Hexachlorobenzene negative ions formation in electron attachment experiments

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Figure caption

Fig. S1. Electron impact ionisation (70 eV) of hexachlorobenzene yielding Cl^+, $Cl_2^{+,}$ $C_6Cl_4^+$, $C_6Cl_5^+$ and $C_6Cl_6^+$ at 44, 48 and 54˚C.

Fig. S2. Shape of several valence molecular orbitals (HOMO–1, HOMO, LUMO, LUMO+1) in C_6Cl_6 of D_{6h} symmetry as calculated at the ωB97XD/aug-cc-pVDZ level.

Table caption

Table S1. Energies for selected reactions (in eV) after electron attachment to C_6Cl_6. The aug-cc-pVDZ basis set was employed for all calculations, CCSD values were single-point calculated in structures optimized at the ωB97XD/aug-cc-pVDZ level, using the zero-point energy correction at the same level.

Table S2. Relative energy of $^2E_{2u}$ and $^2A_{1g}$ states in $C_6Cl_6^-$ in the structure of C_6Cl_6 optimized at the ωB97XD/aug-cc-pVDZ level. The aug-cc-pVDZ basis set was used for the calculations.

Table S3. Experimental and calculated vertical electron affinity (VEA), adiabatic electron affinity (AEA) of chlorobenzene, 1,2-dichlorobenzene and hexachlorobenzene (in eV), calculated at the ωB97XD/aug-cc-pVDZ level. Negative calculated electron affinities are not shown.

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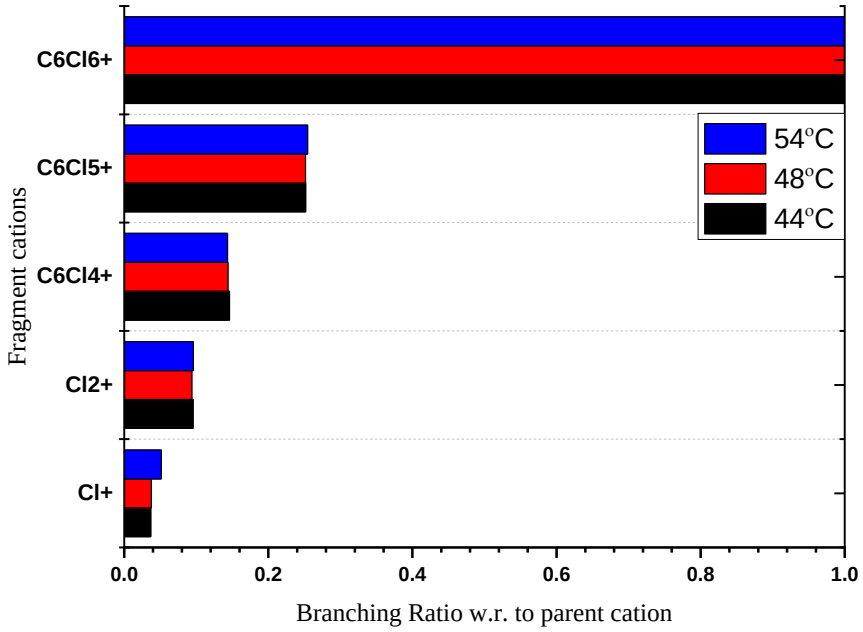

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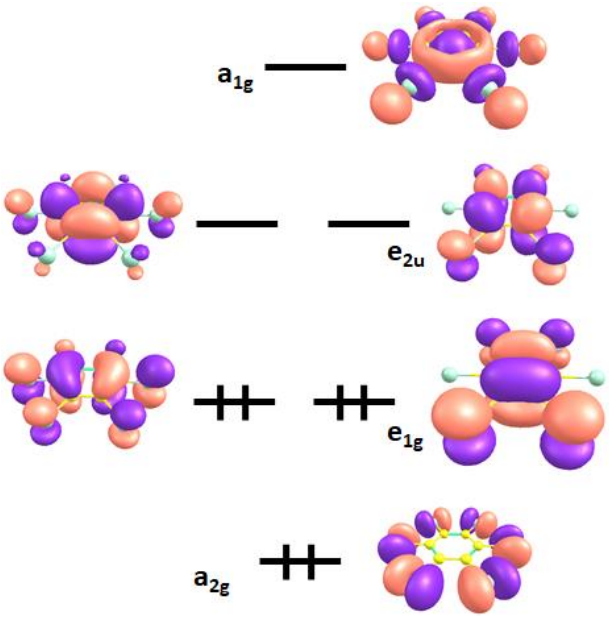

Table S1. Energies for selected reactions (in eV) after electron attachment to C_6Cl_6. The aug-cc-pVDZ basis set was employed for all calculations, CCSD values were single-point calculated in structures optimized at the ωB97XD/aug-cc-pVDZ level, using the zero-point energy correction at the same level.

reaction	ωB97XD	B3LYP	CCSD//ωB97XD
$C_6Cl_6 + e^- \rightarrow C_6Cl_6^-$	–1.07	–1.33	–0.92
$C_6Cl_6 + e^- \rightarrow Cl_2^- + C_6Cl_4$	1.72	1.10	1.97
$C_6Cl_6 + e^- \rightarrow C_6Cl_5^- + Cl$	0.85	0.52	0.77
$C_6Cl_6 + e^- \rightarrow C_6Cl_4^- + Cl_2$	2.13	1.66	2.38
$C_6Cl_6 + e^- \rightarrow C_6Cl_4^- + 2\ Cl$	4.40	3.83	4.13
$C_6Cl_6 + e^- \rightarrow Cl^- + C_6Cl_5$	0.19	–0.07	0.27

Table S2. Relative energy of $^2E_{2u}$ and $^2A_{1g}$ states in $C_6Cl_6^-$ in the structure of C_6Cl_6 optimized at the ωB97XD/aug-cc-pVDZ level. The aug-cc-pVDZ basis set was used for the calculations.

active space	CASSCF		MRCI	
	$^2E_{2u}$	$^2A_{1g}$	$^2E_{2u}$	$^2A_{1g}$
(5,5)	0.00	0.25	0.00	0.21
(5,7)	0.00	–0.03	0.00	–0.05
(5,8)	0.00	0.26	0.00	0.18
(5,10)	0.00	0.19	–	–
(5,13)	0.00	0.08	–	–
(15,13)[a]	0.00	0.25	–	–
(25,18)[a]	0.00	0.21	–	–

a) Active space breaks symmetry slightly, leading to splitting of the $^2E_{2u}$ state of 0.18 meV and 1.7 meV for (15,13) and (25,18), respectively.

Table S3. Experimental and calculated vertical electron affinity (VEA), adiabatic electron affinity (AEA) of chlorobenzene, 1,2-dichlorobenzene and hexachlorobenzene (in eV), calculated at the ωB97XD/aug-cc-pVDZ level. Negative calculated electron affinities are not shown.

	C_6H_5Cl	1,2–$C_6H_4Cl_2$	C_6Cl_6
VEA	–	–	0.27
AEA	–	0.18	1.07
Exp.	–0.14[1]	0.08[1]	0.98[1]

Cartesian coordinates (in Å) of structures optimized at the *ω*B97XD/aug-cc-pVDZ level along with the zero-point corrected energy (in Hartree).

C6Cl4-
E = -2069.294225
C -0.000000 0.672148 -2.082482
C -0.000000 1.382052 -0.905654
C 0.000000 0.702628 0.324202
C -0.000000 -0.702628 0.324202
C -0.000000 -1.382052 -0.905654
C -0.000000 -0.672148 -2.082482
Cl -0.000000 3.168853 -0.907502
Cl 0.000000 1.574114 1.847714
Cl -0.000000 -1.574114 1.847714
Cl -0.000000 -3.168853 -0.907502

C6Cl4
E = -2069.202861
C 0.000000 0.621738 -1.970330
C 0.000000 1.458657 -0.879796
C 0.000000 0.712230 0.320838
C -0.000000 -0.712230 0.320838
C -0.000000 -1.458657 -0.879796
C -0.000000 -0.621738 -1.970330
Cl 0.000000 3.183251 -0.935863
Cl 0.000000 1.564072 1.828553
Cl -0.000000 -1.564072 1.828553
Cl -0.000000 -3.183251 -0.935863

C6Cl5-
E = -2529.565542
C 0.000000 1.158586 -1.144654
C -0.000000 0.000000 -1.887993
C -0.000000 -1.158586 -1.144654
C 0.000000 -1.211551 0.253282
C 0.000000 0.000000 0.958613
C 0.000000 1.211551 0.253282
Cl 0.000000 -2.737463 -2.017917
Cl 0.000000 -2.724947 1.143105
Cl 0.000000 0.000000 2.706845
Cl 0.000000 2.724947 1.143105
Cl 0.000000 2.737463 -2.017917

C6Cl5
E = -2529.452678
C -0.000000 1.222216 -1.122382
C 0.000000 0.000000 -1.737063
C -0.000000 -1.222216 -1.122382
C 0.000000 -1.222421 0.281727
C -0.000000 -0.000000 0.975583
C 0.000000 1.222421 0.281727
Cl 0.000000 -2.678067 -2.061272
Cl 0.000000 -2.723913 1.139572
Cl -0.000000 -0.000000 2.705559
Cl 0.000000 2.723913 1.139572
Cl 0.000000 2.678067 -2.061272

C6Cl6-
E = -2989.776729
C 1.211726 0.688049 -0.057280
C 0.000000 1.398639 0.053689
C -1.211726 0.688049 -0.057280
C -1.211726 -0.688049 -0.057280
C -0.000000 -1.398639 0.053689
C 1.211726 -0.688049 -0.057280
Cl -2.714003 1.595161 -0.358223
Cl -2.714003 -1.595161 -0.358223
Cl 0.000000 -3.048445 0.737931
Cl 2.714003 -1.595161 -0.358223
Cl 2.714003 1.595161 -0.358223
Cl 0.000000 3.048445 0.737931

C6Cl6
E = -2989.737535
C 0.000000 1.400109 0.000000
C -1.212530 0.700055 0.000000
C -1.212530 -0.700055 0.000000
C 0.000000 -1.400109 0.000000
C 1.212530 -0.700055 0.000000
C 1.212530 0.700055 0.000000
Cl -2.709794 -1.564500 0.000000
Cl 0.000000 -3.129001 0.000000
Cl 2.709794 -1.564500 0.000000
Cl 2.709794 1.564500 0.000000
Cl -0.000000 3.129001 0.000000
Cl -2.709794 1.564500 -0.000000

Cl2-
E = -920.471346
Cl 0.000000 0.000000 1.330998
Cl 0.000000 0.000000 -1.330998

Cl2
E = -920.365185
Cl 0.000000 0.000000 1.009249
Cl 0.000000 0.000000 -1.009249

Cl-
E = -460.278011
Cl 0.000000 0.000000 0.000000

Cl
E = -460.140805
Cl 0.000000 0.000000 0.000000

C6Cl5…Cl-, TS
E = -2989.738735
cl -5.296965 0.808948 0.000002
c -0.683655 0.881730 -0.000001
c -0.889884 -0.476170 -0.000001
c 0.268267 -1.273430 -0.000000
c 1.539584 -0.674911 0.000000
c 1.675575 0.721441 0.000000
c 0.523555 1.523254 -0.000001
cl 0.599664 3.259358 -0.000001
cl 3.249300 1.458035 0.000001
cl 2.961933 -1.672446 0.000001
cl 0.116003 -3.001846 -0.000000
cl -2.488795 -1.099785 -0.000001

C6Cl5…Cl-, LM
E = -2989.745650
cl 5.522358 -0.687617 -0.000326
cl 2.578231 -0.468260 0.000317
c 0.845663 -0.322614 0.000144
c 0.041727 -1.431197 0.000117
c -1.324734 -1.462925 0.000038
c -1.990187 -0.228314 -0.000041
c -1.233970 0.954443 -0.000020
c 0.170838 0.912331 0.000073
cl -2.052209 2.487314 -0.000071
cl -3.727931 -0.174355 -0.000199
cl -2.178603 -2.981826 0.000048
cl 1.090153 2.381782 0.000120

References

1 J. R. Wiley, E. C. M. Chen, E. S. D. Chen, P. Richardson, W. R. Reed and W. E. Wentworth, The determination of absolute electron affinities of chlorobenzenes, chloronaphthalenes and chlorinated biphenyls from reduction potentials, *J. Electroanal. Chem.*, 1991, **307**, 169–182.