I. Typical electrochemical behavior of substituted benzyl thiocyanates (1a-h).

The electrochemical characteristics (CV at low and high scan rates as well as the variation of the peak potential and the peak current with the scan rate are reported for the benzyl thiocyanate **1c** and the p-nitrobenzyl thiocyanate **1g** are reported below.

I. 1. Electrochemical characteristics of benzyl thiocyanate (1c).

a- Cyclic voltammetry of **1c**.

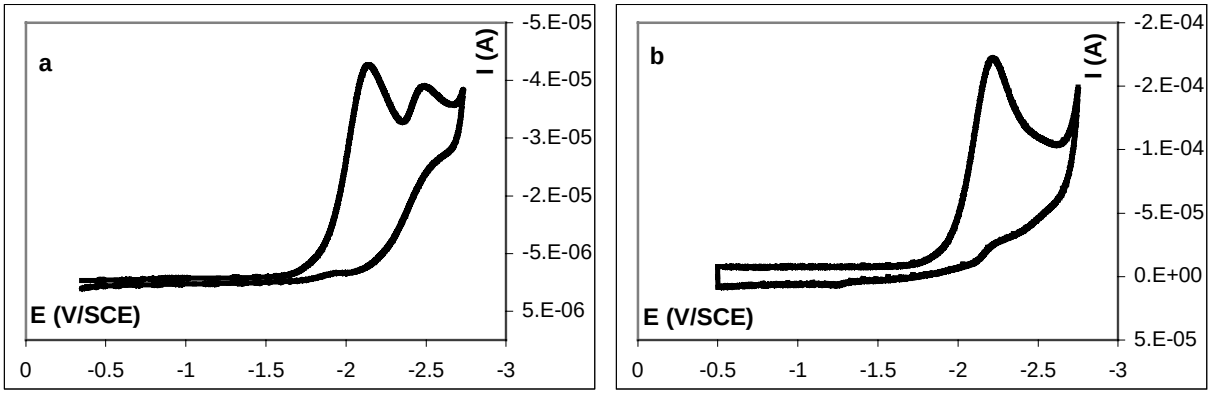

Figure 1: Cyclic voltammetry of **1c** in CH_3CN/TBAF (0.1M) at a glassy carbon electrode at (**a**): v = 0.2 V/s and (**b**) 2.4 V/s.

Two distinct peaks, corresponding to the reduction of benzyl thiocyanate (**1c**) and dibenzyl disulfide (**2c**) respectively, are observed at low scan rate (v = 0.2 V/s). Increasing the scan rate to 2.4 V/s induces the elimination of the second peak indicating that disulfide **2c** results from a slow chemical reaction following the initial electron transfer as per the reported mechanism.

b- Variation of the peak potential (Ep) and the peak current (ip) with Log (v) for **1c**.

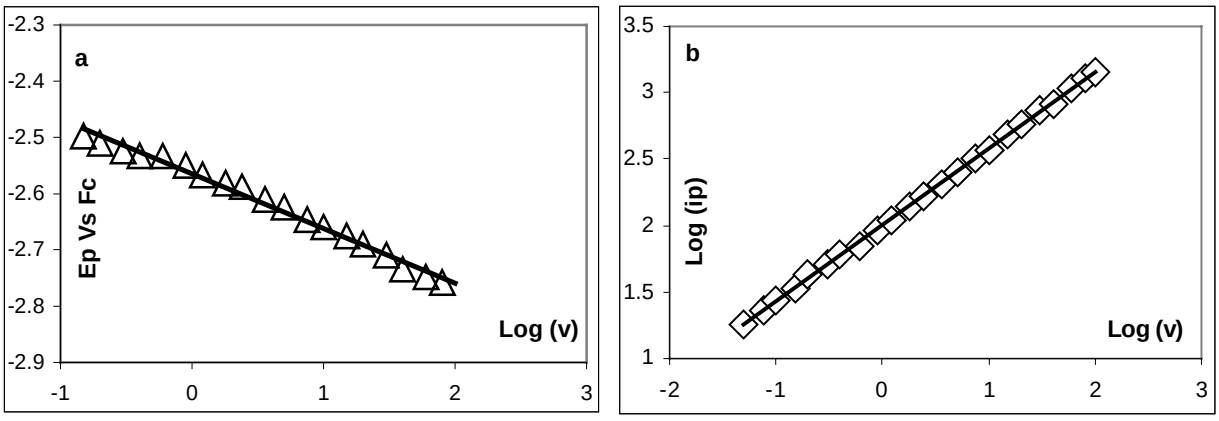

Figure 2: Variation of (**a**) the peak potential (Ep) and (**b**) the peak current (ip) with Log of the scan rate for benzyl thiocyanate (**1c**).

I. 2. Electrochemical characteristics of p-nitrobenzyl thiocyanate (1g).

a- Cyclic voltammetry of **2**.

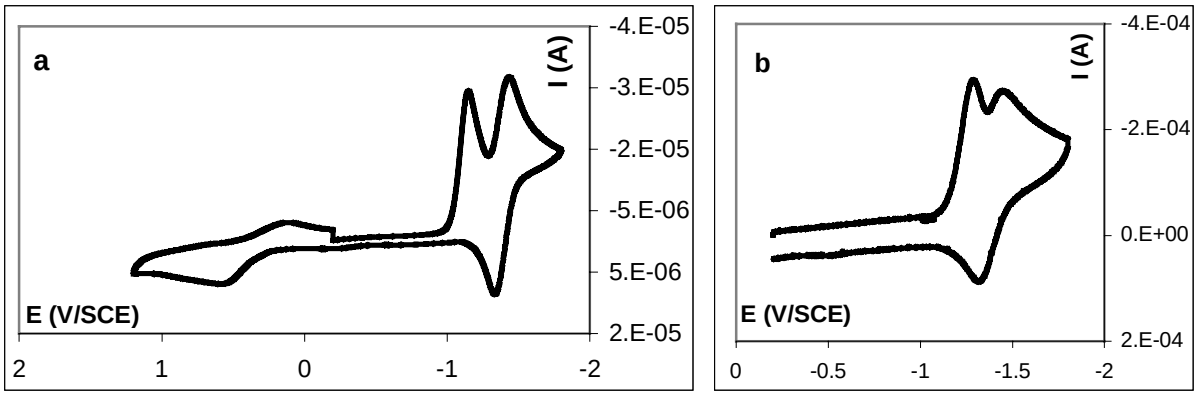

Figure 3: Cyclic voltammetry of **1g** in CH_3CN/TBAF (0.1M) at a glassy carbon electrode at (**a**): v = 0.2 V/s and (**b**) 20 V/s.

For compound **1g**, increasing the scan rate up to 20 V/s does not induce disappearance of the second reduction peak, corresponding to the reduction of 4,4'-dinitrodibenzyl (**3g**). This indicates that compound **3g** is the result of a relatively faster chemical reaction than the one leading to dibenzyl disulfide (**2c**) in the reduction of **1c**. The reduction peak of **3g** disappears only at scan rates higher than 100V/s. When scanning towards the positive potentials one can identify the oxidation peak of thiocyanate anion, as shown by comparison with an authentic sample (see II), indicating an α-cleavage. Both results are in agreement with the proposed mechanism.

b- Variation of the peak potential (Ep) and the peak current (ip) with Log (v) for **1g**.

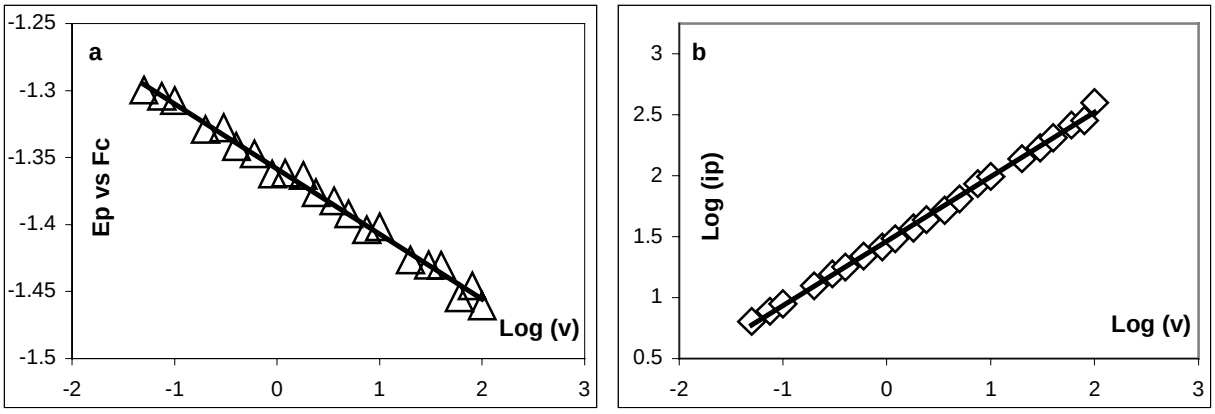

Figure 4: Variation of (**a**) the peak potential (Ep) and (**b**) the peak current (ip) with Log of the scan rate for p-nitrobenzyl thiocyanate (**2**).

III- Electrochemical oxidation of tertabutyl ammonium thiocyanate.

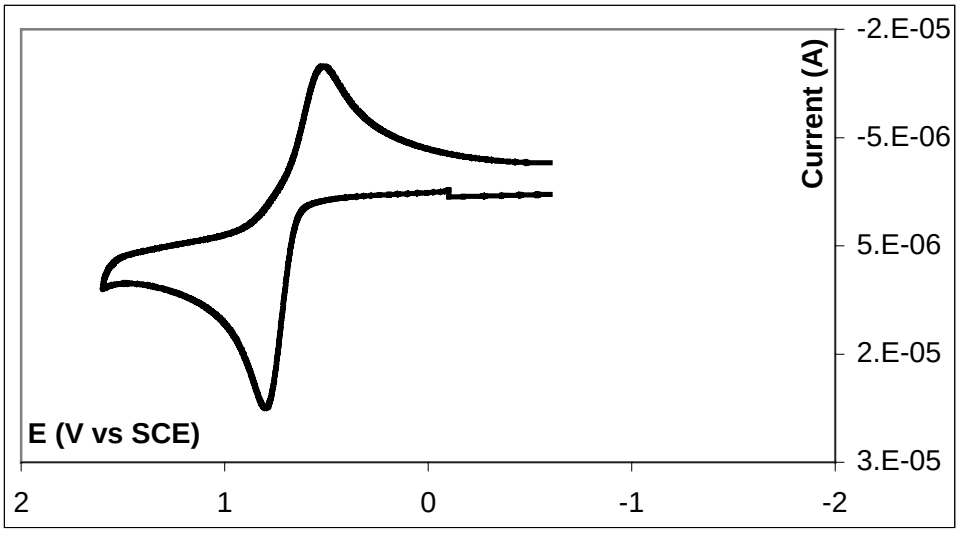

Figure 5: Cyclic voltammetry in CH_3CN/ TBAF (0.1M) at a glassy carbon electrode, v = 0.2 V/s, temperature = 20oC of tetrabutylammonium thiocyanate (2 mM).

III. Computational calculations.

The calculations were performed using the Gaussian 98 package.[1] LUMO and SOMO orbitals were calculated after a full optimization without imposed symmetry of the conformations using the B3LYP method with the 6-31G+(d,p) basis set starting from preliminary optimizations performed with semi-empirical methods. We checked that the conformations obtained were minima by running frequency calculations.

No imaginary vibrational frequencies were seen.

Total Energies and Coordinates.

p-Methoxybenzyl thiocyanate (1a).

Total Energy: -876.53864832 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.910509	-0.984916	0.238728
2	6	0	0.539860	-1.032019	0.508868
3	6	0	-0.239785	0.129334	0.539609
4	6	0	0.391642	1.359549	0.281072
5	6	0	1.751912	1.425339	0.010782
6	6	0	2.522032	0.250739	-0.012686
7	1	0	2.481385	-1.905500	0.230499
8	1	0	0.076042	-1.996051	0.702233
9	1	0	-0.191443	2.276819	0.295751
10	1	0	2.242305	2.373576	-0.182755
11	6	0	-1.710699	0.063899	0.826184
12	1	0	-2.078186	0.974077	1.302735
13	1	0	-1.972562	-0.799992	1.438861
14	16	0	-2.646771	-0.115643	-0.800153
15	6	0	-4.241749	-0.156247	-0.211552
16	7	0	-5.343657	-0.187114	0.174268
17	8	0	3.846871	0.416963	-0.284810
18	6	0	4.686850	-0.732281	-0.329312
19	1	0	4.365051	-1.430784	-1.111371
20	1	0	5.684577	-0.360322	-0.563720
21	1	0	4.708354	-1.247814	0.638663

p-Methybenzyl thiocyanate (1b).

Total Energy: -801.33029166 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.256031	1.202070	0.048302
2	6	0	-0.893762	1.204667	0.348540
3	6	0	-0.193491	0.000420	0.507725
4	6	0	-0.893479	-1.204160	0.348886
5	6	0	-2.255631	-1.202042	0.048643
6	6	0	-2.962744	-0.000057	-0.103895
7	1	0	-2.777741	2.148594	-0.068488
8	1	0	-0.369875	2.150827	0.459780
9	1	0	-0.369281	-2.150117	0.460401
10	1	0	-2.777081	-2.148757	-0.067907
11	6	0	-4.445043	-0.000641	-0.394597
12	1	0	-4.738236	-0.880854	-0.974670
13	1	0	-5.026657	-0.012878	0.535815
14	1	0	-4.742896	0.890833	-0.954623
15	6	0	1.274935	0.000640	0.824664
16	1	0	1.574969	0.892413	1.377003
17	1	0	1.575144	-0.890727	1.377567
18	16	0	2.246635	0.000163	-0.786922
19	6	0	3.829755	-0.000363	-0.165462
20	7	0	4.925491	-0.000733	0.238433

Benzyl thiocyanate (1c).

Total Energy: -762.00888343 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.728402	-1.210528	-0.094013
2	6	0	1.376890	-1.207556	0.255855
3	6	0	0.689913	0.002364	0.435800
4	6	0	1.379911	1.209872	0.251508
5	6	0	2.731472	1.208193	-0.098299
6	6	0	3.408343	-0.002323	-0.272075
7	1	0	3.249631	-2.154157	-0.224928
8	1	0	0.851520	-2.149187	0.393676
9	1	0	0.856903	2.153304	0.385935
10	1	0	3.255074	2.150041	-0.232527
11	1	0	4.460028	-0.004131	-0.542763

12	6	0	-0.766956	0.004865	0.808197
13	1	0	-1.044588	0.899449	1.367672
14	1	0	-1.045396	-0.883633	1.376924
15	16	0	-1.794885	-0.002921	-0.765775
16	6	0	-3.353525	-0.000414	-0.085302
17	7	0	-4.433100	0.001173	0.359769

p-Chlorobenzyl thiocyanate (1d).

Total Energy:-1221.60218271 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.526201	-0.000204	0.003958
2	6	0	1.853183	1.215742	0.132433
3	6	0	0.484017	1.208690	0.399627
4	6	0	-0.218110	0.003275	0.543891
5	6	0	0.482083	-1.203968	0.405311
6	6	0	1.851189	-1.214471	0.138105
7	1	0	2.392053	2.150897	0.027714
8	1	0	-0.041055	2.154818	0.500101
9	1	0	-0.044519	-2.148766	0.510224
10	1	0	2.388565	-2.150964	0.037736
11	17	0	4.249586	-0.002403	-0.328608
12	6	0	-1.693839	0.005155	0.828381
13	1	0	-2.003748	0.899334	1.371214
14	1	0	-2.004282	-0.882912	1.380879
15	16	0	-2.626891	-0.003486	-0.803374
16	6	0	-4.222045	-0.001606	-0.213625
17	7	0	-5.325115	-0.000207	0.169137

p-Fluorobenzyl thiocyanate (1e).

Total Energy: -861.24856529 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.290023	1.216636	0.034975
2	6	0	-0.931230	1.207245	0.341691
3	6	0	-0.236637	0.000100	0.504843
4	6	0	-0.931140	-1.207118	0.341833

5	6	0	-2.289927	-1.216653	0.035112
6	6	0	-2.946791	-0.000042	-0.113466
7	1	0	-2.840898	2.142381	-0.087622
8	1	0	-0.405191	2.150448	0.459856
9	1	0	-0.405026	-2.150268	0.460097
10	1	0	-2.840728	-2.142454	-0.087398
11	9	0	-4.260926	-0.000110	-0.407524
12	6	0	1.230310	0.000151	0.828585
13	1	0	1.528520	-0.890161	1.383755
14	1	0	1.528525	0.890603	1.383526
15	16	0	2.203692	-0.000064	-0.779621
16	6	0	3.787545	-0.000039	-0.157779
17	7	0	4.881631	-0.000031	0.247811

p-Cyanobenzyl thiocyanate (1f).

Total Energy: -854.25092037 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.989982	1.216928	0.127979
2	6	0	-0.623532	1.210992	0.394317
3	6	0	0.075233	0.002597	0.537343
4	6	0	-0.622088	-1.207230	0.399273
5	6	0	-1.988502	-1.215893	0.132913
6	6	0	-2.680430	-0.000165	-0.003714
7	1	0	-2.526125	2.154055	0.023831
8	1	0	-0.094900	2.154623	0.495661
9	1	0	-0.092330	-2.149809	0.504486
10	1	0	-2.523517	-2.154078	0.032554
11	6	0	1.552106	0.004063	0.821555
12	1	0	1.860123	-0.884761	1.374203
13	1	0	1.859892	0.898042	1.365931
14	16	0	2.479322	-0.003440	-0.810658
15	6	0	-4.089987	-0.001560	-0.274913
16	7	0	-5.232703	-0.002684	-0.494638
17	6	0	4.073797	-0.001001	-0.219220
18	7	0	5.176705	0.000481	0.163303

p-Nitrobenzyl thiocyanate (1g).

Total Energy: -966.51527082 a.u.

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	1.566823	-1.219810	0.178163
2	6	0	0.196645	-1.210181	0.429126
3	6	0	-0.501446	0.000562	0.560960
4	6	0	0.196764	1.211071	0.427553
5	6	0	1.566960	1.220276	0.176601
6	6	0	2.230624	0.000123	0.056299
7	1	0	2.119833	-2.145614	0.079407
8	1	0	-0.334220	-2.152659	0.527071
9	1	0	-0.334017	2.153724	0.524235
10	1	0	2.120000	2.145933	0.076665
11	7	0	3.683068	-0.000107	-0.205756
12	8	0	4.245343	1.090481	-0.307541
13	8	0	4.245102	-1.090861	-0.307051
14	6	0	-1.981849	0.000910	0.828573
15	1	0	-2.294968	0.893241	1.372552
16	1	0	-2.294896	-0.889654	1.375510
17	16	0	-2.888800	-0.001848	-0.813736
18	6	0	-4.489466	-0.000215	-0.239306
19	7	0	-5.596615	0.001708	0.130507

o-Nitrobenzyl thiocyanate (1h).
Total Energy: -966.50789801 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.438006	-2.095936	0.021821
2	6	0	1.092455	-1.938107	0.354812
3	6	0	0.483774	-0.675217	0.423116
4	6	0	1.298590	0.432199	0.110129
5	6	0	2.641608	0.289908	-0.243471
6	6	0	3.217634	-0.977660	-0.277335
7	1	0	2.871849	-3.090541	-0.006808
8	1	0	0.487996	-2.814543	0.569472
9	1	0	3.216029	1.176497	-0.482436
10	1	0	4.265041	-1.087184	-0.538615
11	7	0	0.790894	1.822268	0.146506
12	8	0	1.327777	2.636251	-0.602888
13	8	0	-0.115312	2.094238	0.935209
14	6	0	-0.983435	-0.613818	0.762324
15	1	0	-1.233794	0.232489	1.395519
16	1	0	-1.296973	-1.548158	1.228723
17	16	0	-1.956627	-0.432879	-0.831342

18	6	0	-3.519964	-0.285652	-0.181157
19	7	0	-4.607443	-0.193799	0.232866

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1) Gaussian 2003, M. J. Frisch, G. W. Trucks, H. B.Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.