268\H,0.006440746,-0.8398275149,-1.8900898195
\H,2.1433989536,-0.7355595423,-0.6538477551\H,2.131024418,-0.716386899
4,1.8147452316\H,-0.0117149394,-0.7039570184,3.0297767399\H,-2.1453972
676,-0.7134870015,1.7988839647\H,-2.1394856833,-0.7326553931,-0.669733
0092\Cl,0.0064438885,1.7898930974,-1.4100381085\\Version=x86-Linux-G03
RevB.04\State=2-A\HF=-692.2373767\S2=0.78169\S2-1=0.\S2A=0.750709\RMSD
=4.301e-09\RMSF=1.450e-05\Dipole=-0.0033626,-1.1273775,0.7004053\PG=C0
1 [X(C6H6Cl1)]\\@

B3PW91/6-31G(d)

1\1\GINC-NODE03\FOpt\UB3PW91\6-31G(d)\C6H6Cl1(2)\CHS60A\10-Jan-2007\0\
\#P B3PW91/6-31G(D) OPT FREQ=NORAMAN\\C6H6---Cl\\0,2\C,-1.2227796556,-
0.6987563189,-0.1130691525\C,-1.2220497047,-0.7061164767,1.2719230666\
C,-0.0077841987,-0.709009806,1.9690784619\C,1.2116220993,-0.707766669,
1.2809495719\C,1.2226357786,-0.700414624,-0.1039990909\C,0.002586572,-
0.6736359982,-0.8205634372\H,0.0064615065,-0.8298026001,-1.8938483439\
H,2.1598100123,-0.698904239,-0.6518701303\H,2.1463510738,-0.7132093024
,1.8343018484\H,-0.0118181824,-0.7127097959,3.0560079475\H,-2.16086418
57,-0.7102887996,1.8183263518\H,-2.1558611281,-0.6959775437,-0.6678769
975\Cl,0.006502098,1.7373583316,-1.4353504232\\Version=x86-Linux-G03Re
vB.04\State=2-A\HF=-692.2563089\S2=0.76436\S2-1=0.\S2A=0.750146\RMSD=2
.357e-09\RMSF=2.070e-05\Dipole=-0.0041277,-1.335016,0.8687754\PG=C01 [
X(C6H6Cl1)]\\@

MPWB1K/6-31+G(d,p)

1\1\GINC-NODE11\FOpt\UmPWB95\6-31+G(d,p)\C6H6Cl1(2)\CHS60A\21-Dec-2006
\0\\#P MPWB95/6-31+G(D,P) OPT IOP(3/76=0560004400)\\C6H6---Cl benzene
chlorine complex\\0,2\C,-1.213437706,-0.7116415846,-0.136951476\C,-1.2
141453608,-0.698090188,1.2400567011\C,-0.0095558574,-0.6929530672,1.93
23940083\C,1.2006913143,-0.7035036009,1.2500572161\C,1.2113279218,-0.7
170775142,-0.1269099087\C,0.0018851741,-0.7039750694,-0.8362448894\H,0
.0060243572,-0.8338138529,-1.9060490861\H,2.142888529,-0.7201995338,-0
.6697256818\H,2.1291252681,-0.6986733338,1.7988084077\H,-0.0139929988,
-0.6787112562,3.0115426837\H,-2.1470614159,-0.6890873023,1.7810995653\
H,-2.1404750515,-0.7105965865,-0.6874644671\Cl,0.0095822586,1.74673694
18,-1.36838949\\Version=x86-Linux-G03RevB.04\State=2-A\HF=-692.3323887
\S2=0.767227\S2-1=0.\S2A=0.75021\RMSD=3.975e-09\RMSF=4.642e-06\Dipole=
-0.0055702,-1.1398256,0.728098\PG=C01 [X(C6H6Cl1)]\\@

MPW1K/6-31+G(d,p)

```
1\1\GINC-GN1\FOpt\UmPWPW91\6-31+G(d,p)\C6H6Cl1(2)\WEBMO\15-Nov-2006\0\
\#P MPWPW91/6-31+G(D,P) OPT IOP(3/76=0572004280 )\\C6H6.Cl\\0,2\C,-1.2
160007191,-0.6942279387,-0.1280581211\C,-1.2147392118,-0.7061225062,1.
2502291746\C,-0.0067587627,-0.7102053022,1.9434458503\C,1.2056624992,-
0.7077969437,1.2580216264\C,1.2158139397,-0.6959201164,-0.1202307642\C
,0.0022119982,-0.6599790058,-0.8325631953\H,0.0055447609,-0.8083185403
,-1.9005885377\H,2.1473551088,-0.6915710588,-0.6643952455\H,2.13513883
72,-0.715917567,1.8065297897\H,-0.010240574,-0.7166580551,3.0233819428
\H,-2.1477370959,-0.7129635709,1.792743372\H,-2.1440122121,-0.68858517
29,-0.6782086016\Cl,0.0056948656,1.7282073437,-1.3885017732\\Version=x
86-Linux-G03RevB.04\State=2-A\HF=-692.3553157\S2=0.791413\S2-1=0.\S2A=
0.751201\RMSD=6.399e-09\RMSF=8.624e-06\Dipole=-0.0032973,-1.1932889,0.
7623053\PG=C01 [X(C6H6Cl1)]\\@
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η_1-σ Complex geometries

BH&HLYP/6-31G(d)

1\1\GINC-NODE04\FOpt\UBHandHLYP\6-31G(d)\C6H6Cl1(2)\CHS60A\02-Feb-2007
\0\\#P BHANDHLYP/6-31G(D) OPT FREQ\\C6H6---Cl bh&hlyp\\0,2\C,-1.247260
2879,-0.4971390901,-0.0069240867\C,-1.2482011403,-0.4816196546,1.35374
61392\C,-0.041987614,-0.4729000485,2.079004399\C,1.1876780262,-0.51447
05934,1.3954687751\C,1.2329096473,-0.5305873465,0.0355571778\C,0.00736
45235,-0.4348595039,-0.7723537021\H,0.0131644853,-1.0947861746,-1.6305
740948\H,2.1723375019,-0.5688872385,-0.4893879777\H,2.105826606,-0.549
479728,1.9593409556\H,-0.0602094765,-0.4567604432,3.1555532664\H,-2.18
5728497,-0.4916026312,1.8858336185\H,-2.16885381,-0.5103407341,-0.5637
45502\Cl,0.0459084859,1.2506655513,-1.6955301459\\Version=x86-Linux-G0
3RevB.04\State=2-A'\HF=-692.2345665\S2=0.857558\S2-1=0.\S2A=0.756943\R
MSD=5.292e-09\RMSF=3.577e-05\Dipole=-0.0253988,-0.9040328,0.7710466\PG
=CS [SG(C2H2Cl1),X(C4H4)]\\@

MPWB1K/6-31+G(d,p)

1\1\GINC-NODE02\FOpt\UmPWB95\6-31+G(d,p)\C6H6Cl1(2)\CHS60A\02-Feb-2007
\0\\#P MPWB95/6-31+G(D,P) OPT IOP(3/76=0560004400)\\C6H6---Cl bb->sb\\
0,2\C,-1.2432284348,-0.4917936707,-0.0128269309\C,-1.2447959979,-0.478
0902562,1.3456737645\C,-0.0417513439,-0.4676266645,2.0693623957\C,1.18
46476724,-0.5108544042,1.3872861708\C,1.229227852,-0.5251378987,0.0295
222114\C,0.007579591,-0.4243152272,-0.7766077274\H,0.0132163968,-1.092
5646488,-1.6318556731\H,2.1706599629,-0.5633332232,-0.4951620095\H,2.1
04552367,-0.5472430864,1.9504860548\H,-0.0599667128,-0.4494094836,3.14
7167961\H,-2.1840919734,-0.489405245,1.8770285744\H,-2.1668304245,-0.5
048366305,-0.569456143\Cl,0.0454343736,1.2372765321,-1.6783922393\\Ver
sion=x86-Linux-G03RevB.04\State=2-A'\HF=-692.3310476\S2=0.802758\S2-1=
0.\S2A=0.751691\RMSD=6.865e-09\RMSF=2.768e-05\Dipole=-0.0229608,-0.815
9354,0.6980761\PG=CS [SG(C2H2Cl1),X(C4H4)]\\@

MPW1K/6-31+G(d,p)

1\1\GINC-NODE03\FOpt\UmPWPW91\6-31+G(d,p)\C6H6Cl1(2)\CHS60A\02-Feb-200
7\0\\#P MPWPW91/6-31+G(D,P) OPT IOP(3/76=0572004280)\\C6H6---Cl bb->s
b 1k\\0,2\C,-1.2473707562,-0.4762559333,-0.0052413776\C,-1.2479339994,
-0.4750783488,1.3561193715\C,-0.0420566319,-0.473464027,2.0825897911\C
,1.1875062305,-0.507923368,1.3978344891\C,1.2335253984,-0.5097139837,0
.0372523258\C,0.0077205277,-0.4116939826,-0.774898465\H,0.0126752619,-
1.1061454349,-1.6109558027\H,2.1762526146,-0.5405336562,-0.4871227395\
H,2.1081769934,-0.546641648,1.9612182504\H,-0.0604294686,-0.4659139609
,3.1611898405\H,-2.1880644169,-0.4887013504,1.8876306445\H,-2.17207836
07,-0.4818908643,-0.5616025547\Cl,0.0455954566,1.2208591044,-1.7007232
029\\Version=x86-Linux-G03RevB.04\State=2-A'\HF=-692.3574799\S2=0.8459
96\S2-1=0.\S2A=0.755349\RMSD=7.536e-09\RMSF=1.873e-06\Dipole=-0.022309
6,-0.792429,0.6785642\PG=CS [SG(C2H2Cl1),X(C4H4)]\\@

MPW1K/6-311+G(3df,2p)

1\1\GINC-NODE01\FOpt\UmPWPW91\6-311+G(3df,2p)\C6H6Cl1(2)\CHS60A\01-Feb
-2007\0\\#P MPWPW91/6-311+G(3DF,2P) OPT IOP(3/76=0572004280)\\C6H6---
Cl 1k opt freq bb\\0,2\C,-1.2379298821,-0.4838315901,-0.0438857835\C,-
1.2203791903,-0.6336076491,1.3012580953\C,-0.0094814717,-0.6980392454,
2.0063959852\C,1.207203104,-0.639159465,1.3107984191\C,1.2360106533,-0
.489489426,-0.0341632732\C,0.0024746046,-0.3192215549,-0.8154404246\H,
0.0046495289,-0.9201202785,-1.7185425656\H,2.1694998511,-0.4472214569,
-0.5691131358\H,2.1330287087,-0.7263405876,1.8552496448\H,-0.013945049
3,-0.8106421266,3.0766480878\H,-2.1508445313,-0.7165434838,1.838414154
7\H,-2.1669825676,-0.4373040373,-0.5861553785\Cl,0.0092474795,1.390486
209,-1.5438987598\\Version=x86-Linux-G03RevB.04\State=2-A'\HF=-692.442
8134\S2=0.840803\S2-1=0.\S2A=0.754828\RMSD=9.977e-09\RMSF=1.183e-05\Di
pole=-0.0038628,-0.7823604,0.5276199\PG=CS [SG(C2H2Cl1),X(C4H4)]\\@

Parameters for optimised DFT geometries
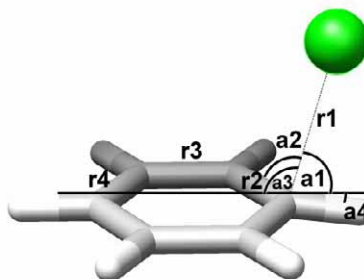
r1=Cl-C(ipso); r2=C(i)-C(ortho); r3=C(o)-C(meta); r4=C(m)-C(para); a1=Cl-C(i)-H(i); a2=Cl-C(i)-C(o); a3=Cl-C(i)-C(p); a4=H(i)-C(i)-C(p).

Table 1. Geometric parameters (as specified in Figure 1) for the π-complex calculated at different levels of density functional theory.

Level of Theory	r1	r2	r3	r4	a1	a2	a3	a4
B3LYP/6-31G(d)	2.579	1.414	1.389	1.402	82.4	97.7	104.6	7.1
B3LYP/6-311+G(d,p)	2.579	1.412	1.385	1.399	82.4	97.7	104.6	7.1
B3LYP/aug-cc-pVTZ	2.554	1.409	1.381	1.396	82.3	97.8	104.8	7.1
BH&HLYP/6-31G(d)	2.579	1.403	1.379	1.391	83.2	97.0	103.1	6.2
BH&HLYP/6-311+G(d,p)	2.594	1.400	1.378	1.389	82.8	96.9	102.9	5.8
BH&HLYP/aug-cc-pVTZ	2.570	1.397	1.374	1.386	82.8	96.9	103.1	5.9
B3PW91/6-31G(d)	2.488	1.415	1.385	1.400	84.0	98.2	105.0	9.0
B3PW91/6-311+G(d,p)	2.485	1.413	1.382	1.398	84.0	98.2	104.9	8.8
B3PW91/aug-cc-pVTZ	2.440	1.411	1.378	1.395	84.0	98.5	105.5	9.5
MPWB1K/6-31+G(d,p)	2.508	1.402	1.377	1.389	84.7	96.6	102.0	6.7
MPWB1K/6-311+G(3df,2p)	2.440	1.398	1.370	1.384	85.1	96.8	102.1	7.2
MPWB1K/aug-cc-pVTZ	2.440	1.398	1.370	1.384	85.1	96.8	102.1	7.2
MPW1K/6-31+G(d,p)	2.452	1.408	1.378	1.392	84.8	97.9	104.2	8.9
MPW1K/6-311+G(3df,2p)	-	-	-	-	-	-	-	-
MPW1K/aug-cc-pVTZ	2.353	1.406	1.370	1.388	85.5	99.1	105.8	11.3
PBE1PBE/6-31+G(d,p)	2.448	1.416	1.384	1.400	84.8	98.3	104.8	10.6
PBE1PBE/6-311+G(3df,2p)	2.361	1.413	1.376	1.394	85.7	99.0	105.7	11.3
PBE1PBE/aug-cc-pVTZ	2.375	1.412	1.377	1.394	85.0	99.1	106.1	11.1
PBE/6-31+G(d,p)	2.462	1.426	1.393	1.410	84.2	98.6	106.0	10.2
PBE/6-311+G(3df,2p)	2.389	1.422	1.385	1.404	84.9	99.4	106.8	11.7
PBE/aug-cc-pVTZ	2.404	1.422	1.386	1.404	84.3	99.4	107.1	11.4

Table 2. Geometric parameters for the σ-complex calculated at different levels of density functional theory.

Level of Theory	r1	r2	r3	r4	a1	a2	a3	a4
BH&HLYP/6-31G(d)	1.922	1.471	1.361	1.407	98.8	107.7	119.5	38.3
BH&HLYP/aug-cc-pVTZ	1.915	1.466	1.354	1.403	98.7	107.5	119.4	38.1
B3PW91/aug-cc-pVTZ	2.000	1.455	2.366	1.404	95.7	106.0	116.0	31.8
MPWB1K/6-31+G(d,p)	1.867	1.464	1.351	1.399	100.1	107.8	119.6	39.6
MPWB1K/aug-cc-pVTZ	1.884	1.461	1.351	1.398	99.4	107.6	119.4	38.8
MPW1K/6-31+G(d,p)	1.877	1.474	1.361	1.408	100.1	108.2	120.8	41.0
MPW1K/6-311+G(3df,2p)	1.858	1.470	1.354	1.403	100.6	108.2	120.7	41.3
MPW1K/aug-cc-pVTZ	1.871	1.468	1.354	1.402	100.0	108.0	120.9	41.0
PBE1PBE/aug-cc-pVTZ	1.922	1.465	1.362	1.406	98.3	107.3	118.7	37.0

Energies of the π-complexes in Hartrees calculated for different DFT methods, with zero point correction energies and counterpoise corrected energies.

Table 3.

Level of Theory	Cl$^{\bullet}$	Benzene	zpe	Complex	zpe	CPC complex
B3LYP/6-31G(d)	-460.1366841	-232.2486611	0.100746	-692.404760	0.101302	-692.4001279
B3LYP/6-311+G(d,p)	-460.1668825	-232.3112362	0.100149	-692.4936911	0.100707	-692.4926034
BH&HLYP/6-31G(d)	-460.127075	-232.1003066	0.104440	-692.2373767	0.10494	-692.2358914
BH&HLYP/6-311+G(d,p)	-460.1554016	-232.1587875	0.103654	-692.3228968	0.104141	-692.3217265
B3PW91/6-31G(d)	-460.0809243	-232.1590497	0.100989	-692.2563089	0.101497	-692.2549924
B3PW91/6-311+G(d,p)	-460.1095778	-232.2157704	0.100393	-692.3409252	0.100851	-692.3395890
MPWB1K/6-31+G(d,p)	-460.1822126	-232.1379445	0.103344	-692.3323887	0.103733	-692.3318755
MPW1K/6-31+G(d,p)	-460.1441181	-232.2001933	0.103547	-692.3553157	0.103869	-692.354693
PBE1PBE/6-31+G(d,p)	-459.969235	-231.9812489	0.101153	-691.9666877	0.101541	-691.9661192
PBE1PBE/6-311+G(3df,2p)	-459.9978384	-232.0346681	0.100438	-692.0500185	0.100837	-692.0480439
PBE/6-31+G(d,p)	-459.929279	-231.953918	0.097792	-691.9069434	0.098181	-691.9064083
PBE/6-311+G(3df,2p)	-459.9591998	-232.0090607	0.097220	-691.9930102	0.097686	-691.9908631

DFT Energies of structures with a fully converged basis set (aug-cc-pVTZ)

Table 4.

DFT Method	Cl$^{\bullet}$	Benzene	zpe	π-complex	zpe	σ-complex	zpe
B3LYP	-460.1753305	-232.3355734	0.100334	-692.5254284	0.100855	n/i	-
BH&HLYP	-460.1649646	-232.1836527	0.103794	-692.356243	0.10426	-692.3541938	0.103248
B3PW91	-460.1189712	-232.2391325	0.100351	-692.372695	0.100807	-692.3716222	0.099953
MPWB1K	-460.2184347	-232.1987781	0.102849	-692.4296331	0.10331	-692.4298246	0.102511
MPW1K	-460.1806047	-232.2619143	0.10301	-692.4532949	0.103172	-692.4565329	0.102642
PBE1PBE	-460.0057068	-232.0424638	0.100792	-692.0641541	0.101061	-692.0648897	0.100446
PBEPBE	-459.9662324	-232.0171272	0.097593	-692.0067246	0.097890	n/i	-