SUPPLEMENTARY INFORMATION

Effects of Charge and Substituent on the S···N Chalcogen Bond

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Table S1: SAPT for XHS···N interaction

	ES	EX	IND	IND+EXIND	DISP	DISP+EXDISP	Tot
CH_3	-2.37	2.80	-1.13	-0.22	-2.02	-1.75	-1.54
NH_2	-4.65	5.37	-3.72	-0.65	-2.76	-3.61	-3.54
CF_3	-6.28	5.34	-.97	-0.82	-2.56	-2.10	-3.86
OH	-10.00	11.70	-10.35	-1.70	-4.19	-3.29	-3.29
Cl	-15.16	18.91	-17.85	-3.15	-5.53	-4.24	-3.64
F	-24.35	30.97	-33.86	-6.08	-7.34	-5.52	-4.98
NO_2	-13.85	13.65	-13.31	-2.57	-4.45	-3.50	-6.27

Table S2: SAPT for XMeS···N interaction

	ES	EX	IND	IND+EXIND	DISP	DISP+EXDISP	Tot
H	-4.17	4.38	-1.79	-0.54	-2.87	-2.44	-2.77
CH_3	-3.89	4.21	-1.58	-0.49	-2.95	-2.53	-2.70
NH_2	-3.95	4.45	-1.94	-0.50	-2.99	-2.54	-2.53
CF_3	-5.74	5.42	-3.02	-0.75	-3.20	-2.68	-3.76
OH	-5.73	6.13	-3.58	-0.75	-3.44	-2.86	-3.20
Cl	-8.02	8.82	-6.29	-1.21	-4.17	-3.37	-3.78
F	-13.00	15.9	-14.30	-2.42	-5.61	-4.38	-3.92
NO_2	-8.01	7.17	-5.09	-1.15	-3.64	-2.99	-4.98

Table S3: SAPT for XMe_2S^+···N interaction

	ES	EX	IND	IND+EXIND	DISP	DISP+EXDISP	Tot
H	-16.99	11.48	-10.54	-3.26	-4.93	-4.03	-12.79
CH_3	-14.31	9.29	-7.65	-2.52	-4.53	-3.74	-11.27
NH_2	-16.78	12.12	-10.89	-3.16	-5.16	-4.19	-12.00
CF_3	-18.60	13.13	-12.60	-3.80	-5.37	-4.35	-13.64
OH	-23.29	20.83	-21.12	-5.24	-6.84	-5.38	-13.08
Cl	-25.81	25.03	-25.38	-6.23	-7.64	-5.97	-12.98
F	-48.33	59.26	-73.01	-17.62	-12.51	-9.42	-16.12
NO_2	-22.93	19.06	-19.98	-5.46	-6.49	-5.15	-14.49

Coordinates of XMeS complexes with NH_3

HMes

S	0	-1.466888	-0.845322	0.065781
C	0	-1.061661	0.938568	0.169846
H	0	-2.799652	-0.730164	0.246445
H	0	0.027588	0.986481	0.036057
H	0	-1.332535	1.346436	1.152664
H	0	-1.558792	1.501923	-0.630814
N	0	1.786591	-0.904800	-0.335037
H	0	1.384140	-1.364822	-1.152649
H	0	1.555237	-1.501907	0.459976
H	0	2.799652	-0.954971	-0.446732

Me_2S

S	0	-1.023941	-0.730057	-0.009537
C	0	-0.601608	1.038727	0.094543
C	0	-2.828690	-0.585052	0.190643
H	0	-0.903534	1.449493	1.070236
H	0	-1.090591	1.599274	-0.717010
H	0	0.490433	1.102631	-0.014343
H	0	-3.252335	-1.599258	0.150604
H	0	-3.075592	-0.131897	1.163010
H	0	-3.261826	0.016464	-0.623123
N	0	2.265366	-0.790955	-0.356430
H	0	1.797318	-1.206482	-1.162994
H	0	1.963623	-1.341202	0.449005
H	0	3.261841	-0.976013	-0.474915

NH_2MeS

S	0	-1.038315	-0.823669	0.030746
C	0	-0.723038	0.962800	0.100174
N	0	-2.790283	-0.785339	0.180939
H	0	0.369171	1.069626	0.013748
H	0	-1.071579	1.372864	1.058151
H	0	-1.223083	1.469345	-0.736969
H	0	-3.061966	-1.326630	1.002975
H	0	-3.200700	-1.237823	-0.637222
N	0	2.185669	-0.898148	-0.246689
H	0	1.797836	-1.381088	-1.058151
H	0	1.935913	-1.469330	0.561661
H	0	3.200714	-0.953308	-0.336166

CF_3MeS

S	0	-0.845032	-0.585022	-0.127274
C	0	-0.486969	1.203293	-0.074570
C	0	-2.618225	-0.473373	0.161026
F	0	-3.143021	-1.723465	0.167145
F	0	-3.275543	0.243118	-0.792908
F	0	-2.934998	0.110458	1.350372
H	0	0.597504	1.262054	-0.236664
H	0	-0.749023	1.615585	0.908432
H	0	-1.023270	1.723480	-0.878738
N	0	2.293091	-0.720947	-0.548264
H	0	3.275543	-0.474762	-0.674393
H	0	2.042343	-1.300705	-1.350372

H 0 2.258621 -1.338500 0.263992

OHMeS
S 0 -0.914047 -0.832535 0.120743
C 0 -0.705582 0.960098 0.259521
O 0 -2.574326 -0.958496 0.576721
H 0 0.361511 1.134293 0.053741
H 0 -0.954651 1.290222 1.277725
H 0 -1.321594 1.489548 -0.481461
H 0 -3.078568 -0.909622 -0.251465
N 0 2.104019 -0.870285 -0.482330
H 0 1.827621 -1.447144 -1.277710
H 0 2.099900 -1.489548 0.329147
H 0 3.078583 -0.612488 -0.641388

ClMeS
S 0 -0.871902 -0.762558 0.141891
C 0 -0.706024 1.043808 0.194641
Cl 0 -2.934982 -0.857651 0.482895
H 0 0.364929 1.224380 0.023529
H 0 -1.006592 1.425125 1.179947
H 0 -1.304855 1.504623 -0.602615
N 0 2.036011 -0.855423 -0.350037
H 0 1.891068 -1.431870 -1.179947
H 0 2.162170 -1.504608 0.427490
H 0 2.934967 -0.389389 -0.480545

FMeS
S 0 -0.832245 -0.693863 0.748505
C 0 -0.874939 0.843582 -0.202438
F 0 -2.506653 -0.686920 1.078200
H 0 0.155853 1.036316 -0.527695
H 0 -1.226868 1.667587 0.433487
H 0 -1.527710 0.724625 -1.078217
N 0 1.859955 -0.824387 0.282135
H 0 2.187500 -1.052185 -0.657288
H 0 1.990936 -1.667587 0.842072
H 0 2.506653 -0.129654 0.657883

NO_2MeS
S 0 -0.767456 -0.566956 -0.120117
C 0 -0.533234 1.222015 0.014664
N 0 -2.567764 -0.599487 -0.152771
O 0 -3.049835 -1.732407 -0.243835
O 0 -3.189896 0.463043 -0.085403
H 0 0.560532 1.332825 0.040695
H 0 -0.983795 1.600555 0.940842
H 0 -0.954269 1.732407 -0.860764
N 0 2.260635 -0.745789 -0.083252
H 0 2.243057 -1.299667 -0.940842
H 0 2.218719 -1.417800 0.684265
H 0 3.189896 -0.325363 -0.038818

Coordinates of XH_2S^+ complexes with NH_3

H_3S^+

S 0	-1.042923	-0.072754	0.072189
H 0	-0.508728	0.585724	1.129623
H 0	-2.311310	0.401962	0.268097
H 0	-0.705521	0.873688	-0.837418
N 0	1.712875	-0.209473	-0.218445
H 0	2.311310	0.617081	-0.138916
H 0	2.094147	-0.873703	0.460266
H 0	1.945648	-0.613068	-1.129608

$CH_3H_2S^+$

S 0	-0.564087	-0.500244	0.044600
C 0	-2.260361	0.129807	0.347443
H 0	0.112488	0.166275	1.008942
H 0	-0.174362	0.334213	-0.947327
H 0	-2.869568	-0.202942	-0.503555
H 0	-2.259857	1.221390	0.441330
H 0	-2.609802	-0.355545	1.268509
N 0	2.273483	-0.612885	-0.380569
H 0	2.869568	0.218552	-0.396469
H 0	2.693985	-1.221375	0.326111
H 0	2.461014	-1.084900	-1.268509

$NH_2H_2S^+$

S 0	-0.532776	-0.260406	0.110077
N 0	-2.191452	0.069977	0.243317
H 0	0.063446	0.382950	1.148500
H 0	-0.210556	0.673828	-0.812256
H 0	-2.437973	0.964020	0.669250
H 0	-2.678238	-0.709076	0.688095
N 0	2.102509	-0.330475	-0.239822
H 0	2.525803	-0.964005	0.443039
H 0	2.302322	-0.756256	-1.148500
H 0	2.678238	0.515213	-0.209976

$CF_3H_2S^+$

S 0	-0.342697	-0.574219	-0.049805
C 0	-2.164108	-0.142273	0.274994
F 0	-2.844223	-0.491623	-0.813980
F 0	-2.547119	-0.853333	1.332489
F 0	-2.295212	1.162491	0.513016
H 0	0.126938	0.105606	1.026184
H 0	-0.144333	0.435593	-0.933838
N 0	2.311768	-0.520905	-0.408264
H 0	2.759705	-1.162476	0.251450
H 0	2.540497	-0.896378	-1.332489
H 0	2.844223	0.350418	-0.335541

OHH_2S^+

S 0	-0.387924	-0.203918	0.017900
O 0	-2.041779	0.050995	0.218750
H 0	-0.010834	0.498138	1.112152
H 0	-0.202316	0.810410	-0.859207
H 0	-2.491684	-0.810410	0.126221

N 0 2.013428 -0.097260 -0.198547
H 0 2.491684 0.803391 -0.102234
H 0 2.448639 -0.719315 0.488205
H 0 2.292892 -0.465073 -1.112152

ClH_2S^+
S 0 -0.393143 -0.236435 0.098206
Cl 0 -2.444305 0.022781 0.437195
H 0 -0.004547 0.528763 1.147964
H 0 -0.297653 0.762283 -0.814011
N 0 1.959976 -0.174026 -0.242752
H 0 2.444305 0.728745 -0.222824
H 0 2.417557 -0.762300 0.459854
H 0 2.180176 -0.599533 -1.147964

FH_2S^+
S 0 -0.527847 -0.127396 0.115494
F 0 -2.148422 0.201950 0.373215
H 0 -0.132446 0.722229 1.093964
H 0 -0.441254 0.764313 -0.900772
N 0 1.635468 -0.214066 -0.222137
H 0 1.821350 -0.720856 -1.093948
H 0 2.148422 0.672409 -0.277908
H 0 2.072403 -0.764328 0.524567

$NO_2H_2S^+$
S 0 -0.285309 -0.194443 -0.156128
N 0 -2.477310 0.421310 0.095444
O 0 -2.811295 0.294006 1.231674
O 0 -2.936127 0.743225 -0.955673
H 0 0.059906 0.470520 0.975357
H 0 -0.050858 0.869247 -0.965607
N 0 2.410004 -0.193451 -0.309784
H 0 2.936111 0.671768 -0.163605
H 0 2.771957 -0.869263 0.366882
H 0 2.680328 -0.543503 -1.231674

Coordinates of XMe_2S^+ complexes with NH_3

HMe_2S^+

S	0	-1.156372	-0.706223	-0.074402
C	0	-1.083435	0.583527	-1.362061
C	0	-0.750488	0.242416	1.429642
H	0	-2.506866	-0.708969	0.086365
H	0	-0.018738	0.823959	-1.464233
H	0	-1.677094	1.452621	-1.052277
H	0	-1.473511	0.138611	-2.287506
H	0	-0.928787	-0.420013	2.287521
H	0	-1.374359	1.143478	1.480942
H	0	0.315414	0.481216	1.336900
N	0	1.787460	-0.770050	-0.433029
H	0	1.920135	-1.245636	-1.329376
H	0	2.100922	-1.452621	0.261887
H	0	2.506882	-0.042358	-0.420303

Me_3S^+

S	0	-0.829437	-0.669250	-0.088669
C	0	-0.550415	0.643494	-1.309402
C	0	-2.646790	-0.665543	-0.009659
C	0	-0.431137	0.202087	1.451828
H	0	0.531937	0.820953	-1.318069
H	0	-1.114532	1.539963	-1.015762
H	0	-0.888382	0.261749	-2.282883
H	0	-2.939575	-1.341812	0.805679
H	0	-3.016205	-1.058900	-0.967133
H	0	-3.014267	0.354721	0.169052
H	0	-0.689865	-0.468811	2.282898
H	0	-1.006851	1.137085	1.500977
H	0	0.650208	0.383591	1.423584
N	0	2.257538	-0.823471	-0.246490
H	0	3.016205	-0.141251	-0.169571
H	0	2.417023	-1.284042	-1.145966
H	0	2.485687	-1.539963	0.447128

$NH_2Me_2S^+$

S	0	-0.728455	-0.556534	-0.088730
C	0	-0.380981	0.759369	-1.277451
C	0	-0.555466	0.348709	1.473572
N	0	-2.403198	-0.698730	-0.347336
H	0	0.660690	1.061478	-1.116119
H	0	-1.081619	1.588104	-1.101517
H	0	-0.524261	0.326385	-2.276367
H	0	-0.888443	-0.323807	2.276352
H	0	-1.173294	1.257660	1.431580
H	0	0.510223	0.587311	1.581009
H	0	-2.950912	0.081329	0.024490
H	0	-2.745377	-1.588104	0.020767
N	0	2.211685	-0.737534	0.060883
H	0	2.458725	-1.184769	-0.825638
H	0	2.385284	-1.459656	0.764618
H	0	2.950928	-0.046539	0.214493

$CF_3Me_2S^+$

S 0 -0.618881 -0.639114 -0.080383
C 0 -0.387970 0.670059 -1.321655
C 0 -2.489487 -0.674820 -0.089340
C 0 -0.393753 0.263458 1.482513
F 0 -2.878738 -1.478531 0.903412
F 0 -2.874313 -1.163422 -1.270966
F 0 -3.009338 0.546158 0.086533
H 0 0.685806 0.891953 -1.305054
H 0 -0.996933 1.542038 -1.050308
H 0 -0.685242 0.248566 -2.291794
H 0 -0.695038 -0.415848 2.291809
H 0 -1.001785 1.177155 1.467361
H 0 0.680038 0.479919 1.534210
N 0 2.280365 -0.826614 -0.101990
H 0 2.509186 -1.273575 -0.993744
H 0 2.491486 -1.542023 0.598755
H 0 3.009338 -0.119339 0.025238

$OHMe_2S^+$
S 0 -0.724533 -0.533066 -0.104996
C 0 -0.560181 0.854675 -1.251419
O 0 -2.405029 -0.628983 -0.168427
C 0 -0.633041 0.326141 1.482727
H 0 0.430542 1.299118 -1.103851
H 0 -1.372559 1.558090 -1.020340
H 0 -0.667389 0.448364 -2.266251
H 0 -2.639908 -1.558090 -0.354004
H 0 -0.787521 -0.428040 2.266235
H 0 -1.439835 1.072449 1.489151
H 0 0.359329 0.784119 1.562103
N 0 1.989243 -0.581924 -0.042038
H 0 2.281830 -0.983948 -0.936508
H 0 2.240707 -1.290268 0.652496
H 0 2.639908 0.190948 0.123764

$ClMe_2S^+$
S 0 -0.625748 -0.689270 -0.104721
C 0 -0.545792 0.694031 -1.283386
Cl 0 -2.685593 -0.911819 -0.090805
C 0 -0.472198 0.186264 1.482468
H 0 0.484756 1.067917 -1.266602
H 0 -1.271469 1.455582 -0.968719
H 0 -0.804443 0.280502 -2.268127
H 0 -0.683716 -0.552292 2.268143
H 0 -1.206009 1.003021 1.496338
H 0 0.559570 0.551575 1.546448
N 0 2.026764 -0.750519 -0.186554
H 0 2.266113 -1.161728 -1.092926
H 0 2.308000 -1.455582 0.500122
H 0 2.685577 0.023407 -0.061127

FMe_2S^+
S 0 -0.585373 -0.752686 0.069748
C 0 -0.707260 0.276000 -1.422913
F 0 -2.256241 -0.808823 0.259781
C 0 -0.338928 0.501312 1.363831

H 0 0.245697 0.782318 -1.609039
H 0 -1.518387 0.991898 -1.233093
H 0 -0.972473 -0.397293 -2.249695
H 0 0.065430 -0.006042 2.249710
H 0 -1.336792 0.910934 1.570358
H 0 0.343567 1.278091 0.999237
N 0 1.719543 -0.743546 -0.165573
H 0 1.957611 -1.278091 -1.006775
H 0 2.110031 -1.277618 0.616806
H 0 2.256241 0.128021 -0.214722

$NO_2Me_2S^+$
S 0 -0.452850 -0.724365 -0.145935
C 0 -0.466965 0.688477 -1.283310
C 0 -0.212769 0.067520 1.463104
N 0 -2.432770 -0.853668 -0.039093
O 0 -2.874985 -0.892502 1.086578
O 0 -2.949280 -0.888367 -1.133423
H 0 0.582657 0.961700 -1.449448
H 0 -1.035736 1.512726 -0.831451
H 0 -0.947891 0.391129 -2.226135
H 0 -0.271835 -0.720062 2.226151
H 0 -0.994064 0.824783 1.615311
H 0 0.767654 0.560165 1.482208
N 0 2.280563 -0.816589 -0.368027
H 0 2.469269 -1.242218 -1.279312
H 0 2.591660 -1.512726 0.314453
H 0 2.949280 -0.045578 -0.287796