Supporting Information

for

Aromaticity of Unsaturated BEC_4 Heterocycles

(E = N, P, As, Sb, O, S, Se, Te)

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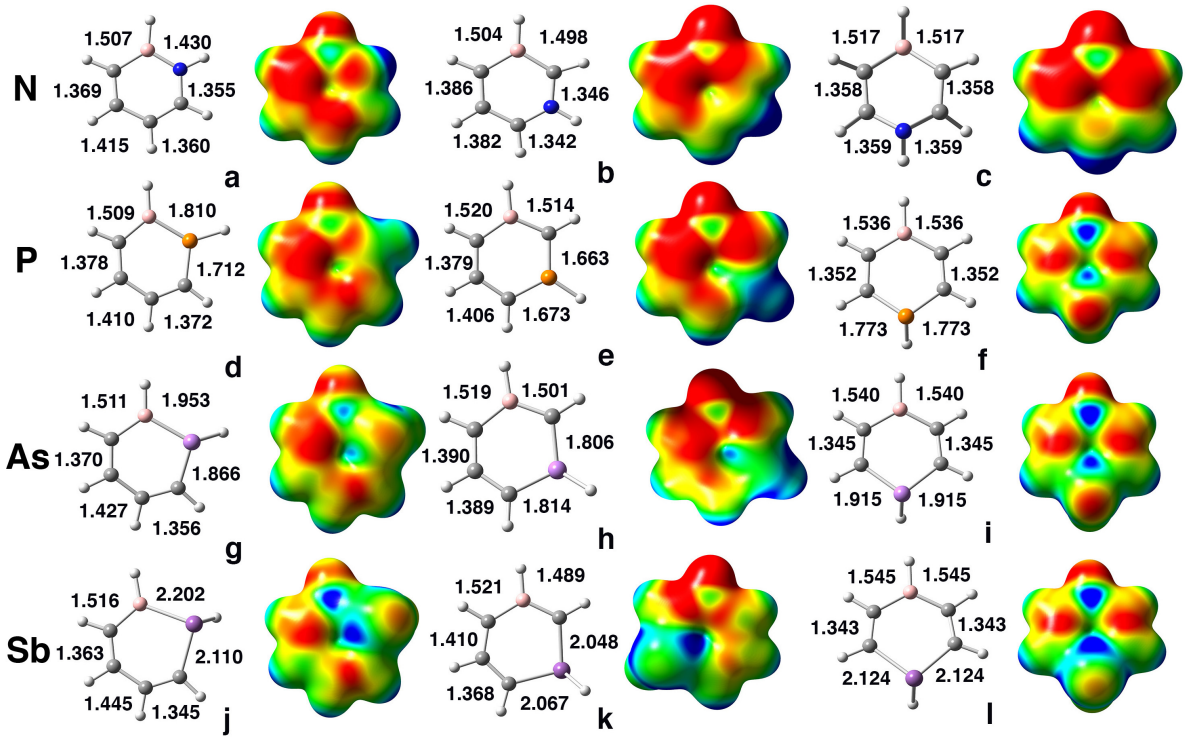


Figure 1: Optimized structures and electrostatic potential maps for pnictoborines. Note the potential for m-BSb (panel k) is rotated 180^o to orient the lone pair towards the viewer for clarity. The electrostatic potential maps are projected onto the ground state electron density to identify regions of charge inhomogeneity. Isosurface values range from -1.0×10^{-4}–$1.0\times10^{-1}$$a.u.$ (blue to red).

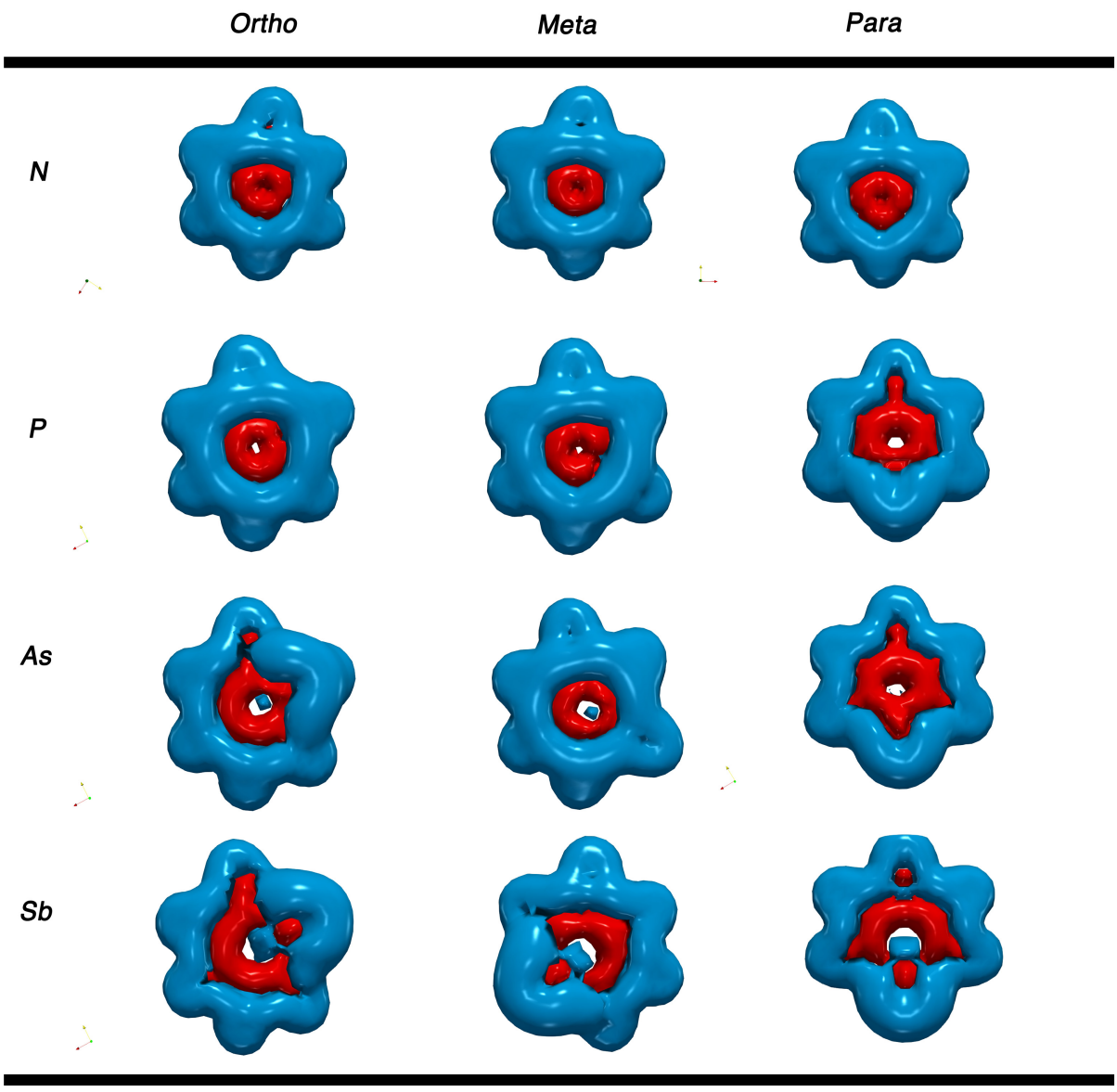


Figure 2: Signed modulus of the ring current for pnictoborines. The blue coloring indicates diatropic current, and red coloring marks paratropic current. The isosurface value ranges ± 0.01 nAT^{-1}. Locations of elemental substitutions correspond to positions shown in SI Fig. 1 except m-BSb, which is rotated 180^o.

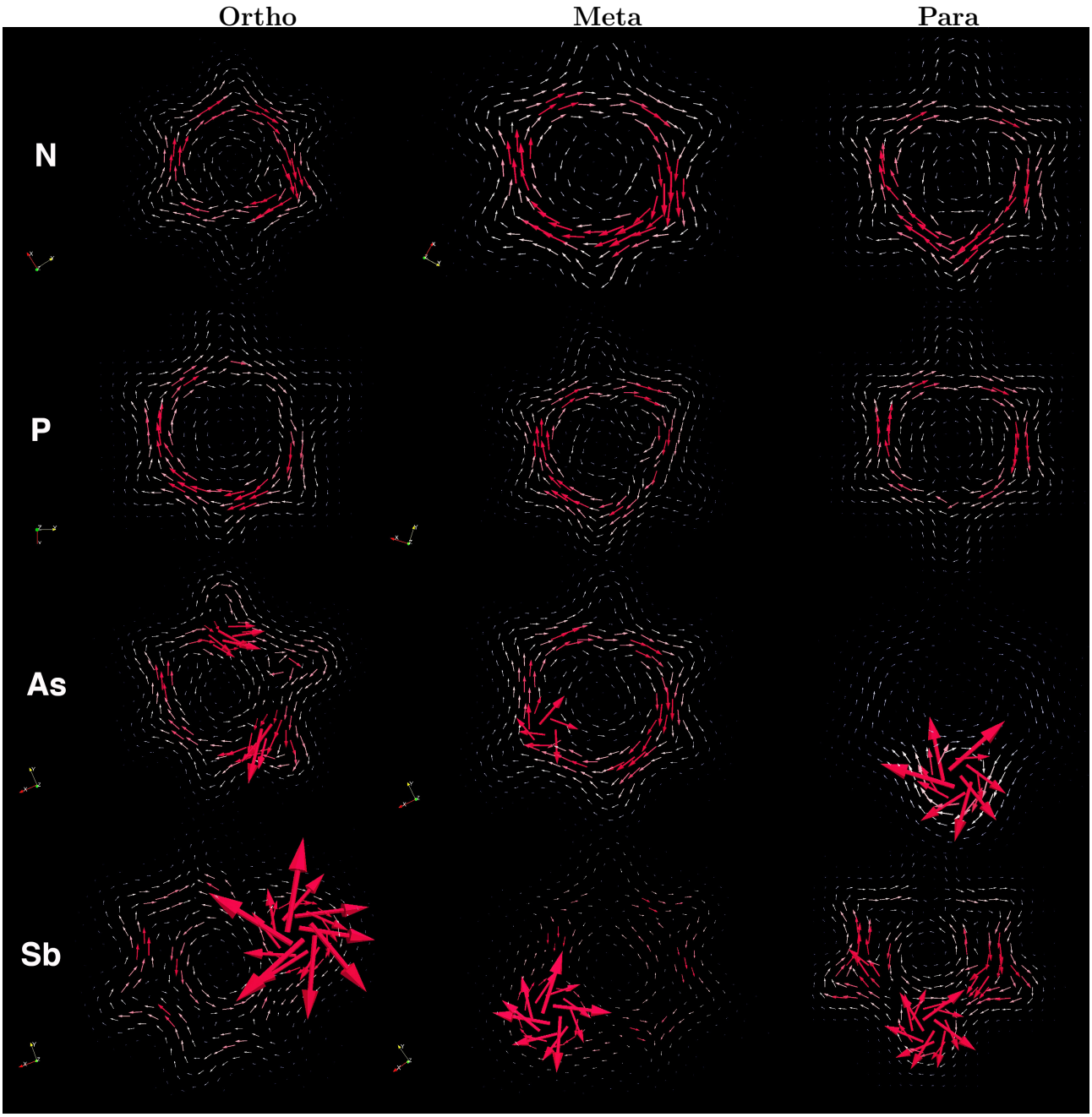


Figure 3: GIMIC ring current vector field set at 1 Å above the molecular plane of each pnictoborine. The plane was set to 2.0 Å for p-BAs to mitigate oversized vectors from the lone pair over the arsenic atom. The scale is 0.00-0.07 $a.u.$ (white-red) of the magnetic field strength. Locations of elemental substitutions correspond to positions shown in SI Fig. 1 except m-BAs and m-BSb which are rotated 180^o.

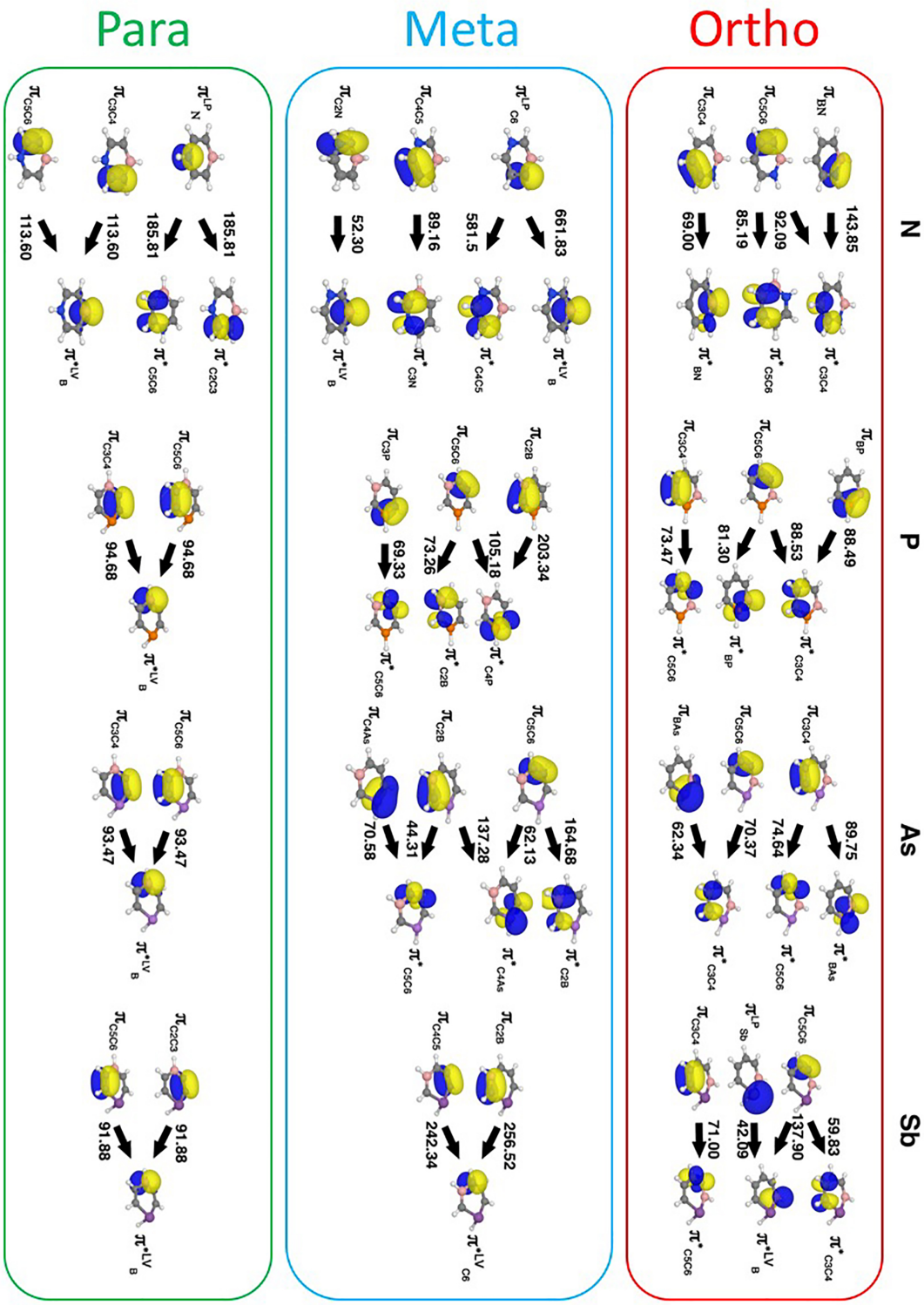


Figure 4: Donor-acceptor interactions among Lewis and non-Lewis type NBOs for all pnictoborines. Each NBO is labeled with an arrow pointing from the Lewis bonding NBOs (principle donor) to antibonding non-Lewis NBOs (principle acceptor). Above the arrows is the stabilization energy resulting from charge delocalization among NBOs in $kJ\ mol^{-1}$.

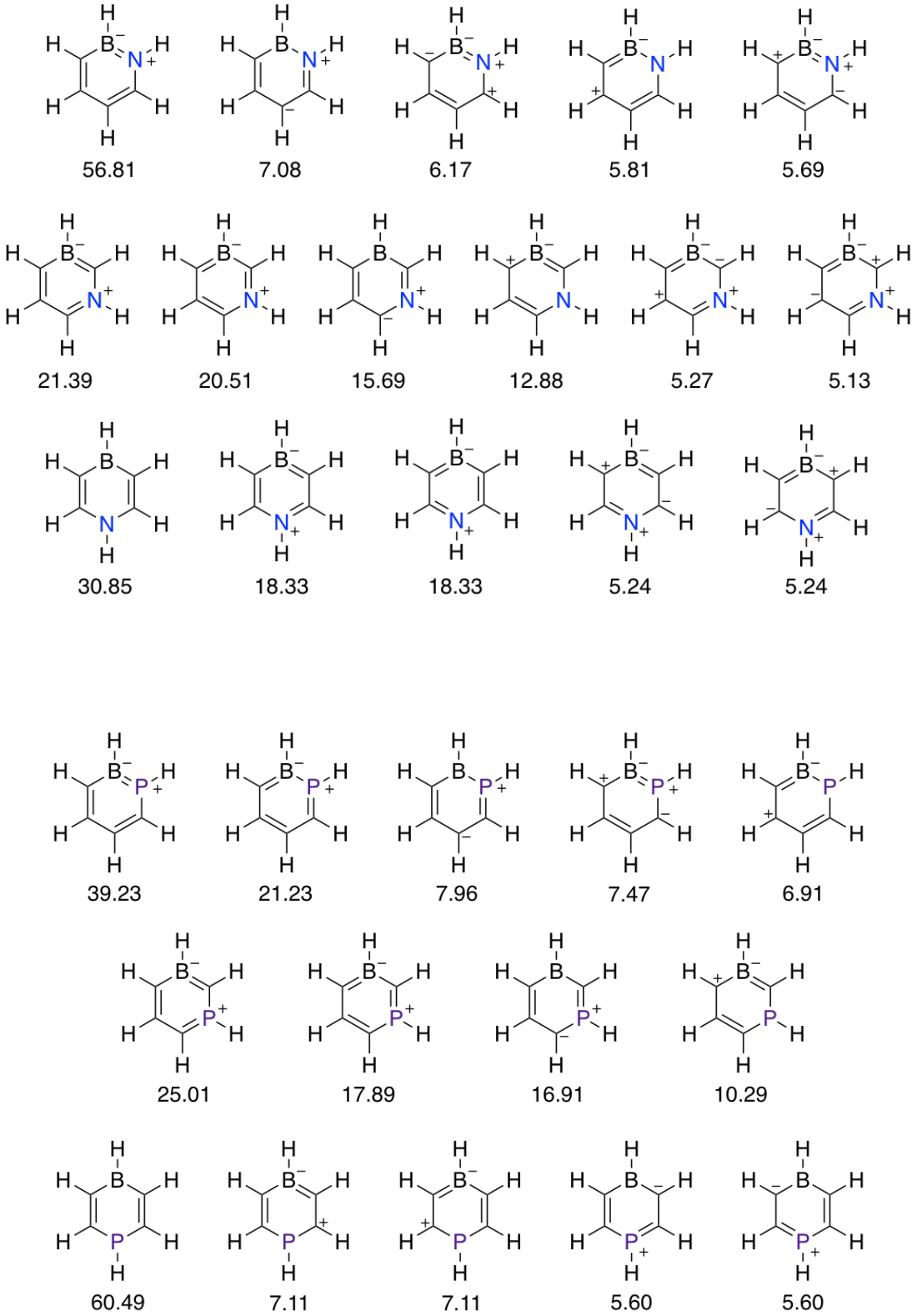


Figure 5: Major resonance contributors of nitrogen (top) and phosphorus (bottom) substituted boron heterocycles resulting from NRT analysis. The numeric values are the contribution of each structure (%). Structures contributing less than 5% are not shown.

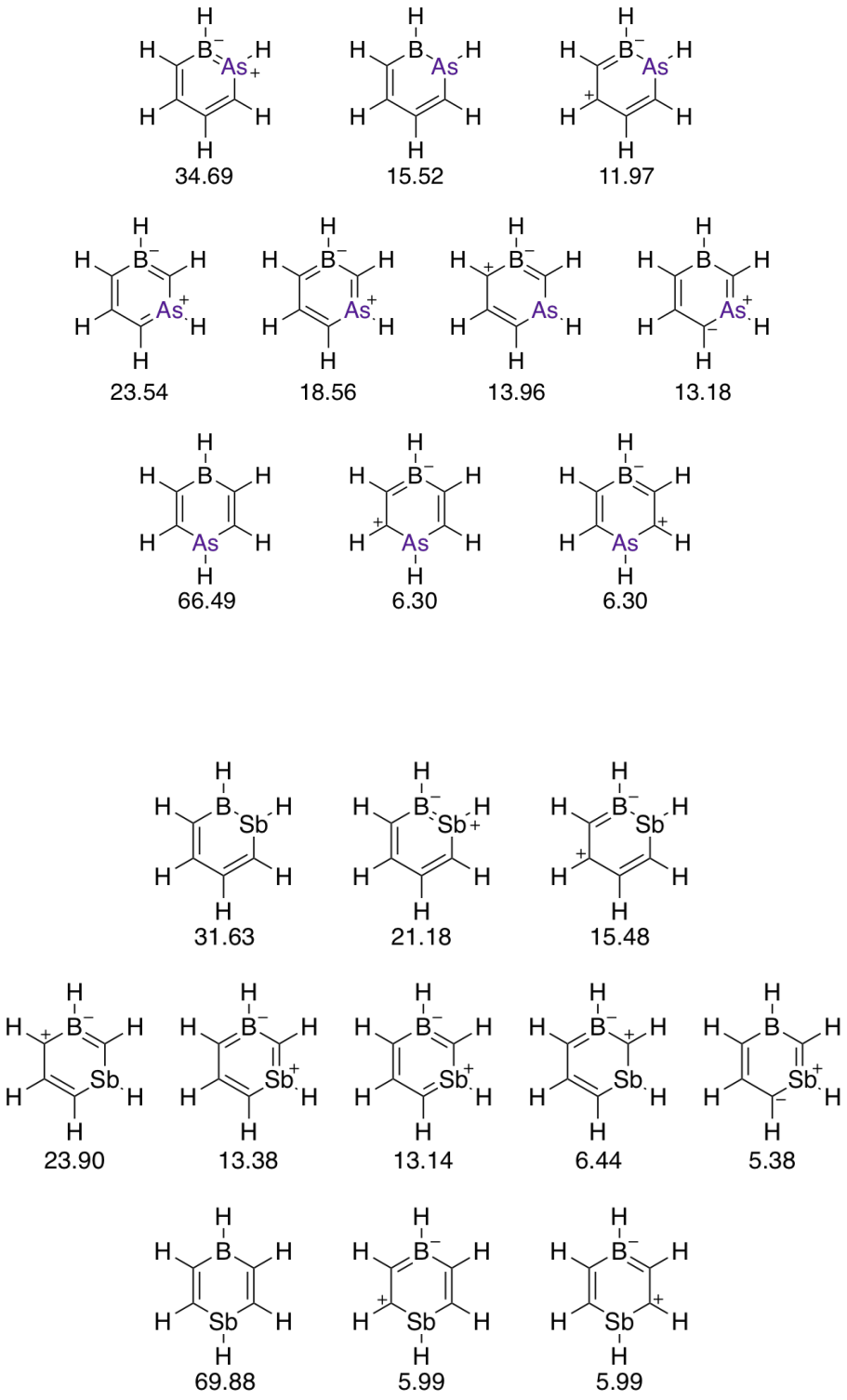


Figure 6: Major resonance contributors of arsenic (top) and antimony (bottom) substituted boron heterocycles resulting from NRT analysis. The numeric values are the contribution of each structure (%). Structures contributing less than 5% are not shown.

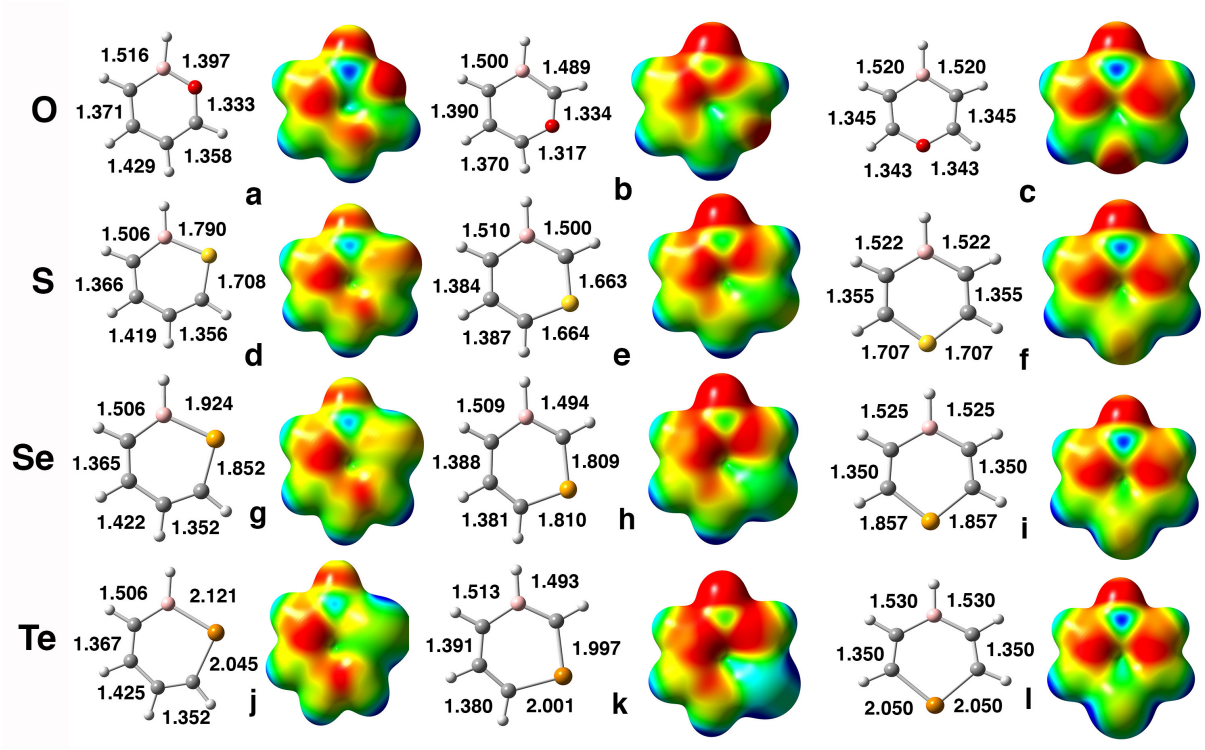


Figure 7: Optimized structures and electrostatic potential maps for chalcogenaborines. The electrostatic potential maps are projected onto the ground state electron density to identify regions of charge inhomogeneity. Isosurface values range from -1.0×10^{-4}–1.0×$10^{-1}$$a.u.$ (blue to red).

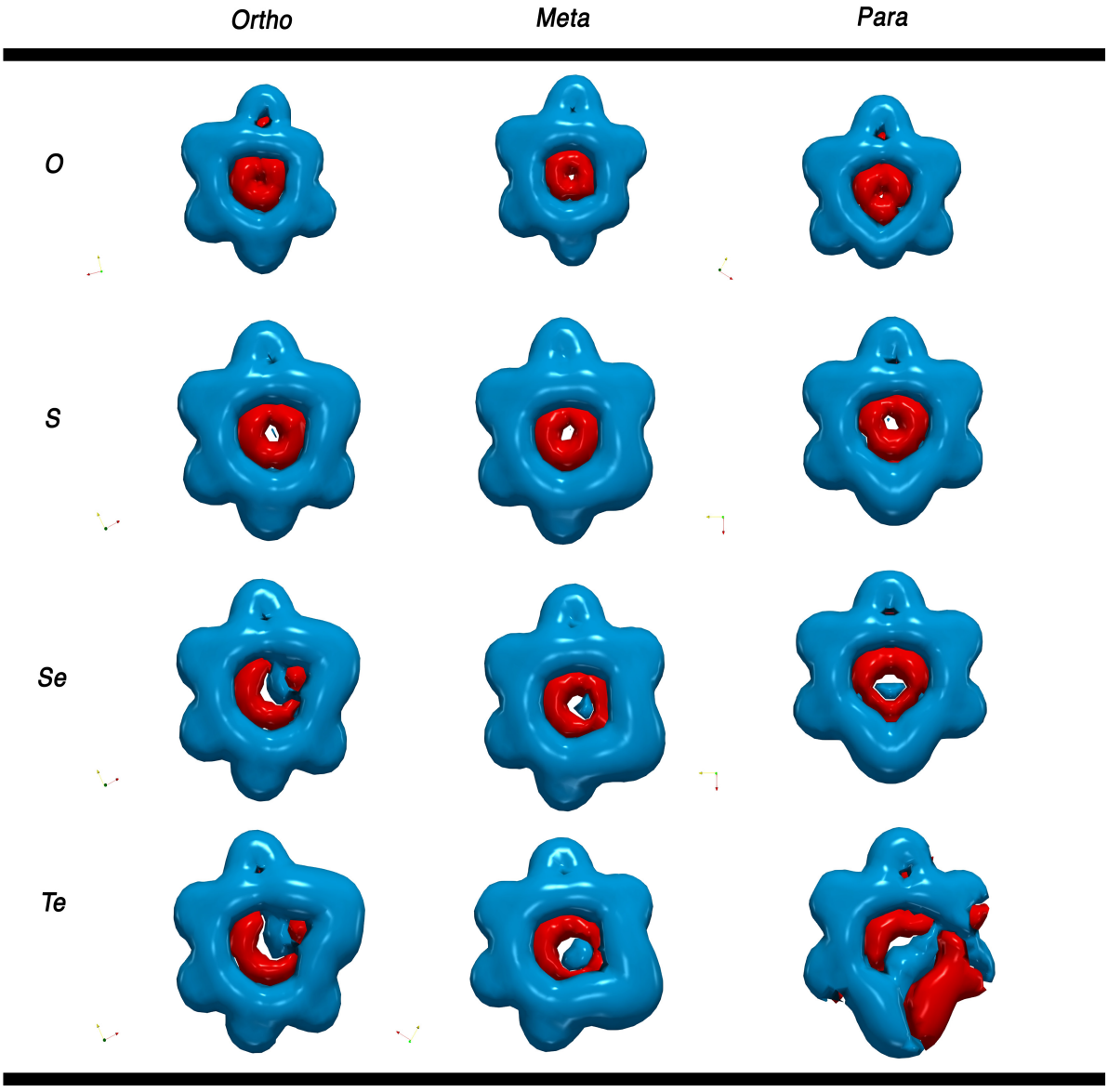


Figure 8: Signed modulus of the ring current for chalcogenaborines. The blue coloring indicates diatropic current, and red coloring marks paratropic current. The isosurface value ranges $\pm$ 0.01 nAT^{-1}. Locations of elemental substitutions correspond to positions shown in SI Fig. 7.

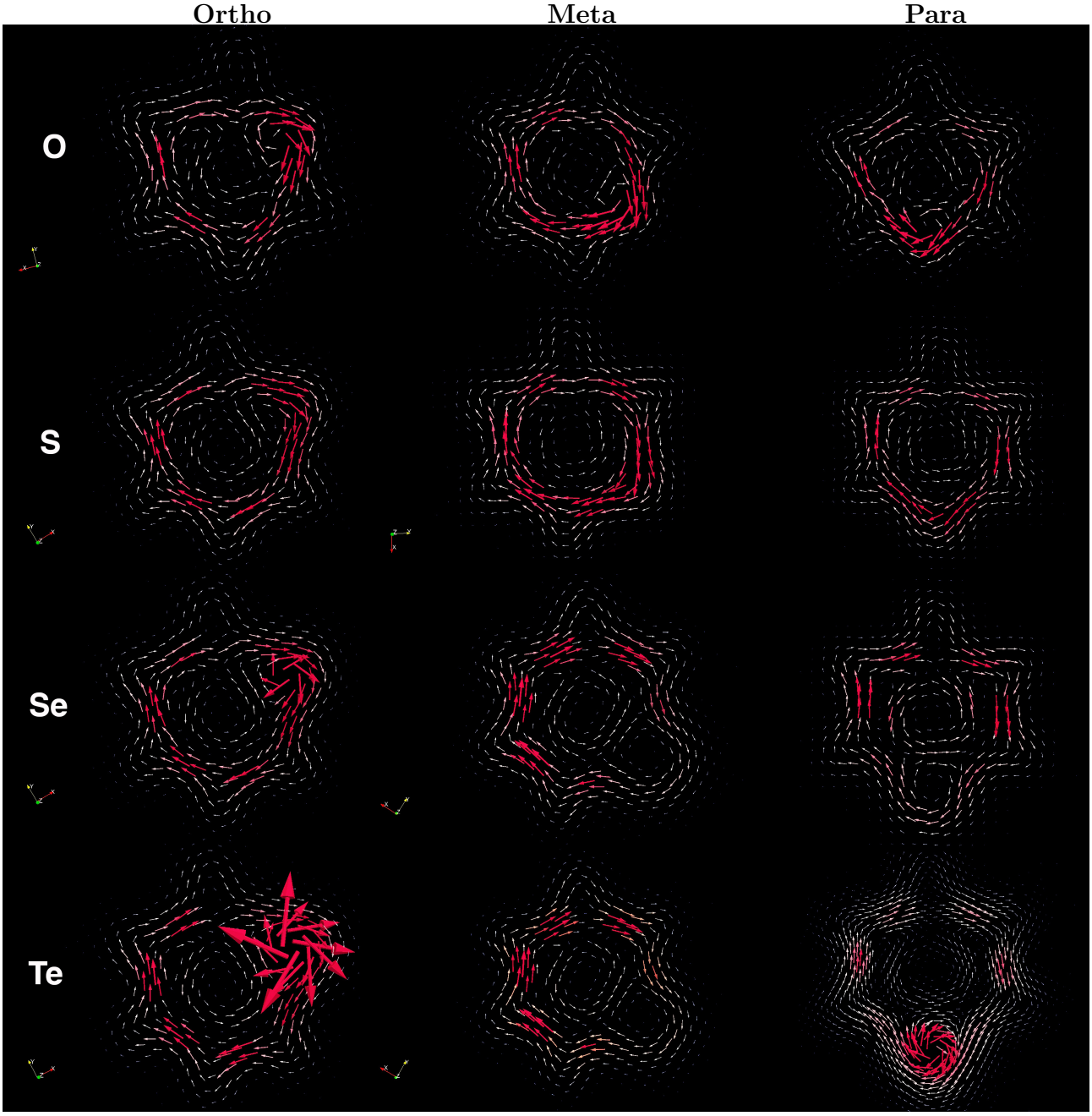


Figure 9: GIMIC ring current vector field set at 1 Å above the molecular plane of each chalcogenaborine. The scale is 0.00-0.07 *a.u.* (white-red) of the molecular magnetic field strength. Locations of elemental substitutions correspond to positions shown in SI Fig. 7.

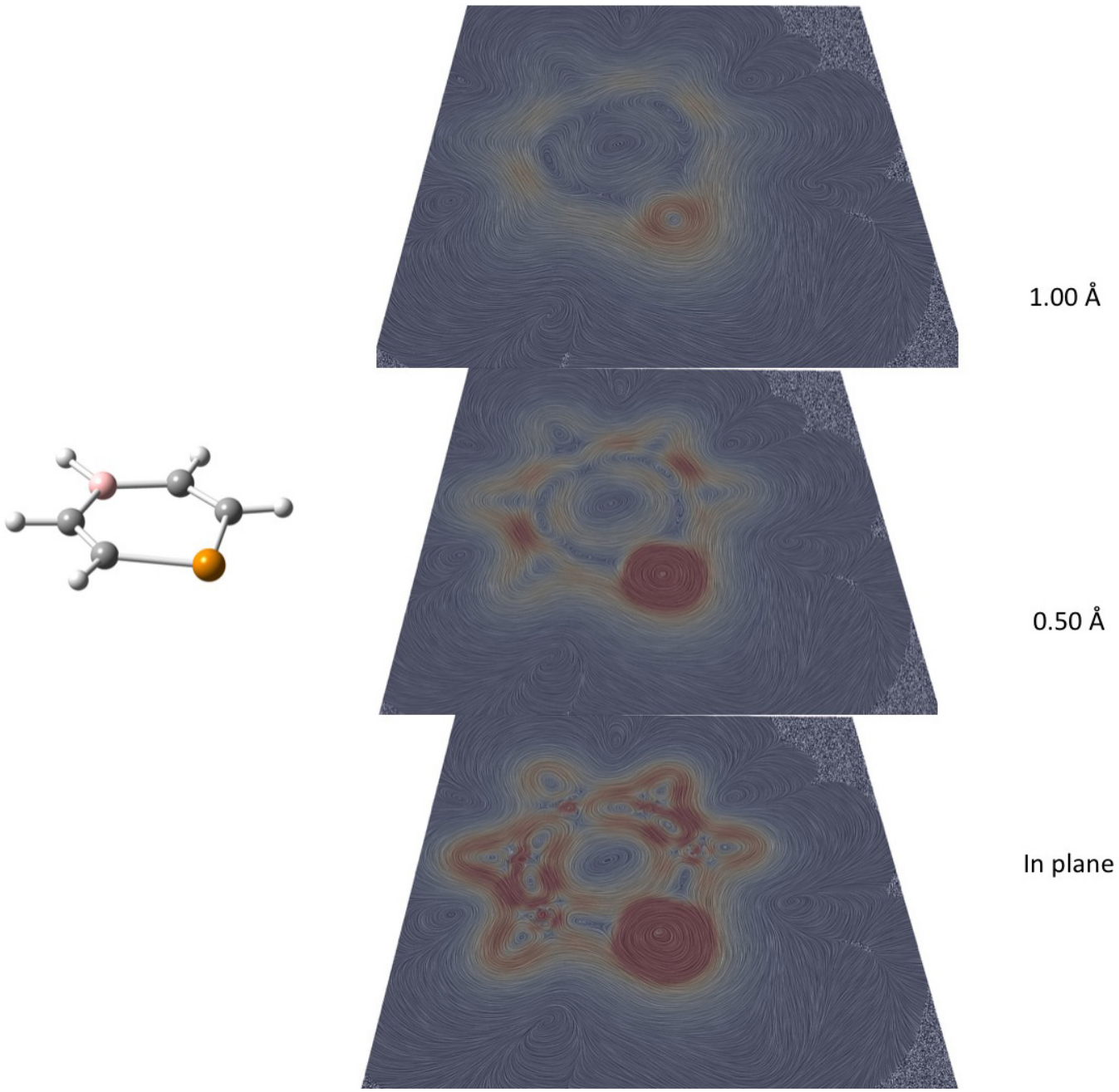


Figure 10: Representation of current magnitude in 1,4-telluraborine various distances from the molecular plane. Note the presence of vortices throughout the streamline slices. The color scale is set to a max of 0.1 nAT^{-1}. The large red-spot indicates the lone pair over tellurium, but also shown in-plane are smaller separatrices that contribute to the disjointed appearance of the vector current map 1 Å from the plane.

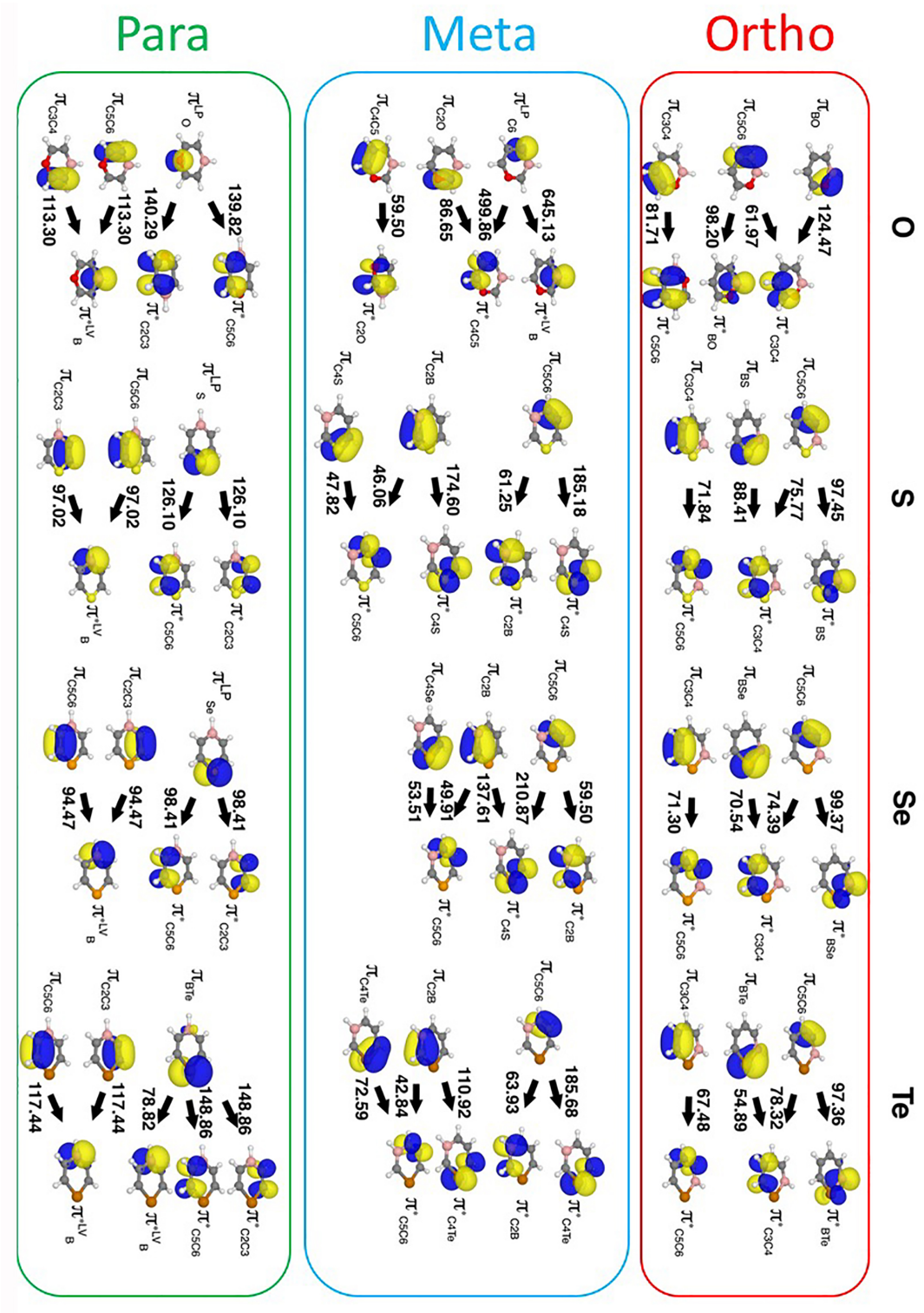


Figure 11: Donor-acceptor interactions among Lewis and non-Lewis type NBOs for all chalcogenaborines. Each NBO is labeled with an arrow pointing from the Lewis bonding NBOs (principle donor) to antibonding non-Lewis NBOs (principle acceptor). Above the arrows is the stabilization energy resulting from charge delocalization among NBOs in $kJ\ mol^{-1}$.

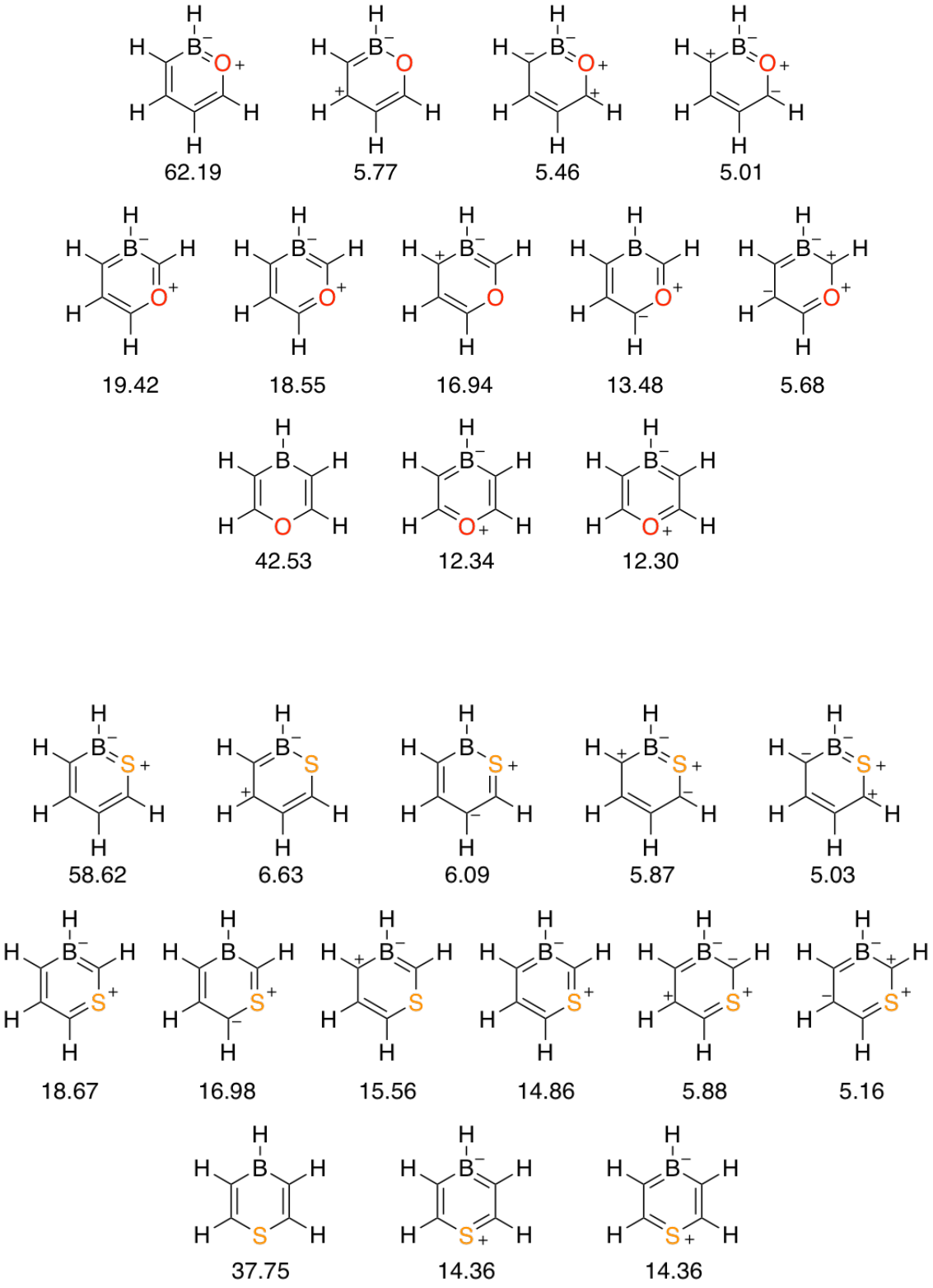
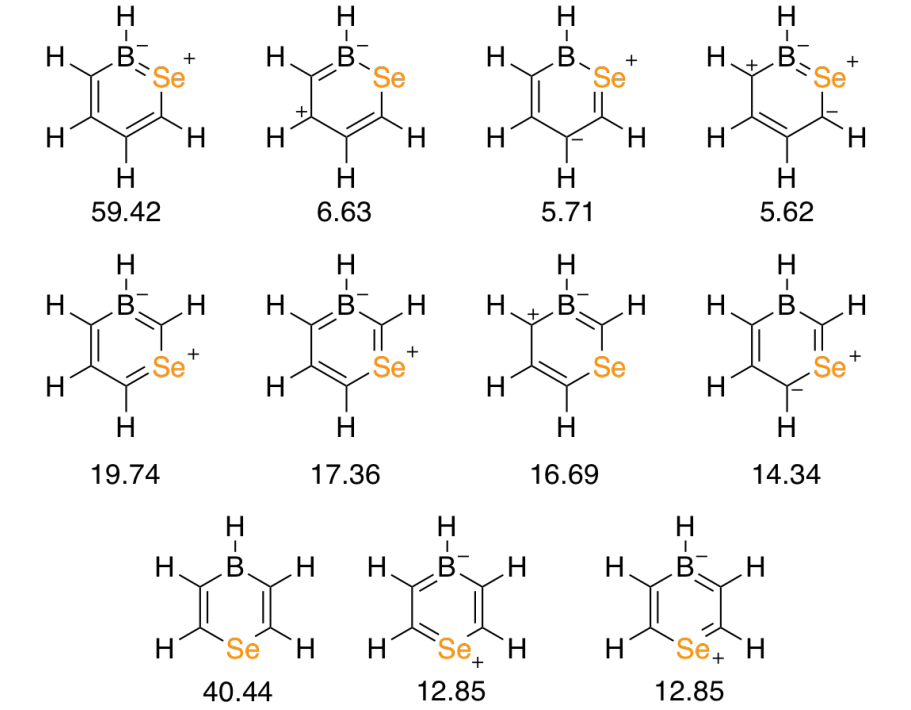


Figure 12: Major resonance contributors of oxygen (top) and sulfur (bottom) substituted boron heterocycles resulting from NRT analysis. The numeric values are the contribution of each structure (%). Structures contributing less than 5% are not shown.



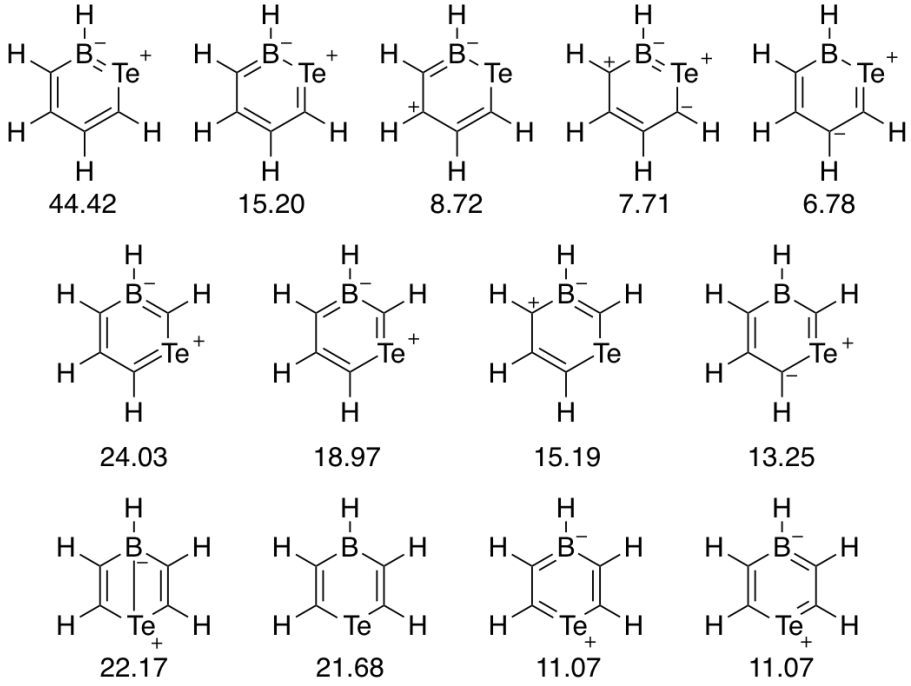


Figure 13: Major resonance contributors of selenium (top) and tellurium (bottom) substituted boron heterocycles resulting from NRT analysis. The numeric values are the contribution of each structure (%). Structures contributing less than 5% are not shown.

Cartesian coordinates of optimized structures in .xyz format

***o*-BN**

12

C 1.1844716384 0.6849659615 0.0000000000
C -0.0002494300 1.3527600631 0.0000000000
C 0.0494967537 -1.4678343813 0.0000000000
C 1.2023324818 -0.7302156646 0.0000000000
H 2.1064178776 1.2486565735 0.0000000000
H -0.0472101536 2.4340882717 0.0000000000
H 0.1343832203 -2.5483623204 0.0000000000
H 2.1719946017 -1.2194155405 0.0000000000
N -1.1773112987 0.6804523389 0.0000000000
H -2.0068728531 1.2498122754 0.0000000000
B -1.2741648166 -0.7468028842 0.0000000000
H -2.3651841392 -1.2317950442 0.0000000000

***m*-BN**

12

C -1.1678351577 0.6372438576 0.0000000000
C 0.0045538603 -1.4722602610 0.0000000000
C -1.1755687868 -0.7447783367 0.0000000000
H -2.0622172843 1.2414556353 0.0000000000
H -0.0540004638 2.3064486132 0.0000000000
H -0.0957461071 -2.5536783822 0.0000000000
H -2.1447124612 -1.2311067116 0.0000000000
B 1.3341511906 -0.7699967177 0.0000000000
H 2.3975068729 -1.3165786218 0.0000000000
C 1.2164217996 0.7232981167 0.0000000000
H 2.0250832922 1.4448686973 0.0000000000
N -0.0000052700 1.2993665655 0.0000000000

***p*-BN**

12

C -1.2765318370 0.7229050439 0.0000000000
C -1.1962205904 -0.6327213660 0.0000000000
H 0.0000010500 -2.2818189737 0.0000000000
H 2.0555322251 -1.2933589168 0.0000000000
H -2.2765043301 1.1409816560 0.0000000000
H -2.0555310239 -1.2933608165 0.0000000000
B -0.0000007200 1.5429248286 0.0000000000
H -0.0000012800 2.7400221070 0.0000000000
C 1.2765311649 0.7229062239 0.0000000000
H 2.2765032612 1.1409837674 0.0000000000
C 1.1962211619 -0.6327202600 0.0000000000
N 0.0000005900 -1.2780150467 0.0000000000

***o*-BP**

12

C	0.9578523125	-1.2701354970	0.0000000400
C	-0.4107569711	-1.3725735441	0.0000002500
C	1.1236224250	1.2159164829	0.0000000400
C	1.6667467537	-0.0509312938	-0.0000000500
H	1.5350957571	-2.1874899223	-0.0000000500
H	-0.8957749370	-2.3394227271	0.0000003200
H	1.8485325215	2.0264062406	-0.0000000700
H	2.7486779386	-0.1396717108	-0.0000002300
H	-2.7143518563	-0.1459127108	0.0000006000
B	-0.3403375258	1.5838802372	0.0000002600
H	-0.8121161786	2.6744411441	0.0000003300
P	-1.3333368715	0.0701501851	0.0000003800

***m*-BP**

12

C	1.2479274360	-1.0410594075	0.0000008500
C	-0.1050226980	-1.4247117961	0.0000004000
C	-0.6915114237	1.3783527523	0.0000001300
C	1.6927865871	0.2641077201	0.0000009800
H	1.9706632066	-1.8525442671	0.0000011200
H	-0.4187865214	-2.4577900042	0.0000003100
H	-1.4068610547	2.1896722440	-0.0000001300
H	1.3045721562	2.6018985053	0.0000007900
H	2.7729394984	0.3780212484	0.0000013500
B	0.8175103998	1.5067961622	0.0000006500
P	-1.2370577755	-0.1925338445	-0.0000000100
H	-2.5855504950	-0.5611379509	-0.0000004900

***p*-BP**

12

C	0.3492397762	1.4050391239	-0.0991232475
C	-0.9963194238	-1.3304826428	0.0042038703
C	-0.9963193868	1.3304826693	0.0042038903
H	0.8673768569	2.3608453355	-0.0908102968
H	2.3303309645	-0.0000000400	0.5298194209
H	-1.5278730856	-2.2728574416	0.1135344384
H	-2.9586282552	0.0000000400	0.0889773866
H	-1.5278730274	2.2728574840	0.1135344786
B	-1.7634076140	0.0000000200	0.0201563815
H	0.8673767934	-2.3608453567	-0.0908103470
C	0.3492397365	-1.4050391239	-0.0991232776
P	1.3559245642	-0.0000000100	-0.4945121974

***o*-BAs**

12

C	1.4053364950	-1.2682879064	0.0120715509
C	0.0663101850	-1.4329325858	0.1531278114
C	1.5544483776	1.2425233245	0.0084515006
C	2.0890019294	-0.0174011213	-0.0603400946
H	2.0280603640	-2.1569034350	-0.0082727606
H	-0.3557606269	-2.4259723437	0.2388861180
H	2.2825017340	2.0501482858	0.0067902705
H	3.1690747179	-0.0998448976	-0.1445719609
H	-2.2297297287	-0.1651686623	0.8714194536
B	0.0930970368	1.5898356509	0.1763301932
H	-0.3554770366	2.6890783403	0.2539844392
As	-1.0664537029	0.0352019426	-0.0546398740

***m*-BAs**

12

C	-1.5838749401	-1.1548552864	-0.0011794001
C	-0.2250761572	-1.4431193167	-0.0145066711
C	0.0832422165	1.5231307526	-0.0127359709
C	-2.1392087215	0.1193357487	0.0127536710
H	-2.2508237022	-2.0133726631	0.0245860119
H	0.1491764015	-2.4562532364	-0.0369028928
H	2.2961121305	-0.3041005627	0.2545808389
H	0.6939855125	2.4165206824	-0.0415189731
H	-2.0438900029	2.4774010961	0.0429388833
H	-3.2255365809	0.1260916594	0.0487843437
B	-1.4166822352	1.4556569492	-0.0015960601
As	0.9164041182	-0.0572023645	-0.2744243005

***p*-BAs**

12

C	-1.4452124984	-1.1536726176	-0.1309408397
C	0.3163642840	1.4086799057	0.0123482909
C	-2.0096306709	0.0591562944	0.0047862204
H	-2.0443683420	-2.0606102629	-0.1269820896
H	0.8382044635	-2.1734204645	0.6514137109
H	2.1746840922	0.3871913890	-0.1131082385
H	0.8354860429	2.3551219449	0.1538258115
H	-1.8239076181	2.4179980818	0.0893965468
H	-3.0896631308	0.0778746759	0.1405219303
B	-1.2238516916	1.3838129037	0.0223493617
C	1.0900187596	0.3172796040	-0.1228792895
As	0.3974278598	-1.4066515164	-0.5866424157

***o*-BSb**

12

C	1.8322857163	-1.2887149472	0.0110867008
C	0.5145902585	-1.5120838918	0.1636557022
C	2.0123304221	1.2496218721	0.0048240004
C	2.5116863895	-0.0161596212	-0.0721287555
H	2.4943303494	-2.1512408627	-0.0117001309
H	0.1721147731	-2.5377395317	0.2433638085
H	2.7662052575	2.0340001034	-0.0101038108
H	3.5904347002	-0.1129265185	-0.1702856026
H	-1.6300994618	-0.0713169654	1.4815751406
B	0.5587185525	1.6409647460	0.1868706340
H	0.2067860557	2.7749767514	0.2982911823
Sb	-0.9144386587	0.0233122118	-0.0576970844

***m*-BSb**

12

C	-1.8620698121	-1.2217114130	0.0180608713
C	-0.5351298628	-1.5050834218	0.1945832146
C	-0.3296038950	1.6145705491	0.2219007269
C	-2.4304142522	0.0655778947	-0.0753405556
H	-2.5456600398	-2.0685796352	-0.0106079008
H	-0.2115304362	-2.5377458395	0.2507680989
H	1.8282361980	-0.2193979265	1.3360863283
H	0.1668062024	2.5783419420	0.2772842310
H	-2.5119743307	2.4044161392	-0.0404726131
H	-3.5133655745	0.0368686428	-0.1838322539
B	-1.7919807777	1.4434874600	0.0012240301
Sb	0.8772441975	-0.0165876012	-0.0588345546

***p*-BSb**

12

C	-0.5236502197	-1.5593298790	0.1421372106
C	-1.8471409282	1.3651803346	0.0261412020
C	-1.8471408806	-1.3651803717	0.0261411020
H	-0.1199637292	-2.5652503138	0.2326072675
H	1.3864749351	-0.0000000300	1.5769745800
H	-0.1199638091	2.5652503138	0.2326074575
H	-2.4687679873	2.2608212786	0.0507899338
H	-3.7441015448	-0.0000000400	-0.2846852812
H	-2.4687679238	-2.2608213527	0.0507897639
B	-2.5590345238	-0.0000000300	-0.1059797278
C	-0.5236502694	1.5593298684	0.1421373307
Sb	0.9028339657	0.0000000200	-0.0659944847

***o*-BO**

11

C	0.3307397952	-1.3467633418	-0.0057697305
C	-0.9542238235	-0.9070034008	-0.0193208015
C	1.1500252158	0.9466796504	0.0155550412
C	1.4011766274	-0.4007689400	0.0119472409
H	0.5223858295	-2.4188836811	-0.0086393707
H	-1.8227548795	-1.5669863806	-0.0331133425
H	1.9927280511	1.6405529932	0.0292261922
H	2.4244847418	-0.7886153482	0.0225026717
B	-0.2993969728	1.3891589433	-0.0000099300
H	-0.7315551075	2.5096598099	0.0001867100
O	-1.2727938665	0.3876235394	-0.0169007113

***m*-BO**

11

C	-1.3013359092	-1.7134706494	0.0000587400
C	0.0680022049	-1.6664529969	0.0004283700
C	0.1197018288	0.6565518897	-0.0010891701
C	-2.0544667161	-0.5440861824	-0.0009356401
H	-1.7575931044	-2.6966304034	0.0005777400
H	0.7223064862	-2.5250258790	0.0011864601
H	0.8763427441	1.4326545296	-0.0013789101
H	-1.8995369636	1.8533655819	-0.0024813402
H	-3.1338519288	-0.6622299298	-0.0011701601
B	-1.3637981131	0.7870615568	-0.0016158601
O	0.7314507325	-0.5290804800	-0.0001252200

***p*-BO**

11

C	-1.2822794375	-1.6573189530	0.0000427800
C	0.1604224419	0.7201721556	-0.0011377501
C	-2.0420967217	-0.5471966810	-0.0009202901
H	-1.6464136418	-2.6770082624	0.0006227600
H	0.8379460451	1.5656758890	-0.0015098201
H	-1.9522070653	1.8442748777	-0.0024900002
H	-3.1135952460	-0.7078166818	-0.0011171101
B	-1.3565850197	0.8088896209	-0.0016310701
C	0.7384081063	-0.4946763275	-0.0001588200
H	1.8029336937	-0.6925074728	0.0002763000
O	0.0601567146	-1.6532714932	0.0004234100

***o*-BS**

11

C	-0.3442021861	-1.5829373069	0.0006618000
C	1.0397818308	-1.5724060605	0.0004947400
C	1.8109195658	-0.4194283716	-0.0007057601
C	-0.4727082257	0.9812591928	-0.0017907201
H	-0.8005096599	-2.5693367211	0.0016683901
H	1.5889459081	-2.5102015710	0.0013390201
H	2.8923366497	-0.4524476143	-0.0007959301
H	-0.9392969134	1.9613533754	-0.0026811202
H	-2.3894377824	-0.3672598575	-0.0002829700
B	-1.1928882925	-0.3343511552	-0.0004463400
S	1.1841166980	1.1223817848	-0.0021141302

***m*-BS**

11

C	-0.3442021861	-1.5829373069	0.0006618000
C	1.0397818308	-1.5724060605	0.0004947400
C	1.8109195658	-0.4194283716	-0.0007057601
C	-0.4727082257	0.9812591928	-0.0017907201
H	-0.8005096599	-2.5693367211	0.0016683901
H	1.5889459081	-2.5102015710	0.0013390201
H	2.8923366497	-0.4524476143	-0.0007959301
H	-0.9392969134	1.9613533754	-0.0026811202
H	-2.3894377824	-0.3672598575	-0.0002829700
B	-1.1928882925	-0.3343511552	-0.0004463400
S	1.1841166980	1.1223817848	-0.0021141302

***p*-BS**

11

C	-0.3585337670	-1.6190770596	0.0009837901
C	0.9954001847	-1.6662888037	0.0004612400
C	-0.3553166567	0.9889540438	-0.0018028901
H	-0.8544047223	-2.5863000428	0.0022323102
H	1.5542470998	-2.5974622378	0.0012221201
H	-0.8488051432	1.9573952302	-0.0026303102
H	-2.3395333463	-0.3126134836	0.0004223400
B	-1.1426354460	-0.3140928135	-0.0000813900
C	0.9987275137	1.0328320295	-0.0024219502
H	1.5598677771	1.9626260361	-0.0036528503
S	2.0416405550	-0.3180165839	-0.0014231301

***o*-BSe**

11

C	-1.5229502661	-1.2395651125	-0.0017834901
C	-0.1788199933	-1.3855172831	-0.0017816301
C	-1.6587747937	1.2412310313	-0.0017835301
C	-2.2231320473	-0.0018953701	-0.0017843901
H	-2.1193989395	-2.1455708820	-0.0017843901
H	0.2709589102	-2.3693405566	-0.0017810501
H	-2.3510052582	2.0784130556	-0.0017844301
H	-3.3061977882	-0.0808524060	-0.0017859101
B	-0.1776572935	1.5116923959	-0.0017814401
H	0.3385439456	2.5843940469	-0.0017806401
Se	1.0318311860	0.0156742612	-0.0017798601

***m*-BSe**

11

C	1.5542335581	-1.1905397880	0.0000001800
C	0.1856915837	-1.3747300631	0.0000001900
C	0.0375716629	1.4522394484	-0.0000002200
C	2.2028983467	0.0364699628	0.0000000100
H	2.1472894803	-2.1015871772	0.0000003200
H	-0.2584717094	-2.3602162391	0.0000003200
H	-0.5642997744	2.3544108154	-0.0000003600
H	2.1649478658	2.4035369694	-0.0000003200
H	3.2876530203	-0.0266067220	0.0000000400
B	1.5301663864	1.3875938169	-0.0000001800
Se	-1.0140564080	-0.0194230915	-0.0000000200

***p*-BSe**

11

C	-0.1641344923	1.4248975585	0.0000003000
C	-1.5101200515	-1.3196498183	0.0000002100
C	-1.5101200621	1.3196497972	0.0000002300
H	0.3559003768	2.3769816168	0.0000003700
H	-2.0424322518	-2.2679579535	0.0000002100
H	-3.4718624092	-0.0000000200	0.0000000200
H	-2.0424322042	2.2679579324	0.0000002100
B	-2.2751351528	0.0000000100	0.0000001300
C	-0.1641344822	-1.4248975585	0.0000003100
H	0.3559004170	-2.3769816115	0.0000004000
Se	1.0221308379	0.0000000300	0.0000003600

***o*-BTe**

11

C	-1.7779586125	-1.2526686260	-0.0001911800
C	-0.4428786836	-1.4678185483	-0.0001905800
C	-1.9026338412	1.2532292629	-0.0001912000
C	-2.4526562123	0.0020079602	-0.0001914700
H	-2.4144537425	-2.1328392690	-0.0001914900
H	-0.0585767643	-2.4795108252	-0.0001904000
H	-2.6210857791	2.0696804985	-0.0001915100
H	-3.5363577650	-0.0715112554	-0.0001919600
B	-0.4381788228	1.6054592387	-0.0001905600
H	0.0035845203	2.7110577544	-0.0001903700
Te	0.9651939748	0.0156936212	-0.0001899400

***m*-BTe**

11

C	1.8817105697	-1.2165223433	-0.0000001200
C	0.5228230294	-1.4577225608	-0.0000021400
C	0.3842995988	1.5565771466	-0.0000011600
C	2.5105644702	0.0243458018	0.0000012600
H	2.5075255111	-2.1068802303	0.0000004000
H	0.1370685704	-2.4682248451	-0.0000030900
H	-0.1451905807	2.5032580511	-0.0000015300
H	2.5556461648	2.3779918796	0.0000022600
H	3.5960166312	-0.0354940527	0.0000027700
B	1.8684797414	1.3938154226	0.0000008900
Te	-0.8565234527	-0.0075272005	-0.0000035400

***p*-BTe**

11

C	-4.0699699051	-0.0940552169	-0.1440023709
C	-2.2668335101	2.4949001992	-0.1568225417
C	-4.5854130778	1.1532292359	-0.1464426210
H	-4.6953173131	-0.9811253163	-0.1395993003
H	-1.7593525447	3.4585587609	-0.1611985021
H	-4.3960172808	3.5003916247	-0.1541147619
H	-5.6737954890	1.1938565016	-0.1436506607
B	-3.7963037638	2.4636798052	-0.1525759716
C	-1.4424613588	1.4263296868	-0.1557160316
H	-0.3616828273	1.5261796655	-0.1589470418
Te	-2.0657898869	-0.5265648396	-0.1480000113