Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Stabilizing Otherwise Unstable Anions with Halogen Bonding

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Methods

Experimental

Anion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency photon beam and energy-analyzing the resultant photodetached electrons. It is governed by the energy-conserving relationship, hv = EBE + EKE, where h is the photon energy, EBE is the electron binding (transition) energy, and EKE is the electron kinetic energy. Our anion photoelectron spectrometer, which has been described previously,[1] consists of a laser photo emission anion source, a linear time-of-flight mass analyzer/selector, a pulsed Nd:YAG photodetachment laser, and a magnetic bottle electron energy analyzer. Photoelectron spectra were calibrated against the well-known photoelectron spectrum of Cu^-.[2] The $Pz(BrPh)_{1,2}^-$ anions were generated by placing several drops of Pz/BrPh solution in the pulsed valve, which is backed by ~60 psi ultra-high purity helium. Once the solution was supersonically expanded into the gas phase by the helium in the pulsed valve, it encountered a plume of electrons, which were generated by ablating a copper rod with a pulsed Nd:YAG laser beam operating at a wavelength of 532 nm, and formed anions. Negatively charged anions were then extracted into the spectrometer prior to mass selection and photodetachment.

Theoretical

Density functional theory calculations were conducted by applying M06-2X functional[3] using the Gaussian09 software package[4] to determine the geometries of $Pz(BrPh)_{1,2}^{0/-}$ clusters, the electron affinity (EA) and vertical detachment energy (VDE) values, and the charge distribution. The M06-2X is a widely accepted method to describe halogen bonding.[5,6] All geometries, including that of the anion and its corresponding neutral molecule, were fully optimized without any geometrical constraints using the 6-31++G (d, p) basis set and then improved by single point energy calculations with the 6-311++G (3df, 3pd) basis set.[7] The EA value is the energy difference between the ground state of the neutral and the ground state of the anion with zero point energy correction. The VDE is the energy difference between the ground state of the anion and the neutral with the same structure as the anion. The zero point energies are scaled by a factor of 0.95.[8] Natural population analysis (NPA), as implemented in the Gaussian09 code, was also carried out to determine the charge distribution of the anions. The NPA method has been found to be satisfactory in calculating the charge distribution within a cluster.[9-14] We also mapped the electrostatic potential surfaces (ESP) of Pz, Pz^- and $Pz(BrPh)_{1,2}^-$ to visualize the σ-hole, the halogen bond, and the effect that the halogen bond has on the charge distribution of the Pz^- kernel.

Figure S1. Experimental mass spectra and simulated isotopic distributions of $Pz(BrPh)_{1,2}^-$.

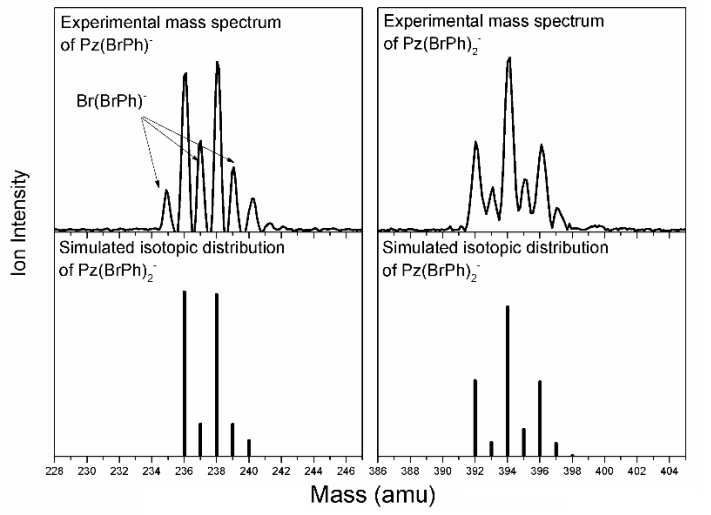

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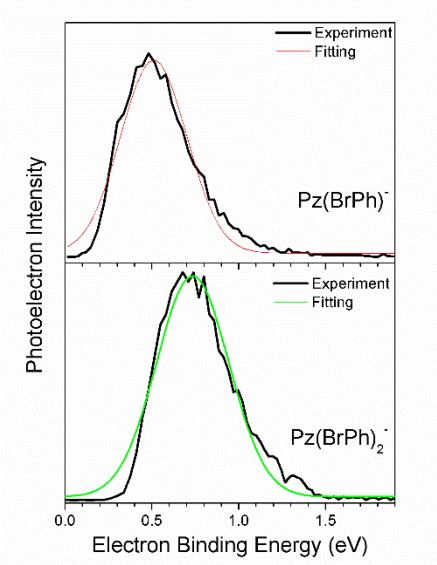
Figure S2. Gaussian fittings of the photoelectron spectra of $Pz(BrPh)_{1,2}^-$.



The calculated 3D coordinates of all the studied species

Pz

C	-1.12728300	-0.69468400	0.00000100
C	-1.12733800	0.69459700	0.00000200
C	1.12727800	0.69468800	-0.00000400
C	1.12734300	-0.69459300	-0.00000200
H	-2.05672500	-1.24964700	-0.00000400
H	-2.05683800	1.24950200	-0.00000500
H	2.05673200	1.24967000	0.00001000
H	2.05683100	-1.24948100	0.00001000
N	0.00005900	-1.39620000	0.00000000
N	-0.00005900	1.39618700	0.00000100

Pz^-

C	-1.12893900	-0.68468100	0.00000100
C	-1.12887900	0.68477400	0.00000100
C	1.12894500	0.68467000	0.00000000
C	1.12887300	-0.68478500	0.00000100
H	-2.08075300	-1.21007500	0.00000200
H	-2.08060700	1.21029900	0.00000200
H	2.08072000	1.21010900	0.00000200
H	2.08064000	-1.21026500	0.00000300
N	-0.00006700	-1.46245600	-0.00000200
N	0.00006700	1.46246500	-0.00000200

Pz(BrPh)

C	3.30300100	-0.00012400	-1.13292200
C	4.69830400	-0.00004400	-1.12727500
C	4.68985000	0.00029100	1.13585100
C	3.29453200	0.00021400	1.13115200
H	2.74348200	-0.00029800	-2.06493600
H	5.26017400	-0.00014600	-2.05713500
H	5.24479000	0.00051400	2.06988900
H	2.72801800	0.00035200	2.05891800
N	2.59630100	-0.00000800	-0.00349600
N	5.39948200	0.00015800	0.00690600

C	-4.38184200	1.20545200	0.00254400
C	-2.98835500	1.20896300	0.00029000
C	-2.29914100	-0.00011100	-0.00077400
C	-2.98874800	-1.20894800	0.00060000
C	-4.38224000	-1.20495200	0.00289200
C	-5.08184100	0.00036100	0.00384700
H	-4.91851000	2.14909300	0.00326500
H	-2.43689600	2.14324900	-0.00077200
H	-2.43760200	-2.14342300	-0.00019500
H	-4.91922600	-2.14841100	0.00389100
H	-6.16705700	0.00053200	0.00558200
Br	-0.40710800	-0.00026100	-0.00398900

$Pz(BrPh)^-$

C	-3.16674700	-0.30830300	-1.09470600
C	-4.54072500	-0.30737500	-1.08932200
C	-4.53794200	0.30789900	1.09198300
C	-3.16394900	0.30828400	1.09401100
H	-2.62847600	-0.56539100	-2.00847200
H	-5.07588800	-0.56489800	-2.00439000
H	-5.07079000	0.56561700	2.00833900
H	-2.62335300	0.56507200	2.00650200
N	-2.39294200	-0.00014100	-0.00128900
N	-5.31702800	0.00042100	0.00227100
C	4.31533900	-1.16702700	0.29501800
C	2.92166900	-1.16679000	0.29514500
C	2.21497700	-0.00022100	-0.00010500
C	2.92148300	1.16666700	-0.29472300
C	4.31513000	1.16745400	-0.29354100
C	5.01918000	0.00032400	0.00098700
H	4.85153300	-2.08341300	0.52587000
H	2.37084700	-2.07413100	0.52407000
H	2.37044000	2.07376700	-0.52403400
H	4.85112100	2.08406800	-0.52397100
H	6.10517700	0.00050400	0.00137500
Br	0.31510500	-0.00024600	-0.00116100

$Pz(BrPh)_2$

C	0.69483900	-0.17049500	-1.13479800
C	-0.70012800	-0.17044800	-1.13157700
C	-0.69478600	-0.17072200	1.13578700
C	0.70017800	-0.17081000	1.13256600
H	1.25756800	-0.16962600	-2.06472800
H	-1.26722600	-0.16957000	-2.05884500
H	-1.25751200	-0.17002800	2.06571900
H	1.26727300	-0.17023000	2.05983500
N	1.39745300	-0.16989000	-0.00275300
N	-1.39740200	-0.16975300	0.00374600
C	-6.88223400	1.29983900	-0.00081700
C	-8.27298700	1.38336700	-0.00280700
C	-9.04682300	0.22403400	-0.00354700
C	-8.42364700	-1.02247000	-0.00227300
C	-7.03308500	-1.11362300	-0.00029300
C	-6.26977700	0.05024600	0.00045300
H	-6.27407300	2.19817000	-0.00021300
H	-8.74970500	2.35874800	-0.00381100
H	-10.12992900	0.29187600	-0.00510400
H	-9.01843400	-1.93055300	-0.00279900
H	-6.54151200	-2.08083300	0.00078200
C	8.42368600	-1.02233700	0.00112100
C	7.03312900	-1.11355200	-0.00052400

C	6.26976000	0.05028000	-0.00076700
C	6.88214800	1.29990200	0.00066100
C	8.27289900	1.38349100	0.00232200
C	9.04679700	0.22420100	0.00256200
H	9.01851700	-1.93039200	0.00127100
H	6.54160600	-2.08078700	-0.00172800
H	6.27394000	2.19820200	0.00043600
H	8.74956700	2.35889600	0.00347100
H	10.12989900	0.29210400	0.00386300
Br	4.38036900	-0.06272200	-0.00300300
Br	-4.38037300	-0.06253300	0.00318900

$Pz(BrPh)_2^-$

C	0.68295400	-0.22364100	-1.13954200
C	-0.68950100	-0.22365300	-1.13565600
C	-0.68299600	-0.22425800	1.14169700
C	0.68947700	-0.22440300	1.13781800
H	1.22210200	-0.22327500	-2.08757400
H	-1.23415600	-0.22327400	-2.08053700
H	-1.22209800	-0.22440000	2.08976600
H	1.23399900	-0.22463600	2.08278600
N	1.45388700	-0.22214200	-0.00303600
N	-1.45390900	-0.22201600	0.00521700
C	-6.68195000	1.31597900	-0.00138500
C	-8.07185700	1.41476200	-0.00371100
C	-8.85890500	0.26347900	-0.00426000
C	-8.24223000	-0.98705400	-0.00250100
C	-6.85204900	-1.08577900	-0.00024400
C	-6.06356100	0.06544600	0.00036300
H	-6.06630500	2.21026800	-0.00092400
H	-8.53977400	2.39539700	-0.00511300
H	-9.94213700	0.34036200	-0.00606000
H	-8.84396500	-1.89166600	-0.00289900
H	-6.36861100	-2.05809500	0.00117800
C	8.24222800	-0.98702900	0.00006100
C	6.85204000	-1.08572800	-0.00155600
C	6.06356100	0.06550000	-0.00101200
C	6.68197400	1.31602200	0.00119900
C	8.07187900	1.41477800	0.00291600
C	8.85892400	0.26349000	0.00234300
H	8.84394800	-1.89165200	-0.00042800
H	6.36861900	-2.05805300	-0.00339600
H	6.06633100	2.21031300	0.00162700
H	8.53979100	2.39541600	0.00469300
H	9.94215400	0.34037400	0.00365000
Br	4.16897400	-0.06367600	-0.00327600
Br	-4.16896500	-0.06362200	0.00352700

BrPh

C	2.16470000	-1.20005500	0.00000100
C	0.77696100	-1.20814600	-0.00000200
C	0.09835700	0.00000600	-0.00000300
C	0.77696600	1.20815000	-0.00000200
C	2.16470800	1.20004900	0.00000100
C	2.86115500	-0.00000400	0.00000000
H	2.69979000	-2.13912700	0.00000300
H	0.22763500	-2.13777700	0.00000100
H	0.22764900	2.13778700	0.00000000
H	2.69980200	2.13911800	0.00000300
H	3.94148400	-0.00000600	0.00000000
Br	-1.79581300	0.00000000	0.00000000

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