Sulfur K-edge X-ray Absorption Spectroscopy and Time-Dependent Density Functional Theory of Arsenic Dithiocarbamates

Courtney M. Donahue, Juan S. Lezama, Jason M. Keith,* Scott R. Daly*

Supporting Information

Complete reference 39: Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian 09, Revision D.01, Wallingford, CT.

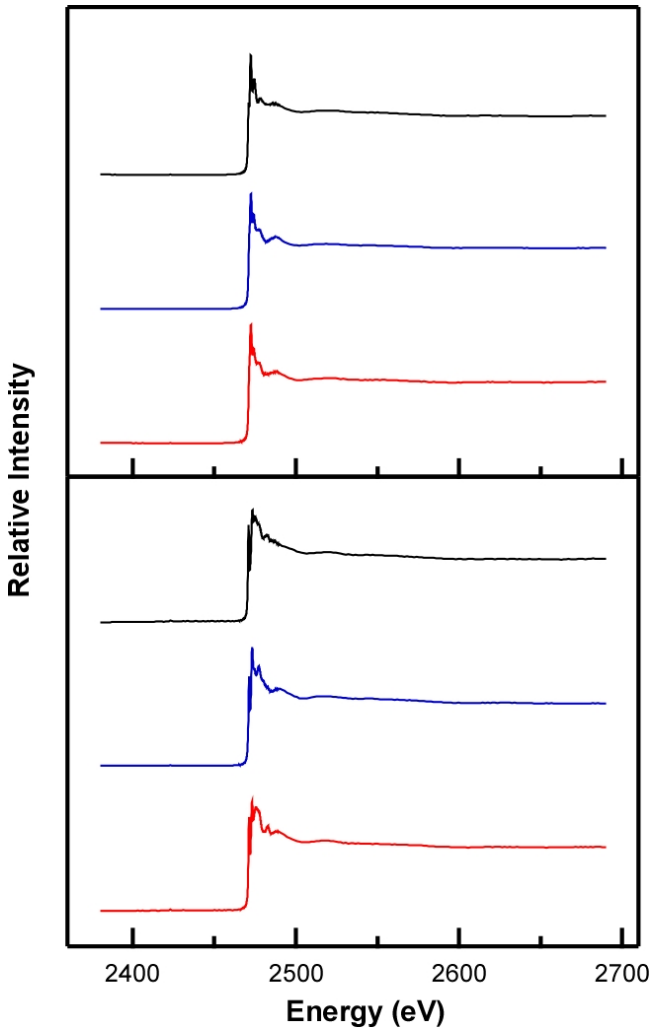

Figure S1. Complete S K-edge XAS spectra of phosphonium and arsenic dithiocarbamates. Top pane – $[PPh_4][S_2CNEt_2]$ (**1a**, red), $[PPh_4][S_2CN(CH_2)_5]$ (**1b**, blue) and $[PPh_4][S_2CNPh_2]$ (**1c**, black). Bottom pane – $As[S_2CNEt_2]_3$ (**2a**, red), $As[S_2CN(CH_2)_5]_3$ (**2b**, blue) and $As[S_2CNPh_2]_3$ (**2c**, black).

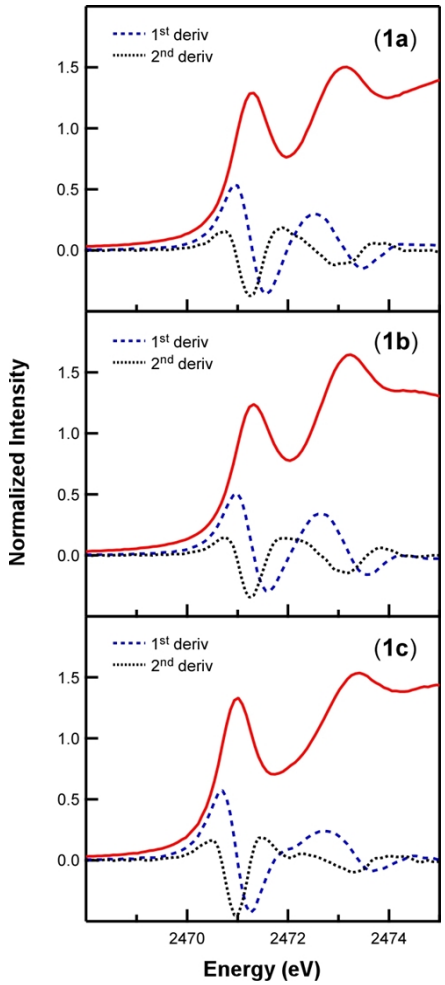

Figure S2. S K-edge X-ray absorption spectra with 1st and 2nd derivative traces of $[PPh_4][S_2CNEt_2]$ (**1a**, top), $[PPh_4][S_2CN(CH_2)_5]$ (**1b**, middle) and $[PPh_4][S_2CNPh_2]$ (**1c**, bottom).

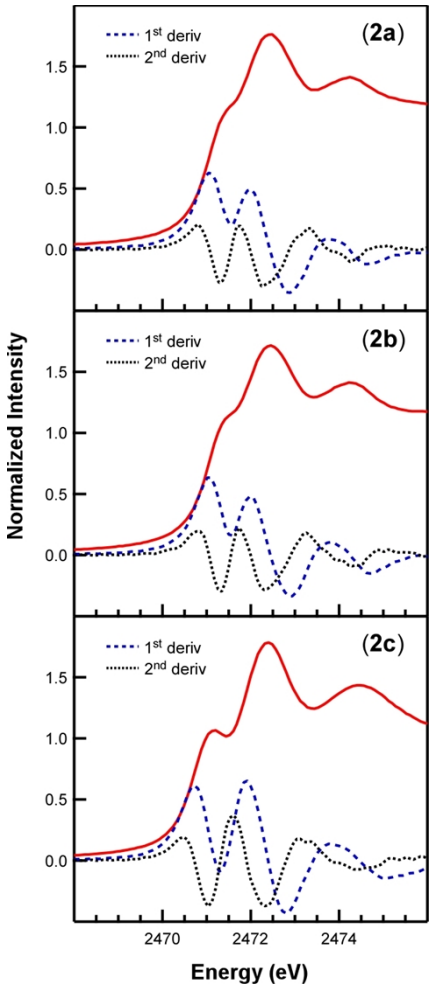

Figure S3. S K-edge X-ray absorption spectra with 1st and 2nd derivative traces of $As[S_2CNEt_2]_3$ (**2a**, top), $As[S_2CN(CH_2)_5]_3$ (**2b**, middle) and $As[S_2CNPh_2]_3$ (**2c**, bottom).

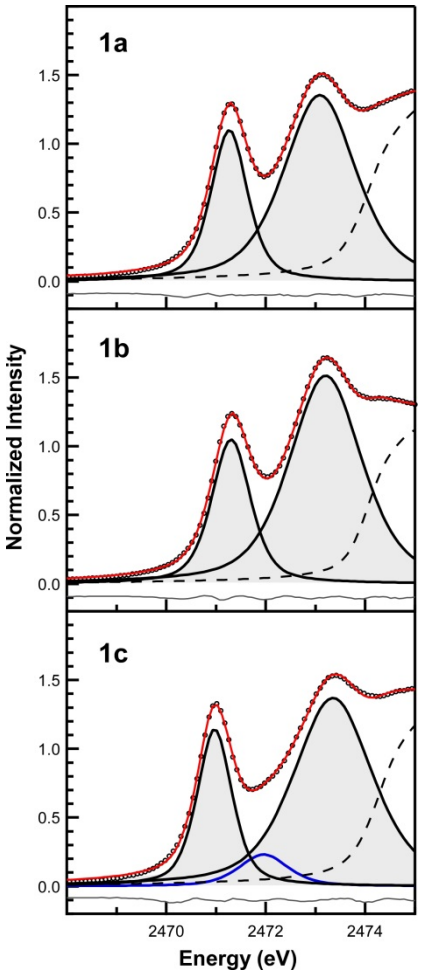

Figure S4. S K-edge X-ray absorption spectra of (top) $[PPh_4][S_2CNEt_2]$ (**1a**), (middle) $[PPh_4][S_2CN(CH_2)_5]$ (**1b**), and (bottom) $[PPh_4][S_2CNPh_2]$ (**1c**). The experimental data is represented as black circles and the model is overlaid as a red trace. The pre-edge functions used to generate the model are shown (outlined grey pseudo-Voigt functions) as well as the post edge residual (dashed line). The least-square residuals for each fit are represented as the grey line at the bottom of each pane.

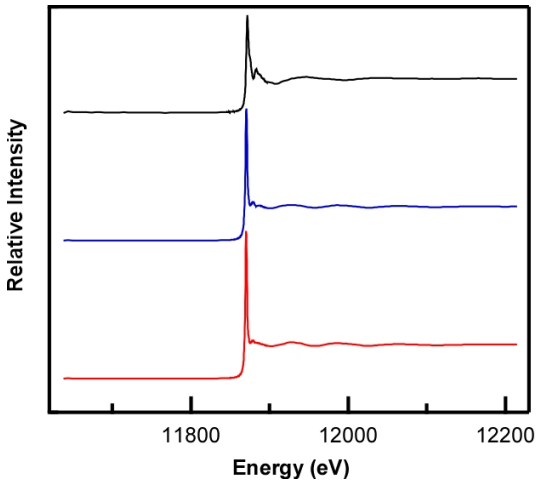

Figure S5. Complete As K-edge XAS spectra of $As[S_2CNEt_2]_3$ (**2a**, red), $As[S_2CN(CH_2)_5]_3$ (**2b**, blue) and $As[S_2CNPh_2]_3$ (**2c**, black).

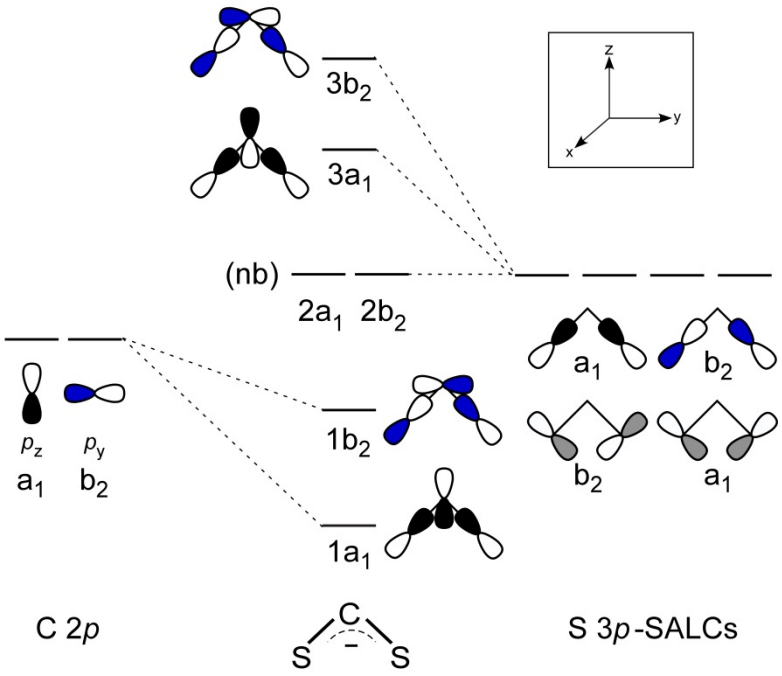

Figure S6. Qualitative MO diagram of the σ-type arrangements (a_1 and b_1 symmetry only) between the S 3p and C 2p orbitals in the dithiocarbamate anions (nb = non-bonding). The π-type arrangements involving the orbitals of b_1 and a_2 symmetry are provided in Figure 6.

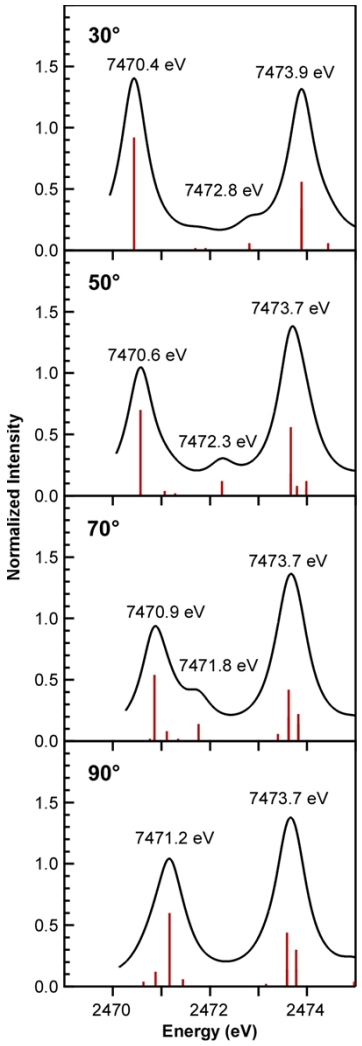

Figure S7. Simulated S K-edge X-ray absorption spectra (black lines) and calculated transitions (red bars) for $S_2CNPh_2^-$ with C-N-C-C dihedral angles set to 30°, 50°, 70°, and 90°. Oscillator strengths have been multiplied by a factor of 200 to bring them on scale with the experimental data.

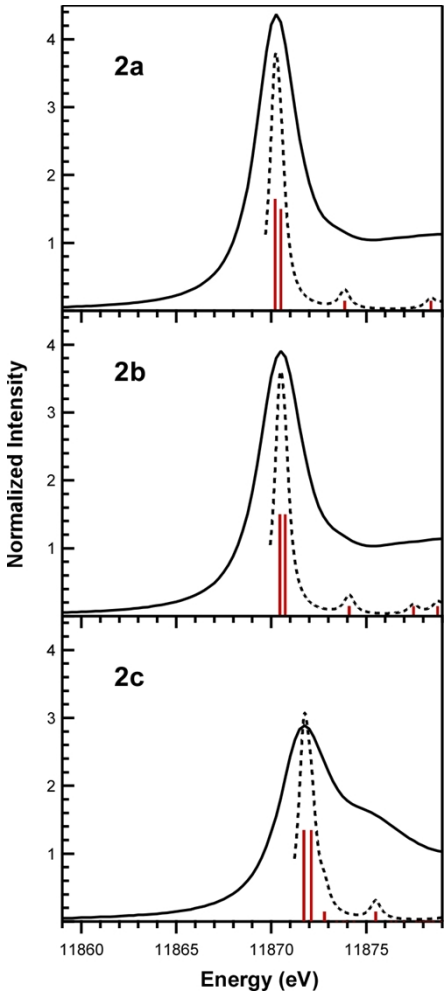

Figure S8. As K-edge X-ray absorption spectra (solid lines), TDDFT simulated spectra (dotted lines), and calculated transitions (red bars) for $As[S_2CNR_2]_3$: (top) $As[S_2CNEt_2]_3$ (**2a**), (middle) $As[S_2CN(CH_2)_5]_3$ (**2b**), and (bottom) $As[S_2CNPh_2]_3$ (**2c**). Oscillator strengths have been multiplied by a factor of 1500 to bring them on scale with the experimental data.

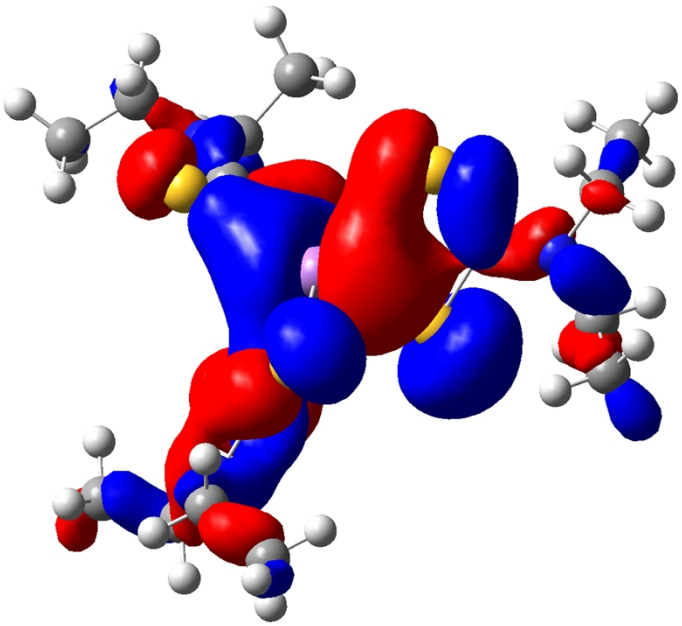

Figure S9. Kohn-Sham orbital showing the As-S σ bond and the constructive mixing between the S 3p orbital on the thiocarbonyl and the As-S σ orbital.

Table S1. Atomic coordinates and Mulliken charges for the calculated structures of $S_2CNR_2^-$ and $As[S_2CNR_2]_3$ from the DFT calculations.

Compound	Atom Type	Atom Number	Cartesian Coordinates			Mulliken Populations
			x	y	z	
$S_2CNEt_2^-$ (1a)	C	1	-1.235386	-1.245361	0.659524	-0.025254
	C	2	-1.233886	1.246777	0.659494	-0.025245
	C	3	-1.862505	-1.838816	-0.609064	-0.296482
	H	4	-0.534474	-1.974492	1.073415	0.128944
	C	5	-1.859159	1.841535	-0.609389	-0.296476
	H	6	-2.018294	1.047985	1.402736	0.047921
	H	7	-1.070984	-2.052835	-1.33156	0.138598
	H	8	-2.37623	2.781522	-0.373515	0.056709
	C	9	0.851588	-0.000616	0.092949	0.023456
	S	10	1.647496	1.517154	-0.115344	-0.469169
	S	11	1.645473	-1.519319	-0.11571	-0.469139
	N	12	-0.496979	0.000254	0.446454	-0.334142
	H	13	-0.532353	1.974882	1.074177	0.128921
	H	14	-1.066637	2.055087	-1.330926	0.138643
	H	15	-2.380376	-2.778355	-0.373208	0.056741
	H	16	-2.019018	-1.045854	1.403407	0.04792
	H	17	-2.588604	-1.157786	-1.066258	0.074025
	H	18	-2.585587	1.161582	-1.067659	0.074029
$S_2CN(CH_2)_5^-$ (1b)	C	1	0.8908	1.213262	0.612651	-0.02347
	C	2	0.890857	-1.213176	0.61284	-0.023488
	C	3	2.063114	1.262922	-0.379943	-0.166587
	H	4	0.219302	2.063015	0.481904	0.133166
	C	5	2.06292	-1.26296	-0.380028	-0.166573
	H	6	1.288082	-1.231144	1.644008	0.05105
	C	7	2.931761	-0.000091	-0.279016	-0.169283
	H	8	1.650275	1.35244	-1.392985	0.10141
	H	9	2.667238	-2.162203	-0.194678	0.054631
	H	10	3.715267	-0.000117	-1.049437	0.058095
	C	11	-1.241887	0.000013	0.057849	0.027761
	S	12	-2.035072	-1.5165	-0.162469	-0.467969
	S	13	-2.035104	1.516475	-0.162474	-0.467949
	N	14	0.103356	0.000038	0.430249	-0.344257
	H	15	0.219315	-2.06295	0.482496	0.133164
	H	16	1.649727	-1.352142	-1.392957	0.101437
	H	17	3.449429	-0.000166	0.693134	0.063183
	H	18	2.667545	2.162011	-0.194181	0.054633
	H	19	1.287759	1.231588	1.643922	0.051046

$S_2CNPh_2^-$ (1c)	C	1	-0.000067	1.82346	-0.000044	-0.009622
	S	2	1.300225	2.596165	-0.784967	-0.402269
	S	3	-1.300453	2.595782	0.785144	-0.402271
	N	4	0.00006	0.380284	-0.000262	-0.493205
	C	5	-1.21067	-0.365965	0.013248	0.25571
	C	6	-2.255491	-0.056908	-0.874443	-0.060785
	C	7	-1.361506	-1.465377	0.872005	-0.092271
	C	8	-3.415251	-0.82606	-0.893363	-0.104405
	H	9	-2.14437	0.794484	-1.535469	0.107606
	C	10	-2.523706	-2.237282	0.84291	-0.100566
	H	11	-0.560895	-1.707736	1.563187	0.080202
	C	12	-3.559642	-1.923362	-0.037361	-0.087541
	H	13	-4.21206	-0.569937	-1.587785	0.056936
	H	14	-2.620101	-3.082509	1.5208	0.052466
	H	15	-4.466586	-2.522509	-0.057908	0.04635
	C	16	1.210751	-0.365844	-0.013471	0.255763
	C	17	2.25558	-0.056654	0.874153	-0.060826
	C	18	1.361644	-1.465492	-0.871997	-0.092291
	C	19	3.415323	-0.825865	0.893274	-0.104406
	H	20	2.144555	0.79489	1.534998	0.107612
	H	22	0.561077	-1.707911	-1.563211	0.080188
	C	23	3.559715	-1.923368	0.037572	-0.087551
	H	24	4.212091	-0.56956	1.58768	0.056933
	H	25	2.620179	-3.082829	-1.520366	0.05246
	H	26	4.466617	-2.522571	0.058278	0.046346
$As[S_2CNEt_2]_3$ (2a)	As	1	0.003521	-0.001929	0.44765	0.251888
	S	2	-1.966903	1.912294	1.44402	-0.184217
	S	3	2.646161	0.742479	1.445283	-0.183938
	S	4	-0.672337	-2.667737	1.4358	-0.184266
	S	5	-0.136914	1.954855	-0.934328	-0.004186
	S	6	-1.620664	-1.098334	-0.93903	-0.004601
	S	7	1.767809	-0.853005	-0.939666	-0.004298
	C	8	3.055231	-0.24603	0.122864	-0.050736
	C	9	-1.739523	-2.518962	0.119904	-0.050841
	C	10	-1.312516	2.762655	0.124425	-0.050741
	N	11	-2.688501	-3.429588	-0.170919	-0.309586
	N	12	4.320063	-0.604443	-0.17124	-0.309584
	N	13	-1.636728	4.036392	-0.171469	-0.30969
	C	14	-3.611135	-3.295116	-1.31184	-0.082453
	H	15	-3.823884	-4.307829	-1.669568	0.112039
	H	16	-3.095469	-2.774402	-2.121781	0.147983

	C	17	-2.87432	-4.6328	0.660356	-0.07076
	H	18	-2.60877	-4.378536	1.687607	0.154711
	H	19	-3.942384	-4.872883	0.6378	0.105756
	C	20	-2.591123	4.795314	0.657201	-0.070758
	H	21	-2.499805	4.4447	1.686407	0.154642
	H	22	-2.273843	5.842857	0.628628	0.105785
	C	23	-1.065306	4.768275	-1.315547	-0.082386
	H	24	-1.841946	5.450785	-1.675729	0.112066
	H	25	-0.866354	4.059392	-2.122403	0.148054
	C	26	4.668364	-1.45858	-1.320084	-0.082385
	H	27	3.95705	-1.268601	-2.126949	0.147972
	H	28	5.649579	-1.127681	-1.675812	0.112049
	C	29	5.453755	-0.166617	0.663253	-0.070758
	H	30	5.101466	-0.074635	1.691789	0.154657
	H	31	6.199018	-0.968391	0.632625	0.105805
	C	32	-4.909058	-2.57031	-0.946069	-0.310121
	H	33	-5.567746	-2.523509	-1.819374	0.10925
	H	34	-5.444889	-3.09085	-0.145987	0.109423
	C	35	-2.041805	-5.819346	0.170941	-0.310246
	H	36	-2.234117	-6.694011	0.800754	0.109291
	H	37	-0.97615	-5.583958	0.224379	0.141937
	C	38	0.204397	5.54333	-0.953584	-0.310156
	H	39	0.567067	6.092414	-1.828694	0.109324
	H	40	0.015466	6.267501	-0.154687	0.10946
	C	41	4.698755	-2.948434	-0.968937	-0.31021
	H	42	4.990284	-3.532095	-1.848207	0.109359
	C	43	6.059387	1.154796	0.186044	-0.310363
	H	44	6.915319	1.420643	0.814882	0.109272
	H	45	5.320698	1.95722	0.252643	0.142038
	H	46	5.419608	-3.155512	-0.171593	0.109389
	H	47	-2.28929	-6.086016	-0.861951	0.10275
	H	48	-4.701032	-1.549499	-0.615937	0.145335
	H	49	3.713355	-3.288292	-0.640803	0.145293
	H	50	6.409397	1.086861	-0.849387	0.102833
	C	51	-4.034654	4.653516	0.170807	-0.310304
	H	52	-4.699409	5.256776	0.797665	0.109261
	H	53	-4.146611	4.992906	-0.864327	0.102822
	H	54	-4.35594	3.610978	0.232624	0.14196
	H	55	0.992153	4.86183	-0.62333	0.145177
$As[S_2CN(CH_2)_5]_3$	As	1	-0.003073	-0.011349	-0.660409	0.253485
(2b)	S	2	1.781991	-0.793932	0.722833	-0.005494
	S	3	-1.583069	-1.163453	0.713192	-0.006553

S	4	-0.21994	1.933521	0.710807	-0.006283
S	5	1.17243	-2.53667	-1.647878	-0.185398
S	6	1.601252	2.260496	-1.657011	-0.185302
S	7	-2.767233	0.232197	-1.669802	-0.186018
C	8	-2.950707	-0.808207	-0.354476	-0.047827
C	9	0.778939	2.940274	-0.350244	-0.047825
C	10	2.168701	-2.156227	-0.340758	-0.04781
N	11	0.822501	4.270975	-0.048642	-0.324706
N	12	-4.127664	-1.429356	-0.05016	-0.325325
N	13	3.30694	-2.847124	-0.039593	-0.324956
C	14	3.841113	-3.860257	-0.921504	-0.061547
C	15	3.929155	-5.18004	-0.473877	0.153768
C	16	4.324915	-3.507407	-2.184761	0.105852
C	17	4.497061	-6.152449	-1.297684	-0.068454
H	18	3.5565	-5.438148	0.511997	0.147943
C	19	4.888565	-4.485055	-3.002784	0.110972
H	20	4.246126	-2.479227	-2.520569	-0.068092
C	21	4.976131	-5.808078	-2.562478	0.148025
H	22	4.562044	-7.179093	-0.949621	0.111044
H	23	5.261614	-4.211031	-3.985098	-0.061148
H	24	5.417549	-6.56636	-3.202441	0.1538
C	25	4.052913	-2.620015	1.176988	0.106015
C	26	5.34552	-2.093175	1.102628	-0.060509
C	27	3.504861	-2.977823	2.413304	0.106023
C	28	6.085927	-1.914633	2.270442	0.15371
H	29	5.759559	-1.828216	0.135343	-0.067879
C	30	4.250174	-2.790678	3.577401	0.148081
H	31	2.502019	-3.389855	2.455351	0.111184
C	32	5.53999	-2.260474	3.508677	-0.18036
H	33	7.088621	-1.50179	2.212321	0.10147
H	34	3.822776	-3.064955	4.537204	0.119795
H	35	6.119066	-2.119462	4.416497	-0.179474
C	36	1.447723	5.232239	-0.928973	0.101159
C	37	2.559751	5.948493	-0.48165	0.120547
C	38	0.90111	5.488355	-2.189874	-0.180543
C	39	3.131673	6.920364	-1.303368	0.101592
H	40	2.96891	5.744528	0.50248	0.119316
C	41	1.479769	6.458813	-3.005943	-0.179234
H	42	0.039636	4.921445	-2.5256	0.10125
C	43	2.594603	7.176584	-2.565795	0.120057
H	44	3.998458	7.47449	-0.955539	-0.180677
H	45	1.056559	6.655265	-3.986507	0.101573
H	46	3.041439	7.932998	-3.204197	-0.179217

	C	47	0.253168	4.811201	1.164669	0.101277
	C	48	-0.838649	5.680319	1.084093	-0.184631
	C	49	0.82786	4.510589	2.404093	-0.184791
	C	50	-1.362114	6.240611	2.24857	0.101701
	H	51	-1.268026	5.910544	0.114585	0.091017
	C	52	0.294606	5.070966	3.564761	0.091106
	H	53	1.678397	3.838631	2.451199	0.101666
	C	54	-0.798642	5.936203	3.489826	0.119569
	H	55	-2.212747	6.912642	2.185302	0.119012
	H	56	0.738942	4.834376	4.526917	-0.184693
	H	57	-1.208916	6.373594	4.395201	0.091138
	C	58	-5.269008	-1.375565	-0.93566	0.101599
	C	59	-6.447145	-0.76714	-0.497724	0.253485
	C	60	-5.212463	-1.986393	-2.191862	-0.005494
	C	61	-7.571255	-0.763451	-1.324198	-0.006553
	H	62	-6.479209	-0.303636	0.482874	-0.006283
	C	63	-6.338913	-1.976252	-3.012676	-0.185398
	H	64	-4.289682	-2.451967	-2.520325	-0.185302
	C	65	-7.519511	-1.365937	-2.582034	-0.186018
	H	66	-8.485855	-0.287152	-0.983608	-0.047827
	H	67	-6.293506	-2.448384	-3.989523	-0.047825
	H	68	-8.395308	-1.361663	-3.224171	-0.04781
	C	69	-4.318801	-2.174721	1.172727	-0.324706
	C	70	-4.541372	-3.55334	1.109993	-0.325325
	C	71	-4.338686	-1.510626	2.403807	-0.324956
	C	72	-4.772627	-4.269224	2.283884	-0.061547
	H	73	-4.53234	-4.052903	0.14684	0.153768
	C	74	-4.564944	-2.235194	3.573937	0.105852
	H	75	-4.170856	-0.439252	2.437281	-0.068454
	C	76	-4.782651	-3.613168	3.516916	0.147943
	H	77	-4.941407	-5.340792	2.234383	0.110972
	H	78	-4.576531	-1.719454	4.529464	-0.068092
	H	79	-4.962155	-4.173595	4.429616	0.148025
$As[S_2CNPh_2]_3$ (2c)	As	1	0.014941	0.001984	-0.311054	0.206233
	S	2	1.971271	0.037329	1.078319	0.028833
	S	3	-0.923186	-1.727472	1.064455	0.029872
	S	4	-1.00455	1.662348	1.091554	0.029378
	S	5	2.124974	-1.73415	-1.331422	-0.156943
	S	6	0.478644	2.707873	-1.290581	-0.157083
	S	7	-2.561152	-0.930848	-1.31323	-0.156576
	C	8	-2.324713	-1.982606	0.003826	-0.052885
	C	9	-0.552819	3.01128	0.028863	-0.052248

C	10	2.906537	-1.020445	0.001339	-0.052631
N	11	-1.053054	4.228491	0.319623	-0.459078
N	12	-3.148225	-3.008884	0.29582	-0.4587
N	13	4.208124	-1.212714	0.293232	-0.458728
C	14	-0.77772	5.41589	-0.506458	0.201667
H	15	-0.04701	5.14414	-1.266427	-0.073763
H	16	-0.331165	6.177895	0.147821	-0.052279
C	17	-2.002332	4.501853	1.41029	-0.097773
H	18	-2.141929	3.60087	2.005974	0.096935
H	19	-1.552051	5.265408	2.060032	-0.101625
C	20	4.918467	-0.564404	1.406928	0.114376
H	21	4.21212	0.010427	2.004174	-0.073203
H	22	5.329076	-1.358177	2.046689	0.091401
C	23	5.091823	-2.047121	-0.537619	0.094532
H	24	4.491334	-2.513807	-1.316768	0.089175
H	25	5.500594	-2.839036	0.106066	0.171904
C	26	-4.335104	-3.328058	-0.514819	-0.06451
H	27	-5.211976	-3.272441	0.145854	-0.056284
H	28	-4.438171	-2.56696	-1.286531	-0.097321
C	29	-2.935254	-3.96176	1.396713	0.104051
H	30	-2.062259	-3.66074	1.974129	-0.099487
H	31	-3.809838	-3.906112	2.060374	0.113905
C	32	-2.07527	5.945984	-1.130009	-0.072936
H	33	-1.849238	6.852233	-1.70367	0.094971
H	34	-2.451747	5.199609	-1.84019	0.095313
C	35	-3.338633	5.006468	0.847373	0.091023
H	36	-4.008133	5.244008	1.682189	0.201163
H	37	-3.806256	4.194011	0.27777	-0.073414
C	38	6.228902	-1.202013	-1.126772	-0.052148
H	39	6.894749	-1.855233	-1.702412	-0.097693
H	40	5.798842	-0.478428	-1.830102	0.096947
C	41	6.051232	0.326618	0.878606	-0.101489
H	42	6.589077	0.758478	1.730507	0.114082
H	43	5.609018	1.159744	0.318703	-0.073234
C	44	-4.213733	-4.734176	-1.116318	0.091454
H	45	-5.128741	-4.960103	-1.675954	0.094546
C	46	-2.773716	-5.388326	0.853254	0.089253
H	47	-2.663616	-6.078164	1.697959	0.172308
C	48	-3.13293	6.232363	-0.054332	-0.064742
C	49	7.006078	-0.468128	-0.023954	-0.056176
H	50	-4.080746	6.528485	-0.517281	-0.097249
H	51	-2.804316	7.082592	0.560342	0.103849
H	52	7.552549	-1.20263	0.584885	-0.099482

H	53	7.758467	0.196667	-0.462549	0.113915
H	54	-1.845322	-5.438207	0.27116	-0.072976
H	55	-3.38604	-4.737225	-1.836026	0.094988
C	56	-3.968439	-5.786217	-0.024992	0.095311
H	57	-4.866717	-5.873219	0.602765	0.091067
H	58	-3.801813	-6.772317	-0.472471	0.201334