Supplementary Information

Bromine-rich complexes of bismuth: experimental and theoretical studies

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Table S1. Cartesian atomic coordinates of model supramolecular clusters.

Atom	X	Y	Z
(4-MePyH)$_3${[Bi$_2$Br$_9$](Br$_2$)} (Type I)			
Bi	3.749082	3.360692	11.844880
Bi	4.291226	7.251331	12.203183
Br	5.606093	1.720178	10.672915
Br	1.658352	2.180338	10.494807
Br	3.531918	1.602722	13.957130
Br	4.333888	5.408114	9.774722
Br	5.801700	4.884610	13.412370
Br	1.939602	5.448053	13.005713
Br	6.510418	8.647056	11.491099
Br	2.688916	8.960558	10.776580
Br	4.050462	8.649418	14.504325
Br	0.142699	10.198459	9.487384
Br	-1.627391	11.216050	8.380122
Bi	-5.913382	14.097042	5.548483
Bi	-6.455526	17.987681	5.190179
Br	-7.770393	12.456528	6.720447
Br	-3.822652	12.916688	6.898555
Br	-5.696218	12.339072	3.436233
Br	-6.498188	16.144464	7.618641
Br	-7.966000	15.620960	3.980993
Br	-4.103902	16.184403	4.387650
Br	-8.674718	19.383406	5.902264
Br	-4.853216	19.696908	6.616783
Br	-6.214762	19.385768	2.889038
(PyH)$_3${[Bi$_2$Br$_9$](Br$_2$)} (Type I)			
Bi	0.613626	7.822113	5.850080
Br	-1.318003	9.354692	6.972889
Br	0.604200	9.511106	3.645105
Br	2.538703	9.336923	7.000637
Br	2.614535	5.845075	4.700857
Br	0.627528	5.845075	8.108505
Br	-1.400174	5.845075	4.708150
Bi	0.613626	3.868037	5.850080
Br	-1.318003	2.335458	6.972889
Br	0.604200	2.179044	3.645105
Br	2.538703	2.353227	7.000637
Br	0.059086	11.046023	0.962281
Br	-0.059086	12.334277	-0.962281
Br	4.602809	11.046023	9.855818
Br	4.484637	12.334277	7.931256
Bi	3.930097	19.512263	3.043457
Br	5.861726	21.044842	1.920648
Br	3.939523	21.201256	5.248432
Br	2.005020	21.027073	1.892900

Br	1.929188	17.535225	4.192680
Br	3.916195	17.535225	0.785033
Br	5.943897	17.535225	4.185387
Bi	3.930097	15.558187	3.043457
Br	5.861726	14.025608	1.920648
Br	3.939523	13.869194	5.248432
Br	2.005020	14.043377	1.892900
$(N\text{-}EtPy)_3\{[Bi_2Br_9](Br_2)_2\}$ (Type II)			
Bi	5.357400	2.366227	7.353592
Br	5.197401	4.721003	8.681588
Br	2.904436	1.376031	8.218313
Br	6.848317	1.220965	9.299215
Br	5.856018	0.033081	5.404509
Br	7.690857	3.476976	5.965930
Bi	6.354636	2.366227	3.455427
Br	6.514634	4.721003	2.127431
Br	8.807600	1.376031	2.590706
Br	4.863719	1.220965	1.509804
Br	4.021178	3.476976	4.843089
Br	10.993250	0.312836	0.645298
Br	12.834170	-0.312836	-0.645298
Br	12.974321	3.836729	5.277828
Br	10.651424	3.836729	5.531191
Bi	17.472784	-2.366227	-3.455427
Br	17.312786	-4.721003	-2.127431
Br	15.019820	-1.376031	-2.590706
Br	18.963701	-1.220965	-1.509804
Br	17.971402	-0.033081	-5.404509
Br	19.806242	-3.476976	-4.843089
Bi	18.470020	-2.366227	-7.353592
Br	18.630019	-4.721003	-8.681588
Br	20.922984	-1.376031	-8.218313
Br	16.979103	-1.220965	-9.299215
Br	16.136563	-3.476976	-5.965930
Bi	17.271110	2.366227	7.353592
Br	17.111111	4.721003	8.681588
Br	14.818146	1.376031	8.218313
Br	18.762027	1.220965	9.299215
Br	17.769728	0.033081	5.404509
Br	19.604567	3.476976	5.965930
Bi	18.268346	2.366227	3.455427
Br	18.428344	4.721003	2.127431
Br	20.721310	1.376031	2.590706
Br	16.777429	1.220965	1.509804
Br	15.934888	3.476976	4.843089
(BPP)$\{[BiBr_5(Br_3)](Br_3)(Br_2)\}$ (Type IV)			
Bi	12.674865	10.489800	2.984272
Br	12.700401	7.625245	2.925265
Br	11.976550	10.489800	0.323471
Br	15.449815	10.489800	2.348625
Br	13.512746	10.489800	5.888310
Br	9.982787	10.489800	3.785259
Br	12.950144	10.489800	8.578907
Br	12.415807	10.489800	10.938437
Br	12.700401	13.354355	2.925265
Br	8.792054	10.489800	12.448685
Br	6.736458	10.489800	11.288978
Br	11.411217	10.489800	14.065068
Br	9.847075	10.489800	16.164809
Br	8.305257	10.489800	18.114985

Bi	4.644565	10.489800	6.752978
Br	4.670101	13.354355	6.811985
Br	3.946250	10.489800	9.413779
Br	7.419515	10.489800	7.388625
Br	5.482446	10.489800	3.848940
Br	1.952487	10.489800	5.951991
Br	4.919844	10.489800	1.158343
Br	4.385507	10.489800	-1.201187
Br	4.670101	7.625245	6.811985
3 (type III)			
Br	7.887913	5.587977	11.742165
Br	8.015831	5.827307	9.430098
Bi	7.272449	5.689585	3.479977
Br	9.390083	7.374074	3.453678
Br	5.704800	8.305990	3.466686
Br	7.301844	5.713610	6.279568
Br	8.914903	3.549927	3.499206
Br	7.200685	5.729295	0.608275
Br	4.431300	4.480390	3.466686
Bi	7.272449	5.787215	17.619327
Br	9.390083	4.102726	17.593028
Br	5.704800	3.170810	17.606036
Br	7.301844	5.763190	20.418918
Br	8.914903	7.926873	17.638556
Br	7.200685	5.747505	14.747625
Br	4.431300	6.996410	17.606036
2 (type III)			
Bi	10.997226	10.534650	2.621276
Br	8.979853	10.534650	0.671688
Br	13.028628	10.534650	4.768636
Br	12.959904	10.534650	0.781453
Br	10.703209	13.367066	2.560809
Br	10.703209	7.702234	2.560809
Br	8.853428	10.534650	4.859914
Br	9.329902	2.352177	2.677700
Br	9.329902	4.670923	2.677700
Bi	10.997226	-3.511550	2.621276
Br	8.979853	-3.511550	0.671688
Br	13.028628	-3.511550	4.768636
Br	12.959904	-3.511550	0.781453
Br	10.703209	-0.679134	2.560809
Br	10.703209	-6.343966	2.560809
Br	8.853428	-3.511550	4.859914

Table S2. Values of the density of all electrons – ρ(**r**), Laplacian of electron density – $\nabla^2\rho(\mathbf{r})$, energy density – H_b, potential energy density – V(**r**), and Lagrangian kinetic energy – G(**r**) (Hartree) at the bond critical points (3, –1), corresponding to the Br•••Br non-covalent interactions, bond lengths – *l* (Å), as well as energies for these contacts E_{int} (kcal/mol), defined by two approaches.

ρ(**r**)	$\nabla^2\rho(\mathbf{r})$	H_b	V(**r**)	G(**r**)	E_{int}[a]	E_{int}[b]	*l*[c]
$(4\text{-MePyH})_3\{[Bi_2Br_9](Br_2)\}$ (Type I)							
0.018	0.047	0.001	-0.010	0.011	3.6	3.9	3.147
0.019	0.051	0.001	-0.011	0.012	4.0	4.3	3.111
$(PyH)_3\{[Bi_2Br_9](Br_2)\}$ (Type I)							
0.019	0.042	0.001	-0.009	0.010	3.3	3.6	3.139
$(N\text{-EtPy})_3\{[Bi_2Br_9](Br_2)_2\}$ (Type II)							
0.019	0.051	0.001	-0.011	0.012	4.0	4.3	3.113
0.023	0.063	0.001	-0.014	0.015	5.1	5.4	3.014
$(BPP)\{[BiBr_5(Br_3)](Br_3)(Br_2)\}$ (Type IV)							
0.013	0.032	0.000	-0.007	0.008	2.5	2.9	3.362
0.016	0.035	0.000	-0.008	0.009	2.9	3.2	3.284
0.021	0.060	0.001	-0.013	0.014	4.7	5.0	3.078
2 (type III)							
0.015	0.032	0.000	-0.008	0.008	2.9	2.9	3.330
3 (type III)							
0.017	0.040	0.000	-0.009	0.010	3.3	3.6	3.232
0.022	0.052	0.000	-0.012	0.013	4.4	4.6	3.087

[a] $E_{int} = 0.58(-V(\mathbf{r}))$ [Russ. Chem. Rev. 83(12) 1181-1203 (2014)]

[b] $E_{int} = 0.57G(\mathbf{r})$ [Russ. Chem. Rev. 83(12) 1181-1203 (2014)]

[c] Sum of Bondi's (the shortest) [Alvarez, S., *Dalton Trans.* **2013,** *42*, 8617–8636.] vdW radii for two Br atoms is 3.66 Å.