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The Bonding Situation in Triethylchalcogenostiboranes - Polarized Single Bond vs. Double Bond

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Single crystal X-ray diffraction

Table S1. Crystallographic data of **1**, **2**, **3**

	1	**2**	**3**
Empirical formula	$C_6H_{15}SSb$	$C_6H_{15}SbSe$	$C_6H_{15}Br_2Sb$
M	240.99	287.89	368.75
Crystal size [mm]	0.12 × 0.08 × 0.05	0.37 × 0.12 × 0.08	0.10 × 0.05 × 0.05
T [K]	150(1)	100(1)	100(1)
Crystal system	trigonal	hexagonal	monoclinic
Space group	$P3_1c$	$P6_3mc$	$P2_1/c$
a [Å]	9.2365(5)	9.2201(11)	11.5607(6)
b [Å]	9.2365(5)	9.2201(11)	10.8911(6)
c [Å]	6.3367(7)	6.5289(8)	8.6408(4)
α [°]	90	90	90
β [°]	90	90	96.575(3)
γ [°]	120	120	90
V [Å^3]	468.18(6)	480.66(10)	1080.80(10)
Z	2	2	4
D_{calc} [g · cm^{-1}]	1.710	1.989	2.266
μ(MoK_α [mm^{-1}])	3.089	6.578	9.881
Transmissions	0.75/0.47	0.75/0.30	0.4330/0.1369
F(000)	236	272	688
Index ranges	$-10 \le h \le 10$	$-13 \le h \le 9$	$-16 \le h \le 16$
	$-10 \le k \le 10$	$-10 \le k \le 13$	$0 \le k \le 15$
	$-4 \le l \le 5$	$-8 \le l \le 9$	$0 \le l \le 12$
θ_{max} [°]	24.98	32.05	30.62
Reflections collected	2573	9591	65251
Independent reflections	424	596	3328
R_{int}	0.0412	0.0258	0.0488
Refined parameter	25	23	85
R_1 [$I > 2\sigma(I)$]	0.0325	0.0195	0.0246
wR_2 [all data]	0.0770	0.0495	0.0473
x(Flack)	0.39(14)	0.622(17)	
GooF	1.155	1.228	1.090
$\Delta\rho_{final}$ (max/min) [e · Å^{-3}]	1.437/-0.361	2.125/-0.840	0.746/-0.499

Computational Studies

All geometries were fully optimized using tightened convergence criteria and improved integration grids at the density functional theory level, employing the BP86 exchange-correlation functional [1] including a third-generation dispersion correction [2] as implemented in the Turbomole V6.3 quantum chemistry program package [3]. A quadruple -zeta valence quality Gaussian type function basis set termed def2-QZVP [4] has been used throughout, in conjunction whit effective core potential for Sb [5]. The resolution-of-the-identity approximation was employed, making use of an appropriate auxiliary basis set [6]. Atom coordinates, energies and atomic partial charges (NPA,[7]) of all optimized geometries are given below. Natural bond orbital results (NBO [7]), Electron localization functions [8] and selected molecular orbitals of the monomers are shown below.

References

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8 a) A. D. Becke and K. E. Edgecombe, *J. Chem. Phys*. 1990, **92**, 5397; b) A. Savin and B. Silvi, *Nature* 1994, **371**, 683.

Et_3Sb-S Monomer, **1a**

Energy (in Hartree) and atomic coordinates (in Å):

Energy = -876.4776080837

Sb	0.0000000	0.0000000	0.3646240
S	0.0000000	0.0000000	2.6212947
C	-1.3238612	-1.4881792	-0.5098382
H	-1.4337096	-1.2394283	-1.5745297
H	-0.7936683	-2.4469224	-0.4356025
C	-2.6569509	-1.5122624	0.2353047
H	-2.4982274	-1.6600700	1.3115231
H	-3.3019643	-2.3213456	-0.1344770
H	-3.2019740	-0.5670282	0.1123134
C	1.9507316	-0.4024078	-0.5098382
H	1.7902312	-0.6219148	-1.5745297
H	2.5159311	0.5361243	-0.4356025
C	2.6381331	-1.5448557	0.2353047
H	2.6867764	-1.3334934	1.3115231
H	3.6613264	-1.6989122	-0.1344770
H	2.0920478	-2.4894767	0.1123134
C	-0.6268704	1.8905870	-0.5098382
H	-0.3565216	1.8613431	-1.5745297
H	-1.7222628	1.9107981	-0.4356025
C	0.0188178	3.0571181	0.2353047
H	-0.1885491	2.9935633	1.3115231
H	-0.3593621	4.0202578	-0.1344770
H	1.1099262	3.0565049	0.1123134

Atomic populations according to NPA:

atom	charge	n(s)	n(p)	n(d)	n(f)	n(g)
1 sb	1.52838	3.31754	8.14695	9.99918	0.00682	0.00113
2 s	-0.73189	5.88249	10.82031	0.02600	0.00297	0.00011
3 c	-0.74655	3.15116	3.58626	0.00689	0.00159	0.00066
4 h	0.22505	0.77217	0.00240	0.00030	0.00009	0.00000
5 h	0.23124	0.76597	0.00240	0.00031	0.00009	0.00000
6 c	-0.65071	3.09914	3.54454	0.00462	0.00133	0.00109
7 h	0.23990	0.75856	0.00105	0.00035	0.00014	0.00000
8 h	0.22211	0.77622	0.00117	0.00036	0.00014	0.00000
9 h	0.21347	0.78474	0.00128	0.00036	0.00014	0.00000
10 c	-0.74655	3.15116	3.58626	0.00689	0.00159	0.00066
11 h	0.22505	0.77217	0.00240	0.00030	0.00009	0.00000
12 h	0.23124	0.76597	0.00240	0.00031	0.00009	0.00000
13 c	-0.65071	3.09914	3.54454	0.00462	0.00133	0.00109
14 h	0.23990	0.75856	0.00105	0.00035	0.00014	0.00000
15 h	0.22211	0.77622	0.00117	0.00036	0.00014	0.00000
16 h	0.21347	0.78474	0.00128	0.00036	0.00014	0.00000
17 c	-0.74655	3.15116	3.58626	0.00689	0.00159	0.00066
18 h	0.22505	0.77217	0.00240	0.00030	0.00009	0.00000
19 h	0.23124	0.76597	0.00240	0.00031	0.00009	0.00000
20 c	-0.65071	3.09914	3.54454	0.00462	0.00133	0.00109
21 h	0.23990	0.75856	0.00105	0.00035	0.00014	0.00000
22 h	0.22211	0.77622	0.00117	0.00036	0.00014	0.00000
23 h	0.21347	0.78474	0.00128	0.00036	0.00014	0.00000

Natural bond orbitals (population, character and atomic contributions; BD = bonding orbital, LP = lone pair orbital, core and Rydberg orbitals not shown).

1. (1.94726) BD (1)Sb 1 - S 2
(46.20%) 0.6797*Sb 1 s(28.87%)p 2.46(71.01%)d 0.00(0.06%)f 0.00(0.04%)g 0.00 (0.02%)
(53.80%) 0.7335* S 2 s(10.57%)p 8.36(88.35%)d 0.10(1.02%)f 0.00(0.05%)g 0.00 (0.00%)

2. (1.94345) BD (1)Sb 1 - C 3
(37.79%) 0.6147*Sb 1 s(23.71%)p 3.21(76.18%)d 0.00(0.07%)f 0.00(0.04%)g 0.00 (0.00%)
(62.21%) 0.7888* C 3 s(18.04%)p 4.53(81.72%)d 0.01(0.23%)f 0.00(0.01%)g 0.00 (0.01%)

3. (1.94345) BD (1)Sb 1 - C 10
(37.79%) 0.6147*Sb 1 s(23.71%)p 3.21(76.18%)d 0.00(0.07%)f 0.00(0.04%)g 0.00 (0.00%)
(62.21%) 0.7888* C 10 s(18.04%)p 4.53(81.72%)d 0.01(0.23%)f 0.00(0.01%)g 0.00 (0.01%)

4. (1.94345) BD (1)Sb 1 - C 17
(37.79%) 0.6147*Sb 1 s(23.71%)p 3.21(76.18%)d 0.00(0.07%)f 0.00(0.04%)g 0.00 (0.00%)
(62.21%) 0.7888* C 17 s(18.04%)p 4.53(81.72%)d 0.01(0.23%)f 0.00(0.01%)g 0.00 (0.01%)

5. (1.98245) BD (1) C 3 - H 4
(61.34%) 0.7832* C 3 s(25.60%)p 2.90(74.26%)d 0.00(0.12%)f 0.00(0.01%)g 0.00 (0.00%)
(38.66%) 0.6218* H 4 s(99.77%)p 0.00(0.22%)d 0.00(0.01%)f 0.00(0.00%)

6. (1.98234) BD (1) C 3 - H 5
(61.64%) 0.7851* C 3 s(25.36%)p 2.94(74.50%)d 0.00(0.13%)f 0.00(0.01%)g 0.00 (0.00%)
(38.36%) 0.6194* H 5 s(99.77%)p 0.00(0.22%)d 0.00(0.01%)f 0.00(0.00%)

7. (1.99350) BD (1) C 3 - C 6
(50.96%) 0.7139* C 3 s(31.06%)p 2.22(68.83%)d 0.00(0.09%)f 0.00(0.01%)g 0.00 (0.01%)
(49.04%) 0.7003* C 6 s(28.73%)p 2.48(71.16%)d 0.00(0.08%)f 0.00(0.01%)g 0.00 (0.01%)

8. (1.98798) BD (1) C 6 - H 7
(62.12%) 0.7881* C 6 s(23.98%)p 3.17(75.90%)d 0.00(0.11%)f 0.00(0.01%)g 0.00 (0.01%)
(37.88%) 0.6155* H 7 s(99.87%)p 0.00(0.12%)d 0.00(0.00%)f 0.00(0.01%)

9. (1.98320) BD (1) C 6 - H 8
(61.13%) 0.7819* C 6 s(24.03%)p 3.16(75.87%)d 0.00(0.09%)f 0.00(0.01%)g 0.00 (0.01%)
(38.87%) 0.6234* H 8 s(99.79%)p 0.00(0.20%)d 0.00(0.01%)f 0.00(0.01%)

10. (1.98877) BD (1) C 6 - H 9
(60.74%) 0.7794* C 6 s(23.33%)p 3.28(76.55%)d 0.00(0.11%)f 0.00(0.01%)g 0.00 (0.01%)
(39.26%) 0.6266* H 9 s(99.85%)p 0.00(0.14%)d 0.00(0.00%)f 0.00(0.01%)

11. (1.98245) BD (1) C 10 - H 11
(61.34%) 0.7832* C 10 s(25.60%)p 2.90(74.26%)d 0.00(0.12%)f 0.00(0.01%)g 0.00 (0.00%)
(38.66%) 0.6218* H 11 s(99.77%)p 0.00(0.22%)d 0.00(0.01%)f 0.00(0.00%)

12. (1.98234) BD (1) C 10 - H 12
(61.64%) 0.7851* C 10 s(25.36%)p 2.94(74.50%)d 0.00(0.13%)f 0.00(0.01%)g 0.00 (0.00%)
(38.36%) 0.6194* H 12 s(99.77%)p 0.00(0.22%)d 0.00(0.01%)f 0.00(0.00%)

13. (1.99350) BD (1) C 10 - C 13
(50.96%) 0.7139* C 10 s(31.06%)p 2.22(68.83%)d 0.00(0.09%)f 0.00(0.01%)g 0.00 (0.01%)
(49.04%) 0.7003* C 13 s(28.73%)p 2.48(71.16%)d 0.00(0.08%)f 0.00(0.01%)g 0.00 (0.01%)

14. (1.98798) BD (1) C 13 - H 14
(62.12%) 0.7881* C 13 s(23.98%)p 3.17(75.90%)d 0.00(0.11%)f 0.00(0.01%)g 0.00 (0.01%)
(37.88%) 0.6155* H 14 s(99.87%)p 0.00(0.12%)d 0.00(0.00%)f 0.00(0.01%)

15. (1.98320) BD (1) C 13 - H 15
(61.13%) 0.7819* C 13 s(24.03%)p 3.16(75.87%)d 0.00(0.09%)f 0.00(0.01%)g 0.00 (0.01%)
(38.87%) 0.6234* H 15 s(99.79%)p 0.00(0.20%)d 0.00(0.01%)f 0.00(0.01%)

16. (1.98877) BD (1) C 13 - H 16
(60.74%) 0.7794* C 13 s(23.33%)p 3.28(76.55%)d 0.00(0.11%)f 0.00(0.01%)g 0.00 (0.01%)
(39.26%) 0.6266* H 16 s(99.85%)p 0.00(0.14%)d 0.00(0.00%)f 0.00(0.01%)

17. (1.98245) BD (1) C 17 - H 18
(61.34%) 0.7832* C 17 s(25.60%)p 2.90(74.26%)d 0.00(0.12%)f 0.00(0.01%)g 0.00 (0.00%)
(38.66%) 0.6218* H 18 s(99.77%)p 0.00(0.22%)d 0.00(0.01%)f 0.00(0.00%)

18. 1.98234) BD (1) C 17 - H 19
(61.64%) 0.7851* C 17 s(25.36%)p 2.94(74.50%)d 0.00(0.13%)f 0.00(0.01%)g 0.00 (0.00%)
(38.36%) 0.6194* H 19 s(99.77%)p 0.00(0.22%)d 0.00(0.01%)f 0.00(0.00%)

19. (1.99350) BD (1) C 17 - C 20
(50.96%) 0.7139* C 17 s(31.06%)p 2.22(68.83%)d 0.00(0.09%)f 0.00(0.01%)g 0.00 (0.01%)
(49.04%) 0.7003* C 20 s(28.73%)p 2.48(71.16%)d 0.00(0.08%)f 0.00(0.01%)g 0.00 (0.01%)

20. (1.98798) BD (1) C 20 - H 21
(62.12%) 0.7881* C 20 s(23.98%)p 3.17(75.90%)d 0.00(0.11%)f 0.00(0.01%)g 0.00 (0.01%)
(37.88%) 0.6155* H 21 s(99.87%)p 0.00(0.12%)d 0.00(0.00%)f 0.00(0.01%)

21. (1.98320) BD (1) C 20 - H 22
(61.13%) 0.7819* C 20 s(24.03%)p 3.16(75.87%)d 0.00(0.09%)f 0.00(0.01%)g 0.00 (0.01%)
(38.87%) 0.6234* H 22 s(99.79%)p 0.00(0.20%)d 0.00(0.01%)f 0.00(0.01%)

22. (1.98877) BD (1) C 20 - H 23
(60.74%) 0.7794* C 20 s(23.33%)p 3.28(76.55%)d 0.00(0.11%)f 0.00(0.01%)g 0.00 (0.01%)
(39.26%) 0.6266* H 23 s(99.85%)p 0.00(0.14%)d 0.00(0.00%)f 0.00(0.01%)

43. (1.98034) LP (1) S 2
s(89.32%)p 0.12(10.68%)d 0.00(0.00%)f 0.00(0.00%)g 0.00(0.00%)

44. (1.83837) LP (2) S 2
s(0.00%)p 1.00(99.50%)d 0.00(0.43%)f 0.00(0.06%)g 0.00(0.00%)

45. (1.83837) LP (3) S 2
s(0.00%)p 1.00(99.50%)d 0.00(0.43%)f 0.00(0.06%)g 0.00(0.00%)

Selected molecule orbitals:

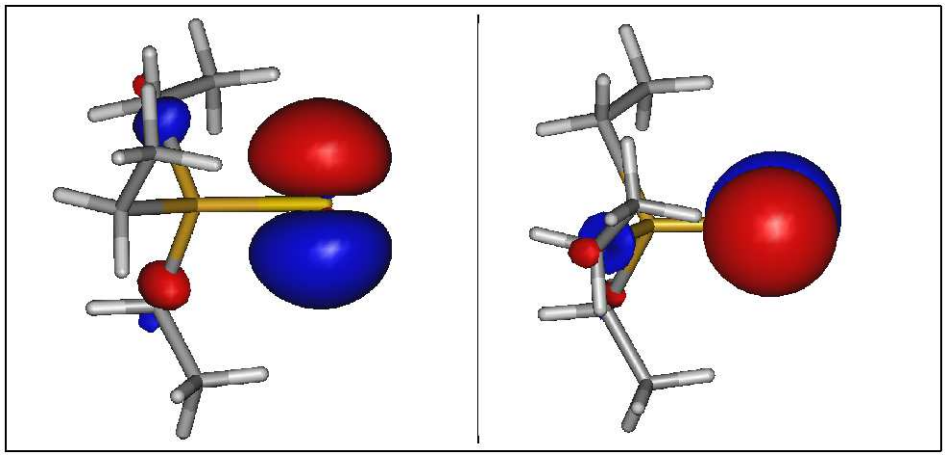

Figure S1: Homo (left) and HOMO-1 (right) of Et_3Sb-S (isovalue ± 0.05 a.u.)

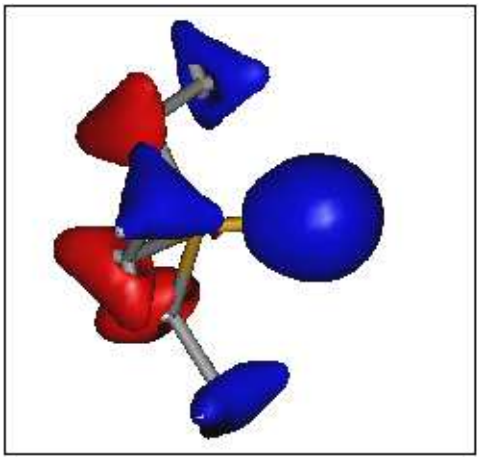

Figure S2: HOMO-20 of Et_3Sb-S (isovalue ± 0.05 a.u.)

Electron localization function:

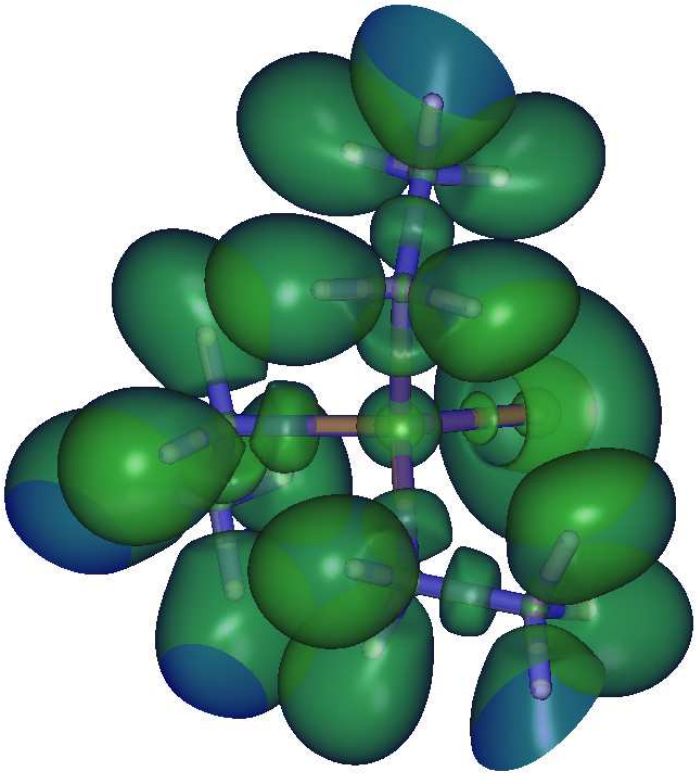

Figure S3: ELF isosurfaces of Et_3Sb-S (isovalue 0.727). The sulfur core electron domain is surrounded by a lone pair domain, the bond electron domain is located on the axis to the antimony core electron domain.

Et_3Sb-S Trimer, **1b**

Energy (in Hartree) and atomic coordinates (in Å):

Energy = -2629.454803311

Sb	0.0000000	0.0000000	6.6963310
S	0.0000000	0.0000000	8.9615511
C	-1.3103181	-1.5061606	5.8426009
H	-1.3400849	-1.3193801	4.7603543
H	-0.8112364	-2.4690423	6.0145668
C	-2.6842225	-1.4473326	6.5063552
H	-2.5972075	-1.5302375	7.5980652
H	-3.3311988	-2.2611255	6.1486980
H	-3.1922680	-0.4985744	6.2873215
C	1.9595324	-0.3816885	5.8426009
H	1.8126592	-0.5008575	4.7603543
H	2.5438716	0.5319698	6.0145668
C	2.5955380	-1.6009386	6.5063552
H	2.6238283	-1.4841289	7.5980652
H	3.6237915	-1.7543401	6.1486980
H	2.0279121	-2.5152980	6.2873215
C	-0.6492143	1.8878491	5.8426009
H	-0.4725743	1.8202376	4.7603543
H	-1.7326352	1.9370725	6.0145668
C	0.0886845	3.0482712	6.5063552
H	-0.0266208	3.0143664	7.5980652
H	-0.2925927	4.0154656	6.1486980
H	1.1643559	3.0138724	6.2873215
Sb	0.0000000	0.0000000	0.3336527
S	0.0000000	0.0000000	2.6037789
C	-1.3029009	-1.5266180	-0.4890845
H	-1.3625341	-1.3380442	-1.5696337
H	-0.7811920	-2.4799625	-0.3324529
C	-2.6602850	-1.4933827	0.2092860
H	-2.5449730	-1.5801814	1.2978333
H	-3.2999002	-2.3176133	-0.1362696
H	-3.1908081	-0.5533791	0.0075400
C	1.9735404	-0.3650363	-0.4890845
H	1.8400473	-0.5109671	-1.5696337
H	2.5383066	0.5634491	-0.3324529
C	2.6234498	-1.5571830	0.2092860
H	2.6409638	-1.4139205	1.2978333
H	3.6570621	-1.6989907	-0.1362696
H	2.0746444	-2.4866313	0.0075400
C	-0.6706395	1.8916543	-0.4890845
H	-0.4775132	1.8490112	-1.5696337
H	-1.7571145	1.9165134	-0.3324529
C	0.0368351	3.0505657	0.2092860
H	-0.0959908	2.9941020	1.2978333
H	-0.3571619	4.0166040	-0.1362696
H	1.1161637	3.0400104	0.0075400
Sb	0.0000000	0.0000000	-5.9812373
S	0.0000000	0.0000000	-3.7169716
C	-1.3042038	-1.5198104	-6.8221189
H	-1.4296634	-1.2829107	-7.8875607
H	-0.7540465	-2.4668055	-6.7444787
C	-2.6283447	-1.5607527	-6.0621690

H	-2.4567426	-1.7018934	-4.9872286
H	-3.2615146	-2.3829605	-6.4223212
H	-3.1912777	-0.6262996	-6.1850050
C	1.9682963	-0.3695684	-6.8221189
H	1.8258650	-0.5966695	-7.8875607
H	2.5133395	0.5803793	-6.7444787
C	2.6658238	-1.4958369	-6.0621690
H	2.7022542	-1.2766548	-4.9872286
H	3.6944616	-1.6330743	-6.4223212
H	2.1380302	-2.4505778	-6.1850050
C	-0.6640926	1.8893788	-6.8221189
H	-0.3962016	1.8795802	-7.8875607
H	-1.7592930	1.8864262	-6.7444787
C	-0.0374791	3.0565896	-6.0621690
H	-0.2455116	2.9785482	-4.9872286
H	-0.4329470	4.0160347	-6.4223212
H	1.0532475	3.0768774	-6.185005

Atomic populations according to NPA:

atom	charge	n(s)	n(p)	n(d)	n(f)	n(g)
1 sb	1.54317	3.31740	8.13240	9.99905	0.00685	0.00113
2 s	-0.76653	5.88229	10.85655	0.02472	0.00286	0.00010
3 c	-0.75064	3.15089	3.59048	0.00703	0.00158	0.00066
4 h	0.24805	0.74909	0.00247	0.00030	0.00008	0.00000
5 h	0.22773	0.76953	0.00235	0.00031	0.00008	0.00000
6 c	-0.64969	3.09801	3.54480	0.00447	0.00132	0.00109
7 h	0.23609	0.76239	0.00102	0.00035	0.00014	0.00000
8 h	0.21718	0.78116	0.00116	0.00037	0.00014	0.00000
9 h	0.21138	0.78688	0.00123	0.00037	0.00014	0.00000
10 c	-0.75064	3.15089	3.59048	0.00703	0.00158	0.00066
11 h	0.24805	0.74909	0.00247	0.00030	0.00008	0.00000
12 h	0.22773	0.76953	0.00235	0.00031	0.00008	0.00000
13 c	-0.64969	3.09801	3.54480	0.00447	0.00132	0.00109
14 h	0.23609	0.76239	0.00102	0.00035	0.00014	0.00000
15 h	0.21718	0.78116	0.00116	0.00037	0.00014	0.00000
16 h	0.21138	0.78688	0.00123	0.00037	0.00014	0.00000
17 c	-0.75064	3.15089	3.59048	0.00703	0.00158	0.00066
18 h	0.24805	0.74909	0.00247	0.00030	0.00008	0.00000
19 h	0.22773	0.76953	0.00235	0.00031	0.00008	0.00000
20 c	-0.64969	3.09801	3.54480	0.00447	0.00132	0.00109
21 h	0.23609	0.76239	0.00102	0.00035	0.00014	0.00000
22 h	0.21718	0.78116	0.00116	0.00037	0.00014	0.00000
23 h	0.21138	0.78688	0.00123	0.00037	0.00014	0.00000
24 sb	1.56945	3.31139	8.11152	9.99964	0.00695	0.00106
25 s	-0.82588	5.87986	10.92209	0.02049	0.00335	0.00010
26 c	-0.74633	3.15075	3.58630	0.00704	0.00158	0.00066
27 h	0.24774	0.74942	0.00246	0.00030	0.00009	0.00000
28 h	0.23040	0.76689	0.00233	0.00031	0.00008	0.00000
29 c	-0.65008	3.09831	3.54484	0.00453	0.00131	0.00109
30 h	0.23638	0.76214	0.00099	0.00035	0.00014	0.00000
31 h	0.22136	0.77699	0.00115	0.00036	0.00014	0.00000
32 h	0.21294	0.78534	0.00121	0.00037	0.00014	0.00000
33 c	-0.74633	3.15075	3.58630	0.00704	0.00158	0.00066
34 h	0.24774	0.74942	0.00246	0.00030	0.00009	0.00000
35 h	0.23040	0.76689	0.00233	0.00031	0.00008	0.00000
36 c	-0.65008	3.09831	3.54484	0.00453	0.00131	0.00109
37 h	0.23638	0.76214	0.00099	0.00035	0.00014	0.00000

38 h	0.22136	0.77699	0.00115	0.00036	0.00014	0.00000
39 h	0.21294	0.78534	0.00121	0.00037	0.00014	0.00000
40 c	-0.74633	3.15075	3.58630	0.00704	0.00158	0.00066
41 h	0.24774	0.74942	0.00246	0.00030	0.00009	0.00000
42 h	0.23040	0.76689	0.00233	0.00031	0.00008	0.00000
43 c	-0.65008	3.09831	3.54484	0.00453	0.00131	0.00109
44 h	0.23638	0.76214	0.00099	0.00035	0.00014	0.00000
45 h	0.22136	0.77699	0.00115	0.00036	0.00014	0.00000
46 h	0.21294	0.78534	0.00121	0.00037	0.00014	0.00000
47 sb	1.55920	3.31101	8.12233	9.99945	0.00695	0.00105
48 s	-0.80762	5.88024	10.90258	0.02120	0.00349	0.00010
49 c	-0.74213	3.15109	3.58182	0.00698	0.00159	0.00066
50 h	0.22905	0.76817	0.00240	0.00030	0.00009	0.00000
51 h	0.23392	0.76330	0.00238	0.00031	0.00009	0.00000
52 c	-0.65053	3.09935	3.54411	0.00466	0.00132	0.00109
53 h	0.23807	0.76042	0.00102	0.00035	0.00014	0.00000
54 h	0.22664	0.77170	0.00116	0.00036	0.00014	0.00000
55 h	0.21521	0.78303	0.00125	0.00036	0.00014	0.00000
56 c	-0.74213	3.15109	3.58182	0.00698	0.00159	0.00066
57 h	0.22905	0.76817	0.00240	0.00030	0.00009	0.00000
58 h	0.23392	0.76330	0.00238	0.00031	0.00009	0.00000
59 c	-0.65053	3.09935	3.54411	0.00466	0.00132	0.00109
60 h	0.23807	0.76042	0.00102	0.00035	0.00014	0.00000
61 h	0.22664	0.77170	0.00116	0.00036	0.00014	0.00000
62 h	0.21521	0.78303	0.00125	0.00036	0.00014	0.00000
63 c	-0.74213	3.15109	3.58182	0.00698	0.00159	0.00066
64 h	0.22905	0.76817	0.00240	0.00030	0.00009	0.00000
65 h	0.23392	0.76330	0.00238	0.00031	0.00009	0.00000
66 c	-0.65053	3.09935	3.54411	0.00466	0.00132	0.00109
67 h	0.23807	0.76042	0.00102	0.00035	0.00014	0.00000
68 h	0.22664	0.77170	0.00116	0.00036	0.00014	0.00000
69 h	0.21521	0.78303	0.00125	0.00036	0.00014	0.00000

Et_3Sb-Se Monomer, **2a**

Energy (in Hartree) and atomic coordinates (in Å):

Energy = -2880.120677896

Sb	0.0000000	0.0000000	0.3976485
Se	0.0000000	0.0000000	2.7902843
C	0.0363390	-3.0583444	0.2138699
H	-0.3375588	-4.0161564	-0.1737487
H	1.1262430	-3.0460562	0.0812001
H	-0.1621264	-3.0207983	1.2931767
C	-0.6252830	-1.8813596	-0.4990429
H	-1.7194681	-1.9094769	-0.4121352
H	-0.3670868	-1.8280304	-1.5659642
C	2.6304344	1.5606427	0.2138699
H	3.6468729	1.7157437	-0.1737487
H	2.0748405	2.4983832	0.0812001
H	2.6971512	1.3699936	1.2931767
C	1.9419467	0.3991689	-0.4990429
H	2.5133896	-0.5343646	-0.4121352
H	1.7666642	0.5961087	-1.5659642
C	-2.6667734	1.4977017	0.2138699
H	-3.3093141	2.3004127	-0.1737487
H	-3.2010835	0.5476730	0.0812001

H	-2.5350249	1.6508047	1.2931767
C	-1.3166637	1.4821907	-0.4990429
H	-0.7939215	2.4438415	-0.4121352
H	-1.3995774	1.2319217	-1.5659642

Atomic populations according to NPA:

atom	charge	n(s)	n(p)	n(d)	n(f)	n(g)
1 sb	1.43662	3.34585	8.20882	9.99988	0.00769	0.00113
2 se	-0.64524	7.90197	16.72614	10.01436	0.00266	0.00012
3 c	-0.65093	3.09894	3.54496	0.00461	0.00132	0.00109
4 h	0.22262	0.77570	0.00118	0.00036	0.00014	0.00000
5 h	0.21348	0.78474	0.00126	0.00037	0.00014	0.00000
6 h	0.23928	0.75919	0.00104	0.00035	0.00014	0.00000
7 c	-0.74427	3.14966	3.58514	0.00719	0.00163	0.00066
8 h	0.23127	0.76588	0.00245	0.00031	0.00009	0.00000
9 h	0.22474	0.77242	0.00245	0.00030	0.00009	0.00000
10 c	-0.65093	3.09894	3.54496	0.00461	0.00132	0.00109
11 h	0.22262	0.77570	0.00118	0.00036	0.00014	0.00000
12 h	0.21348	0.78474	0.00126	0.00037	0.00014	0.00000
13 h	0.23928	0.75919	0.00104	0.00035	0.00014	0.00000
14 c	-0.74427	3.14966	3.58514	0.00719	0.00163	0.00066
15 h	0.23127	0.76588	0.00245	0.00031	0.00009	0.00000
16 h	0.22474	0.77242	0.00245	0.00030	0.00009	0.00000
17 c	-0.65093	3.09894	3.54496	0.00461	0.00132	0.00109
18 h	0.22262	0.77570	0.00118	0.00036	0.00014	0.00000
19 h	0.21348	0.78474	0.00126	0.00037	0.00014	0.00000
20 h	0.23928	0.75919	0.00104	0.00035	0.00014	0.00000
21 c	-0.74427	3.14966	3.58514	0.00719	0.00163	0.00066
22 h	0.23127	0.76588	0.00245	0.00031	0.00009	0.00000
23 h	0.22474	0.77242	0.00245	0.00030	0.00009	0.00000

Natural bond orbitals (population, character and atomic contributions; BD = bonding orbital, LP = lone pair orbital, core and Rydberg orbitals not shown).

1. (1.93957) BD (1)Sb 1 -Se 2
   (50.66%) 0.7118*Sb 1 s(28.64%)p 2.48(71.13%)d 0.00(0.14%)f 0.00(0.07%)g 0.00 (0.02%)
   (49.34%) 0.7024*Se 2 s(7.89%)p11.62(91.74%)d 0.04(0.34%)f 0.00(0.02%)g 0.00 (0.00%)

2. (1.94544) BD (1)Sb 1 - C 7
   (37.96%) 0.6161*Sb 1 s(23.78%)p 3.20(76.10%)d 0.00(0.06%)f 0.00(0.04%)g 0.00 (0.01%)
   (62.04%) 0.7876* C 7 s(18.25%)p 4.47(81.50%)d 0.01(0.24%)f 0.00(0.01%)g 0.00 (0.01%)

3. (1.94544) BD (1)Sb 1 - C 14
   (37.96%) 0.6161*Sb 1 s(23.78%)p 3.20(76.10%)d 0.00(0.06%)f 0.00(0.04%)g 0.00 (0.01%)
   (62.04%) 0.7876* C 14 s(18.25%)p 4.47(81.50%)d 0.01(0.24%)f 0.00(0.01%)g 0.00 (0.01%)

4. (1.94544) BD (1)Sb 1 - C 21
   (37.96%) 0.6161*Sb 1 s(23.78%)p 3.20(76.10%)d 0.00(0.06%)f 0.00(0.04%)g 0.00 (0.01%)
   (62.04%) 0.7876* C 21 s(18.25%)p 4.47(81.50%)d 0.01(0.24%)f 0.00(0.01%)g 0.00 (0.01%)

5. (1.98301) BD (1) C 3 - H 4
(61.15%) 0.7820* C 3 s(24.00%)p 3.16(75.89%)d 0.00(0.09%)f 0.00(0.01%)g 0.00 (0.01%)
(38.85%) 0.6233* H 4 s(99.79%)p 0.00(0.20%)d 0.00(0.01%)f 0.00(0.01%)

6. (1.98871) BD (1) C 3 - H 5
(60.74%) 0.7794* C 3 s(23.34%)p 3.28(76.54%)d 0.00(0.11%)f 0.00(0.01%)g 0.00 (0.01%)
(39.26%) 0.6266* H 5 s(99.85%)p 0.00(0.14%)d 0.00(0.00%)f 0.00(0.01%)

7. (1.98792) BD (1) C 3 - H 6
(62.09%) 0.7880* C 3 s(23.98%)p 3.17(75.90%)d 0.00(0.11%)f 0.00(0.01%)g 0.00 (0.01%)
(37.91%) 0.6157* H 6 s(99.87%)p 0.00(0.12%)d 0.00(0.00%)f 0.00(0.01%)

8. (1.99348) BD (1) C 3 - C 7
(49.05%) 0.7004* C 3 s(28.74%)p 2.48(71.15%)d 0.00(0.08%)f 0.00(0.01%)g 0.00 (0.01%)
(50.95%) 0.7138* C 7 s(31.02%)p 2.22(68.87%)d 0.00(0.09%)f 0.00(0.01%)g 0.00 (0.01%)

9. (1.98212) BD (1) C 7 - H 8
(61.64%) 0.7851* C 7 s(25.28%)p 2.95(74.58%)d 0.01(0.13%)f 0.00(0.01%)g 0.00 (0.00%)
(38.36%) 0.6193* H 8 s(99.77%)p 0.00(0.23%)d 0.00(0.01%)f 0.00(0.00%)

10. (1.98199) BD (1) C 7 - H 9
(61.33%) 0.7831* C 7 s(25.51%)p 2.91(74.35%)d 0.00(0.13%)f 0.00(0.01%)g 0.00 (0.00%)
(38.67%) 0.6219* H 9 s(99.77%)p 0.00(0.22%)d 0.00(0.01%)f 0.00(0.00%)

11. (1.98301) BD (1) C 10 - H 11
(61.15%) 0.7820* C 10 s(24.00%)p 3.16(75.89%)d 0.00(0.09%)f 0.00(0.01%)g 0.00 (0.01%)
(38.85%) 0.6233* H 11 s(99.79%)p 0.00(0.20%)d 0.00(0.01%)f 0.00(0.01%)

12. (1.98871) BD (1) C 10 - H 12
(60.74%) 0.7794* C 10 s(23.34%)p 3.28(76.54%)d 0.00(0.11%)f 0.00(0.01%)g 0.00 (0.01%)
(39.26%) 0.6266* H 12 s(99.85%)p 0.00(0.14%)d 0.00(0.00%)f 0.00(0.01%)

13. (1.98792) BD (1) C 10 - H 13
(62.09%) 0.7880* C 10 s(23.98%)p 3.17(75.90%)d 0.00(0.11%)f 0.00(0.01%)g 0.00 (0.01%)
(37.91%) 0.6157* H 13 s(99.87%)p 0.00(0.12%)d 0.00(0.00%)f 0.00(0.01%)

14. (1.99348) BD (1) C 10 - C 14
(49.05%) 0.7004* C 10 s(28.74%)p 2.48(71.15%)d 0.00(0.08%)f 0.00(0.01%)g 0.00 (0.01%)
(50.95%) 0.7138* C 14 s(31.02%)p 2.22(68.87%)d 0.00(0.09%)f 0.00(0.01%)g 0.00 (0.01%)

15. (1.98212) BD (1) C 14 - H 15
(61.64%) 0.7851* C 14 s(25.28%)p 2.95(74.58%)d 0.01(0.13%)f 0.00(0.01%)g 0.00 (0.00%)
(38.36%) 0.6193* H 15 s(99.77%)p 0.00(0.23%)d 0.00(0.01%)f 0.00(0.00%)

16. (1.98199) BD (1) C 14 - H 16
(61.33%) 0.7831* C 14 s(25.51%)p 2.91(74.35%)d 0.00(0.13%)f 0.00(0.01%)g 0.00 (0.00%)
(38.67%) 0.6219* H 16 s(99.77%)p 0.00(0.22%)d 0.00(0.01%)f 0.00(0.00%)

17. (1.98301) BD (1) C 17 - H 18
(61.15%) 0.7820* C 17 s(24.00%)p 3.16(75.89%)d 0.00(0.09%)f 0.00(0.01%)g 0.00 (0.01%)
(38.85%) 0.6233* H 18 s(99.79%)p 0.00(0.20%)d 0.00(0.01%)f 0.00(0.01%)

18. (1.98871) BD (1) C 17 - H 19
(60.74%) 0.7794* C 17 s(23.34%)p 3.28(76.54%)d 0.00(0.11%)f 0.00(0.01%)g 0.00 (0.01%)
(39.26%) 0.6266* H 19 s(99.85%)p 0.00(0.14%)d 0.00(0.00%)f 0.00(0.01%)

19. (1.98792) BD (1) C 17 - H 20
(62.09%) 0.7880* C 17 s(23.98%)p 3.17(75.90%)d 0.00(0.11%)f 0.00(0.01%)g 0.00 (0.01%)
(37.91%) 0.6157* H 20 s(99.87%)p 0.00(0.12%)d 0.00(0.00%)f 0.00(0.01%)

20. (1.99348) BD (1) C 17 - C 21
(49.05%) 0.7004* C 17 s(28.74%)p 2.48(71.15%)d 0.00(0.08%)f 0.00(0.01%)g 0.00 (0.01%)
(50.95%) 0.7138* C 21 s(31.02%)p 2.22(68.87%)d 0.00(0.09%)f 0.00(0.01%)g 0.00 (0.01%)

21. (1.98212) BD (1) C 21 - H 22
(61.64%) 0.7851* C 21 s(25.28%)p 2.95(74.58%)d 0.01(0.13%)f 0.00(0.01%)g 0.00 (0.00%)
(38.36%) 0.6193* H 22 s(99.77%)p 0.00(0.23%)d 0.00(0.01%)f 0.00(0.00%)

22. (1.98199) BD (1) C 21 - H 23
(61.33%) 0.7831* C 21 s(25.51%)p 2.91(74.35%)d 0.00(0.13%)f 0.00(0.01%)g 0.00 (0.00%)
(38.67%) 0.6219* H 23 s(99.77%)p 0.00(0.22%)d 0.00(0.01%)f 0.00(0.00%)

52. (1.98156) LP (1)Se 2
s(92.06%)p 0.09(7.94%)d 0.00(0.00%)f 0.00(0.00%)g 0.00(0.00%)

53. (1.83593) LP (2)Se 2
s(0.00%)p 1.00(99.89%)d 0.00(0.08%)f 0.00(0.03%)g 0.00(0.00%)

54. (1.83593) LP (3)Se 2
s(0.00%)p 1.00(99.89%)d 0.00(0.08%)f 0.00(0.03%)g 0.00(0.00%)

Selected molecule orbitals:

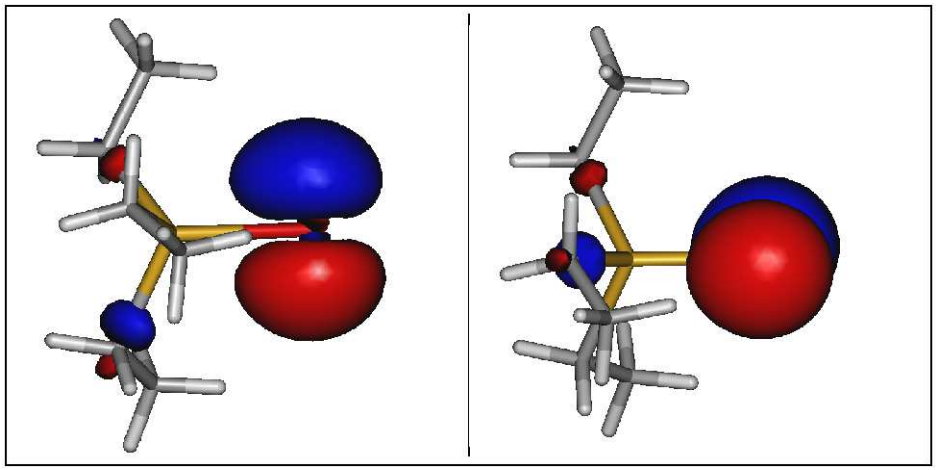

Figure S4: HOMO (left) and HOMO-1 (right) of Et_3Sb-Se (isovalue ± 0.05 a.u.)

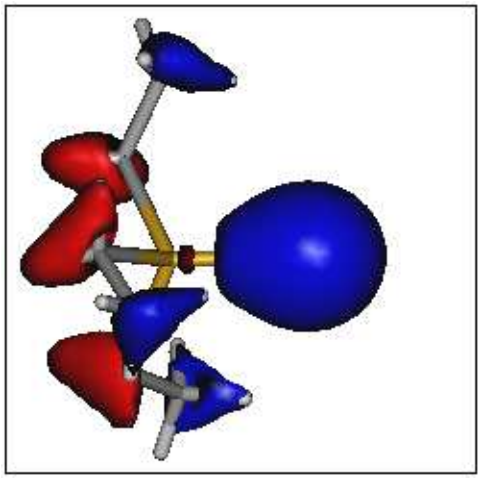

Figure S5: HOMO-20 of Et_3Sb-Se (isovalue ± 0.05 a.u.)

Electron localization function:

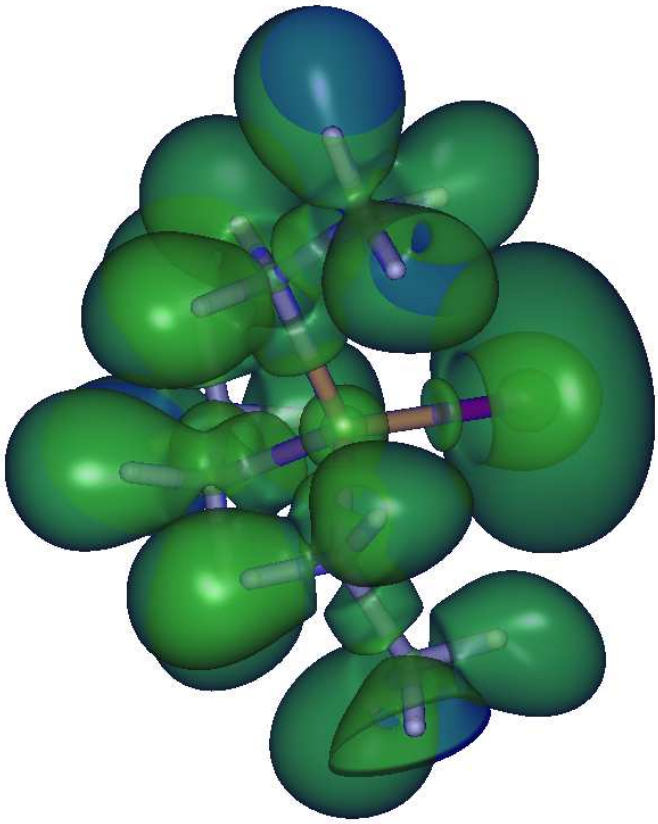

Figure S6: ELF isosurfaces of Et_3Sb-Se (isovalue 0.670). The Se core electron domain is surrounded by a lone pair domain, the bond electron domain is located on the axis to the antimony core electron domain.

Et_3Sb-Se Trimer, **2b**

Energy (in Hartree) and atomic coordinates (in Å):

Energy = -8640.383051191

Sb	0.0000000	0.0000000	7.0285667
Se	0.0000000	0.0000000	9.4294073
C	0.5938421	-1.8984145	6.1554079
H	1.6733541	-1.9855582	6.3357406
H	0.4294704	-1.8131883	5.0720596
C	-0.1881121	-3.0438600	6.7932790
H	-1.2602857	-2.9688330	6.5677561
H	0.1628241	-4.0166246	6.4203953
H	-0.0788357	-3.0334041	7.8861867
C	1.3471542	1.4634896	6.1554079
H	0.8828668	2.4419462	6.3357406
H	1.3555319	1.2785264	5.0720596
C	2.7301162	1.3590201	6.7932790
H	3.2012276	0.3929770	6.5677561
H	3.3970869	2.1493221	6.4203953
H	2.6664228	1.4484284	7.8861867
C	-1.9409962	0.4349249	6.1554079
H	-2.5562208	-0.4563880	6.3357406
H	-1.7850023	0.5346619	5.0720596
C	-2.5420040	1.6848399	6.7932790
H	-1.9409419	2.5758559	6.5677561
H	-3.5599110	1.8673025	6.4203953
H	-2.5875872	1.5849757	7.8861867
Sb	0.0000000	0.0000000	0.3680157
Se	0.0000000	0.0000000	2.7736263
C	0.9484934	-1.7591230	-0.4781917
H	2.0250077	-1.6279823	-0.3075093
H	0.7636417	-1.7260568	-1.5610043
C	0.4104803	-3.0240913	0.1855680
H	-0.6575415	-3.1641835	-0.0274502
H	0.9423137	-3.9141665	-0.1785124
H	0.5267891	-2.9757234	1.2765158
C	1.0491985	1.7009809	-0.4781917
H	0.3973701	2.5676993	-0.3075093
H	1.1129882	1.5243615	-1.5610043
C	2.4136998	1.8675320	0.1855680
H	3.0690341	1.0126441	-0.0274502
H	2.9186108	2.7731509	-0.1785124
H	2.3136575	1.9440745	1.2765158
C	-1.9976919	0.0581421	-0.4781917
H	-2.4223779	-0.9397170	-0.3075093
H	-1.8766299	0.2016953	-1.5610043
C	-2.8241801	1.1565593	0.1855680
H	-2.4114926	2.1515394	-0.0274502
H	-3.8609245	1.1410156	-0.1785124
H	-2.8404466	1.0316490	1.2765158
Sb	0.0000000	0.0000000	-6.2513444
Se	0.0000000	0.0000000	-3.8510278
C	0.9092901	-1.7743957	-7.1154891
H	1.9940753	-1.6312604	-7.0258965
H	0.6502861	-1.7755855	-8.1833383
C	0.4325563	-3.0288057	-6.3872557
H	-0.6462649	-3.1842167	-6.5185714

H	0.9481035	-3.9216925	-6.7662735
H	0.6245543	-2.9506785	-5.3091647
C	1.0820267	1.6746662	-7.1154891
H	0.4156753	2.5425500	-7.0258965
H	1.2125591	1.4509570	-8.1833383
C	2.4067445	1.8890076	-6.3872557
H	3.0807450	1.0324265	-6.5185714
H	2.9222335	2.7819280	-6.7662735
H	2.2430854	2.0162192	-5.3091647
C	-1.9913168	0.0997295	-7.1154891
H	-2.4097506	-0.9112897	-7.0258965
H	-1.8628452	0.3246285	-8.1833383
C	-2.8393008	1.1397981	-6.3872557
H	-2.4344800	2.1517902	-6.5185714
H	-3.8703371	1.1397645	-6.7662735
H	-2.8676397	0.9344594	-5.3091647

Atomic populations according to NPA:

atom	charge	n(s)	n(p)	n(d)	n(f)	n(g)
1 sb	1.45070	3.34483	8.19607	9.99954	0.00771	0.00114
2 se	-0.68050	7.90167	16.76260	10.01357	0.00255	0.00011
3 c	-0.74777	3.14966	3.58849	0.00733	0.00162	0.00066
4 h	0.22869	0.76850	0.00242	0.00031	0.00008	0.00000
5 h	0.24553	0.75160	0.00249	0.00030	0.00009	0.00000
6 c	-0.65004	3.09798	3.54517	0.00448	0.00132	0.00109
7 h	0.21192	0.78636	0.00121	0.00037	0.00014	0.00000
8 h	0.21874	0.77960	0.00116	0.00036	0.00014	0.00000
9 h	0.23589	0.76260	0.00101	0.00035	0.00014	0.00000
10 c	-0.74777	3.14966	3.58849	0.00733	0.00162	0.00066
11 h	0.22869	0.76850	0.00242	0.00031	0.00008	0.00000
12 h	0.24553	0.75160	0.00249	0.00030	0.00009	0.00000
13 c	-0.65004	3.09798	3.54517	0.00448	0.00132	0.00109
14 h	0.21192	0.78636	0.00121	0.00037	0.00014	0.00000
15 h	0.21874	0.77960	0.00116	0.00036	0.00014	0.00000
16 h	0.23589	0.76260	0.00101	0.00035	0.00014	0.00000
17 c	-0.74777	3.14966	3.58849	0.00733	0.00162	0.00066
18 h	0.22869	0.76850	0.00242	0.00031	0.00008	0.00000
19 h	0.24553	0.75160	0.00249	0.00030	0.00009	0.00000
20 c	-0.65004	3.09798	3.54517	0.00448	0.00132	0.00109
21 h	0.21192	0.78636	0.00121	0.00037	0.00014	0.00000
22 h	0.21874	0.77960	0.00116	0.00036	0.00014	0.00000
23 h	0.23589	0.76260	0.00101	0.00035	0.00014	0.00000
24 sb	1.47814	3.33828	8.17522	9.99957	0.00771	0.00108
25 se	-0.74069	7.89948	16.82655	10.01117	0.00339	0.00010
26 c	-0.74403	3.14961	3.58481	0.00733	0.00162	0.00066
27 h	0.23116	0.76606	0.00239	0.00031	0.00008	0.00000
28 h	0.24566	0.75148	0.00248	0.00030	0.00009	0.00000
29 c	-0.65061	3.09828	3.54539	0.00454	0.00131	0.00110
30 h	0.21335	0.78495	0.00119	0.00037	0.00014	0.00000
31 h	0.22253	0.77581	0.00115	0.00036	0.00014	0.00000
32 h	0.23634	0.76219	0.00097	0.00035	0.00014	0.00000
33 c	-0.74403	3.14961	3.58481	0.00733	0.00162	0.00066
34 h	0.23116	0.76606	0.00239	0.00031	0.00008	0.00000
35 h	0.24566	0.75148	0.00248	0.00030	0.00009	0.00000
36 c	-0.65061	3.09828	3.54539	0.00454	0.00131	0.00110
37 h	0.21335	0.78495	0.00119	0.00037	0.00014	0.00000
38 h	0.22253	0.77581	0.00115	0.00036	0.00014	0.00000

39 h	0.23634	0.76219	0.00097	0.00035	0.00014	0.00000
40 c	-0.74403	3.14961	3.58481	0.00733	0.00162	0.00066
41 h	0.23116	0.76606	0.00239	0.00031	0.00008	0.00000
42 h	0.24566	0.75148	0.00248	0.00030	0.00009	0.00000
43 c	-0.65061	3.09828	3.54539	0.00454	0.00131	0.00110
44 h	0.21335	0.78495	0.00119	0.00037	0.00014	0.00000
45 h	0.22253	0.77581	0.00115	0.00036	0.00014	0.00000
46 h	0.23634	0.76219	0.00097	0.00035	0.00014	0.00000
47 sb	1.46913	3.33865	8.18380	9.99964	0.00771	0.00107
48 se	-0.72307	7.89997	16.80783	10.01161	0.00355	0.00011
49 c	-0.74007	3.14967	3.58086	0.00725	0.00163	0.00066
50 h	0.23385	0.76332	0.00243	0.00031	0.00009	0.00000
51 h	0.22858	0.76859	0.00245	0.00030	0.00009	0.00000
52 c	-0.65116	3.09922	3.54488	0.00465	0.00131	0.00110
53 h	0.21519	0.78307	0.00123	0.00037	0.00014	0.00000
54 h	0.22689	0.77144	0.00117	0.00036	0.00014	0.00000
55 h	0.23814	0.76035	0.00101	0.00035	0.00014	0.00000
56 c	-0.74007	3.14967	3.58086	0.00725	0.00163	0.00066
57 h	0.23385	0.76332	0.00243	0.00031	0.00009	0.00000
58 h	0.22858	0.76859	0.00245	0.00030	0.00009	0.00000
59 c	-0.65116	3.09922	3.54488	0.00465	0.00131	0.00110
60 h	0.21519	0.78307	0.00123	0.00037	0.00014	0.00000
61 h	0.22689	0.77144	0.00117	0.00036	0.00014	0.00000
62 h	0.23814	0.76035	0.00101	0.00035	0.00014	0.00000
63 c	-0.74007	3.14967	3.58086	0.00725	0.00163	0.00066
64 h	0.23385	0.76332	0.00243	0.00031	0.00009	0.00000
65 h	0.22858	0.76859	0.00245	0.00030	0.00009	0.00000
66 c	-0.65116	3.09922	3.54488	0.00465	0.00131	0.00110
67 h	0.21519	0.78307	0.00123	0.00037	0.00014	0.00000
68 h	0.22689	0.77144	0.00117	0.00036	0.00014	0.00000
69 h	0.23814	0.76035	0.00101	0.00035	0.00014	0.00000