

**Electrochemical Reduction of N,N'-Thiobisphthalimide and N,N'-Dithiobisphthalimide:  
Ejection of Diatomic Sulfur Through an Autocatalytic Mechanism**

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**Supporting Information**

- I. Application of the extensions of the dissociative electron transfer theory to the case of decomposition of radical anions**
- II. Cyclic Voltammetry**
- III. Computational calculations (method, structures, energies, LUMOs and coordinates)**

## I. Application of the extensions of the dissociative electron transfer theory to the case of decomposition of radical anions

When applying the extensions of the dissociative electron transfer theory to the case of dissociation radical anions, it is important to know the cleavage mechanism. Two possibilities are to be considered. If the cleavage takes place without the transfer of the extra electron from one group to another within the radical anion structure, the cleavage is homolytic. If the cleavage is accompanied by the internal electron transfer of the electron the cleavage is heterolytic.

In the present case, the extra electron resides in the phthalimidyl group for both radical anions (**1**<sup>-</sup> and **2**<sup>-</sup>) and the cleavage leads to the formation of the phthalimidyl anion, so without an intramolecular electron transfer, through a homolytic mechanism.

The activation free energy is similar for both the homolytic and the heterolytic mechanisms. Below are is the general expression showing the involved parameters (eq. 1) for a radical anion (RX<sup>-•</sup>) cleaving to an anion (X<sup>-</sup>) and a radical (R<sup>•</sup>). The intrinsic barrier on the other hand is different from one mechanism to the other. The main difference resides in the involvement of the standard potential of the leaving group (the anion product of the radical anion cleavage) in one case and in that of the other moiety (the radical product of the radical anion cleavage) in the other case. The expressions for the cleavage for both mechanisms are provided below (eqs. 2 and 3).

For a radical anion (RX<sup>-•</sup>) cleaving through a homolytic mechanism to yield R<sup>•</sup> and X<sup>-</sup>, using the extension of the dissociative electron transfer theory to the case of radical anion dissociation, the thermodynamics of the intramolecular homolytic ET could be described by eq.1:

$$\Delta G^0 = E - E_{RX/R^{\bullet}+X^-}^0 = E + D_{R-X} - E_{X^{\bullet}/X^-}^0 - T\Delta S_{RX/R^{\bullet}+X^-} \quad (1)$$

E is the electrode potential,  $E_{RX/R^{\bullet}+X^-}^0$  the standard potential of the RX/R<sup>•</sup>+X<sup>-</sup> couple,  $D_{R-X}$  the bond dissociation energy of the cleaved bond,  $E_{X^{\bullet}/X^-}^0$  the standard potential of the X<sup>•</sup>/X<sup>-</sup> couple and  $\Delta S_{RX/R^{\bullet}+X^-}$  the entropy of the homolytic dissociation reaction.

The intrinsic barrier for the homolytic decomposition of  $\mathbf{1}\cdot$  is described by eq. 2, which depends on the oxidation potential of the leaving group  $E^0_{X/(X)\cdot-}$ , the standard reduction potential of  $\mathbf{1}$ , the bond dissociation energy of the N-SO<sub>2</sub> bond at the level of  $\mathbf{1}$  ( $D_{RX}$ ), and the entropy variation. Here RX represents the initial compound where X represents the phthalimidyl group. The  $(X)\cdot^-$  represents an excited state of the phthalimidyl anion ( $X^-$ ) that results from the injection of an electron into the low lying phthalimidyl radical orbital.

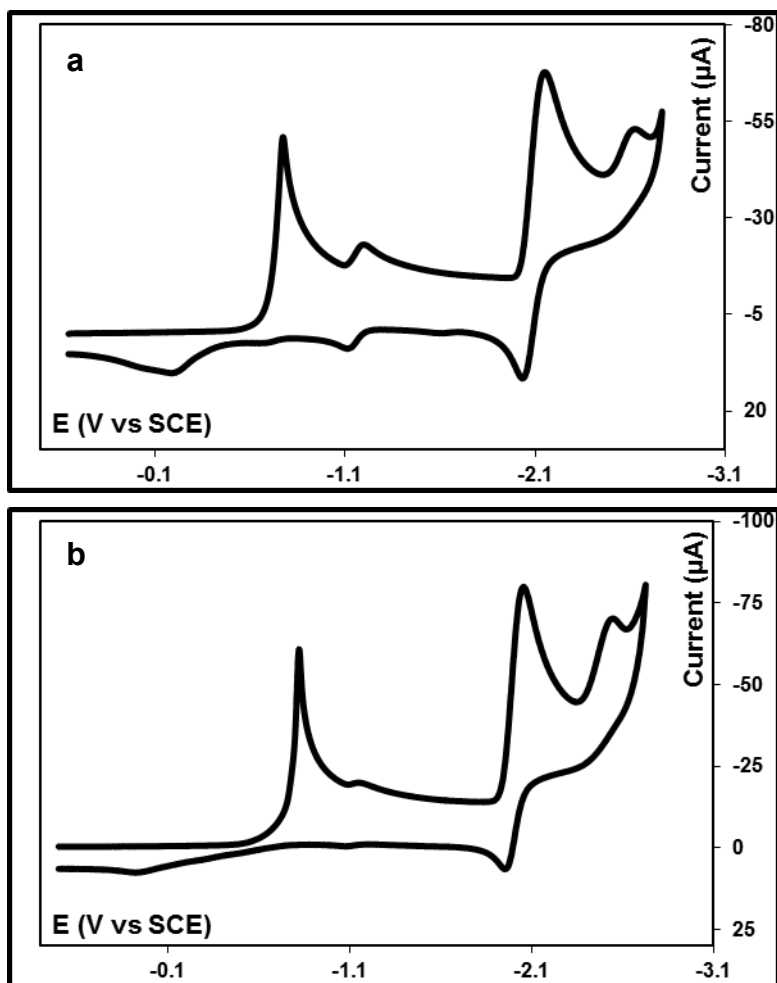
$$\Delta G^{\ddagger}_{0,RX\cdot-/R+X^-} = \frac{1}{4} \left( D_{R-X} + E^0_{RX/RX^-} - E^0_{X/(X)\cdot-} + T\Delta\bar{S}_{RX\cdot-/R+X^-} \right) + \frac{\lambda_0}{4} \quad (2)$$

For a heterolytic cleavage the intrinsic barrier is provided by eq. 3. In this case, the equation involves the standard oxidation potential  $E^0_{R/(R)\cdot-}$ , where  $(R)\cdot^-$  represents an excited state of the anion ( $R^-$ ).

$$\Delta G^{\ddagger}_{0,RX\cdot-/R+X^-} = \frac{1}{4} \left( D_{R-X} + E^0_{RX/RX^-} - E^0_{R/(R)\cdot-} + T\Delta\bar{S}_{RX\cdot-/R+X^-} \right) + \frac{\lambda_0}{4} \quad (3)$$

## II. Cyclic Voltammetry

Cyclic voltammetry of  $N,N'$ -dithiobisphthalimide (**1**) and  $N,N'$ -thiobisphthalimide (**2**):

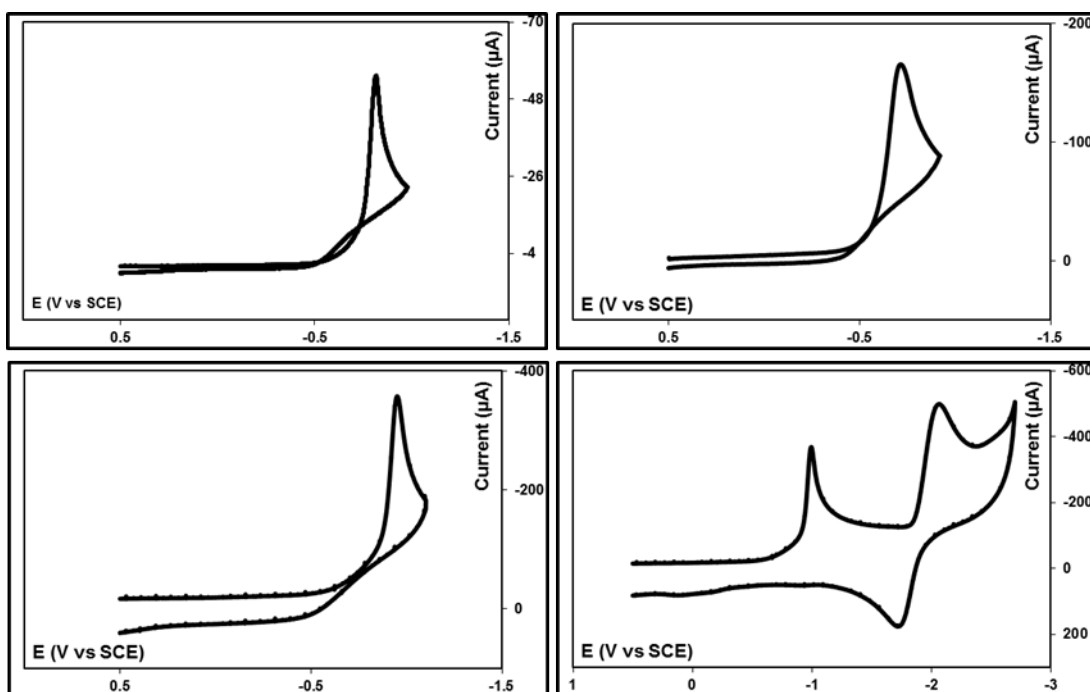


**Figure S1.** Cyclic voltammetry in  $\text{CH}_3\text{CN} + \text{nBu}_4\text{NPF}_6$  (0.1 M), at a glassy carbon electrode and at 0.2 V/s, of (a)  $N,N'$ -dithiobisphthalimide (1.1 mM), and (b)  $N,N'$ -thiobisphthalimide (1.05 mM).

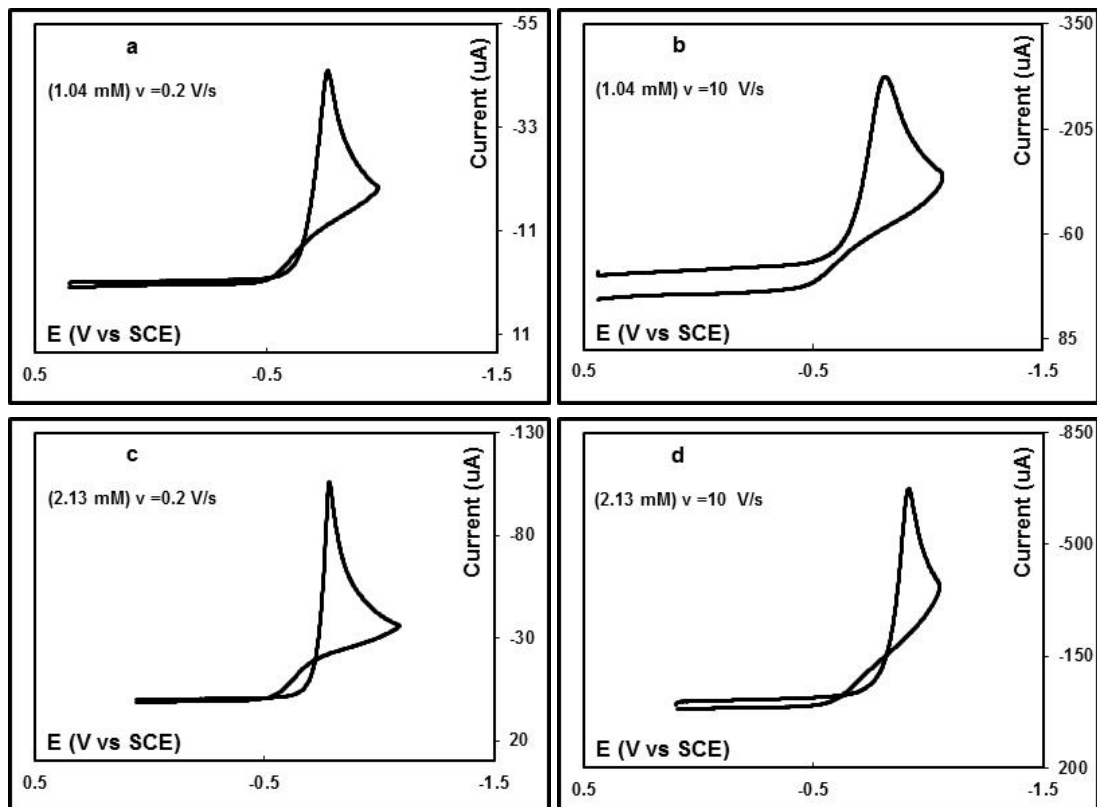
The effects of the scan rate and the concentration on the cyclic voltammetry of  $N,N'$ -thiobisphthalimide (**2**) were investigated. Figure S2 shows the cyclic voltammograms of  $N,N'$ -thiobisphthalimide (**2**) at a low concentration (1.05 mM) at scan rates ranging from 0.2 V/s to 40 V/s. The trace crossing observed at low scan rates disappears at higher scan rates. It is also important to note that the second reversible peak also disappears when the scan rate is high

indicating that the short time scale of the cyclic voltammetry, under these conditions, does not allow formation of the product responsible for this second peak.

Figure S3 shows a comparison of how the scan rate affects the cyclic voltammogram of *N,N'*-dithiobisphthalimide (**1**) at two different concentration (1.1 mM and 2.13 mM). The figure clearly shows that while the trace crossing totally disappears at 10 V/s for the low concentration, it is still clearly visible at the same scan rate at the higher concentration.



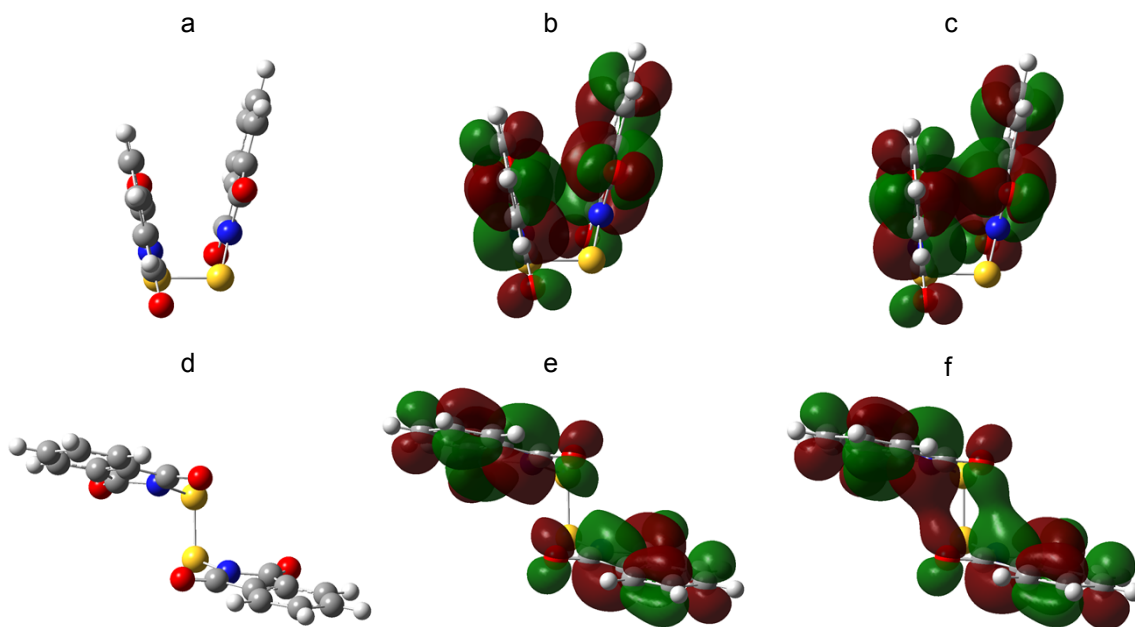
**Figure S2.** Cyclic voltammetry of *N,N'*-thiobisphthalimide (**1**: 1.05 mM) in  $\text{CH}_3\text{CN} + \text{NBu}_4\text{PF}_6$  (0.1 M), at a glassy carbon electrode and at (a) 0.2 V/s; (b) 3.6 V/s; (c) 10 V/s and (d) 10 V/s.



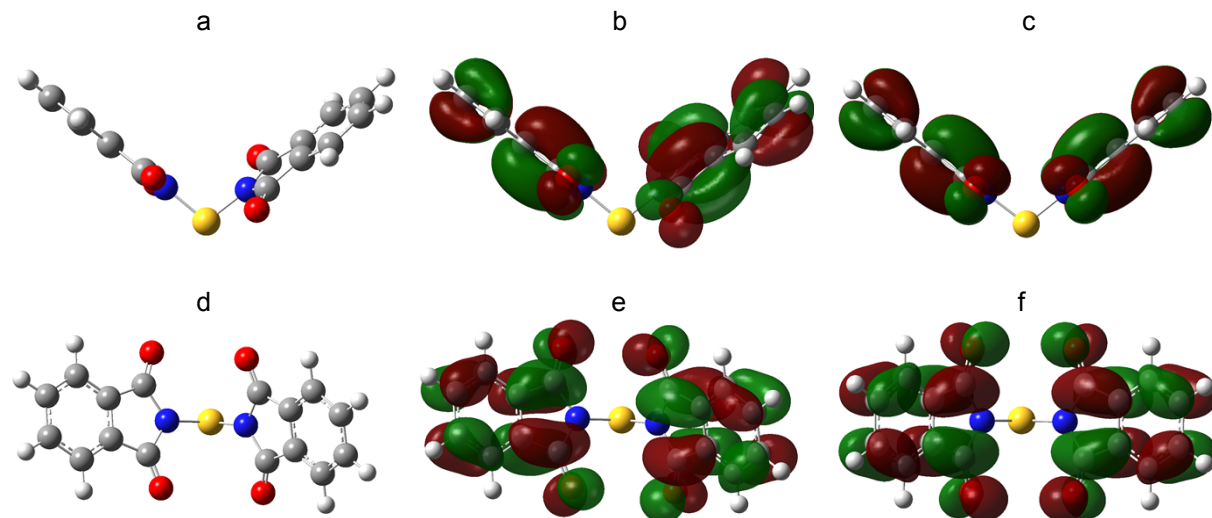
**Figure S3.** Cyclic voltammetry of  $N,N'$ -dithiobisphthalimide (**1**) in  $\text{CH}_3\text{CN} + n\text{Bu}_4\text{NPF}_6$  (0.1 M), at a glassy carbon electrode and at (a) 1.04 mM and 0.2 V/s; (b) 1.04 mM and 10 V/s; (c) 2.13 mM and 0.2 V/s and (d) 1.04 mM and (d) 10 V/s.

## Theoretical Calculations.

All of the calculations were performed using the Gaussian 09 software package.<sup>1</sup> The B3LYP method,<sup>2</sup> with the 6-31G+(d,p) basis set was used starting from preliminary optimizations performed with semi-empirical methods. LUMO orbitals and SOMO orbitals were calculated after a full optimization without imposed symmetry of the conformations. Minimum energy structures were fully optimized and the obtained conformations were checked by running frequency calculations. No imaginary vibrational frequencies were seen.



**Figure S4.** Optimized structures of N,N'-dithiobisphthalimide (a and d), its corresponding LUMO (b and e) and the SOMO of its radical anion (c and f).



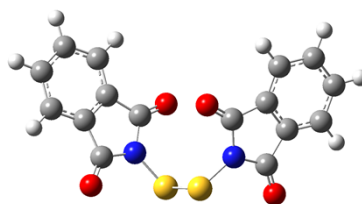
**Figure S5.** Optimized structures of N,N'-thiobisphthalimide (a and d), its corresponding LUMO (b and e) and the SOMO of its radical anion (c and f).



## Total Energies and Coordinates:

### N,N'-Dithiobisphthalimide

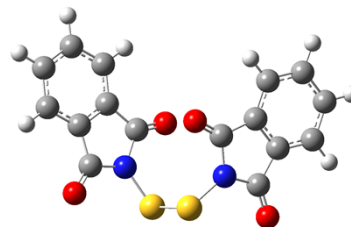
Total Energy: -1821.38913152 a.u.



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
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2	6	0	2.886157	-1.030647	-0.545703
3	6	0	3.280722	-2.354632	-0.694138
4	6	0	4.527283	-2.718102	-0.167965
5	6	0	5.341149	-1.778836	0.482985
6	6	0	4.934467	-0.445884	0.627884
7	6	0	3.005166	1.223657	0.106201
8	6	0	1.633999	-0.358948	-0.989069
9	1	0	2.642076	-3.073471	-1.196727
10	1	0	4.870285	-3.743912	-0.262876
11	1	0	6.301299	-2.092263	0.881472
12	1	0	5.554905	0.288435	1.131035
13	16	0	0.587083	2.209216	-0.860241
14	16	0	-0.586964	2.209055	0.860220
15	6	0	-3.005194	1.223651	-0.106065
16	6	0	-1.633783	-0.359157	0.988589
17	6	0	-3.697107	-0.095095	-0.102059
18	6	0	-2.886109	-1.030744	0.545520
19	6	0	-4.934741	-0.445727	-0.627381
20	6	0	-3.280691	-2.354729	0.693897
21	6	0	-5.341440	-1.778682	-0.482539
22	1	0	-5.555299	0.288687	-1.130245
23	6	0	-4.527425	-2.718072	0.168043
24	1	0	-2.641930	-3.073665	1.196200
25	1	0	-6.301723	-2.092010	-0.880783
26	1	0	-4.870443	-3.743879	0.262916
27	7	0	1.777645	1.004555	-0.591454
28	7	0	-1.777518	1.004407	0.591271
29	8	0	3.364974	2.275482	0.582557
30	8	0	0.678293	-0.826037	-1.566601
31	8	0	-0.677965	-0.826346	1.565868
32	8	0	-3.365143	2.275581	-0.582077

## N,N'-Dithiobisphthalimide Radical Anion

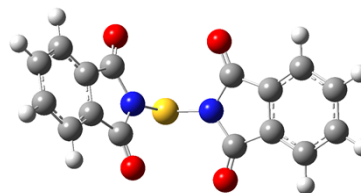
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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
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1	6	0	3.509386	-0.148113	0.051334
2	6	0	2.578238	-1.038440	-0.535290
3	6	0	2.857575	-2.406694	-0.624110
4	6	0	4.069747	-2.867350	-0.115115
5	6	0	4.999243	-1.976803	0.476203
6	6	0	4.723984	-0.612077	0.561752
7	6	0	2.965656	1.214494	0.013711
8	6	0	1.411711	-0.285858	-0.991335
9	1	0	2.136539	-3.083179	-1.073015
10	1	0	4.306920	-3.926980	-0.165831
11	1	0	5.935274	-2.365331	0.868773
12	1	0	5.427256	0.081031	1.014378
13	16	0	0.583372	2.347997	-0.870398
14	16	0	-0.583327	2.347947	0.870443
15	6	0	-2.965637	1.214512	-0.013690
16	6	0	-1.411716	-0.285900	0.991329
17	6	0	-3.509387	-0.148076	-0.051341
18	6	0	-2.578267	-1.038434	0.535299
19	6	0	-4.723986	-0.612012	-0.561788
20	6	0	-2.857653	-2.406682	0.624117
21	6	0	-4.999288	-1.976727	-0.476239
22	1	0	-5.427232	0.081117	-1.014422
23	6	0	-4.069829	-2.867302	0.115105
24	1	0	-2.136643	-3.083189	1.073031
25	1	0	-5.935324	-2.365230	-0.868824
26	1	0	-4.307036	-3.926925	0.165821
27	8	0	3.443029	2.264034	0.431591
28	8	0	0.397879	-0.655852	-1.572843
29	8	0	-3.442956	2.264067	-0.431596
30	8	0	-0.397873	-0.655922	1.572815
31	7	0	1.706451	1.083709	-0.649243
32	7	0	-1.706415	1.083683	0.649239

## N,N'-Thiobisphthalimide

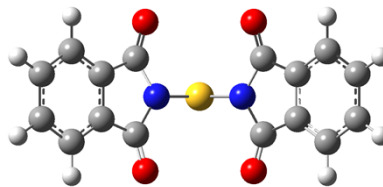
Total Energy: -1423.18691900 a.u.



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
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2	6	0	3.232551	-0.573628	0.170530
3	6	0	4.304919	-1.247685	0.743100
4	6	0	5.136341	-0.520877	1.604982
5	6	0	4.894464	0.835181	1.873323
6	6	0	3.812141	1.506203	1.289736
7	6	0	1.784461	1.211723	-0.317891
8	6	0	2.196710	-1.075564	-0.775485
9	1	0	4.483085	-2.296067	0.527326
10	1	0	5.983139	-1.013028	2.073729
11	1	0	5.558841	1.371472	2.544121
12	1	0	3.616338	2.554834	1.488481
13	16	0	0.000001	-0.000181	-2.087573
14	6	0	-1.784479	-1.211808	-0.317670
15	6	0	-2.196713	1.075392	-0.775722
16	6	0	-2.991371	-0.775566	0.438320
17	6	0	-3.232534	0.573663	0.170422
18	6	0	-3.812179	-1.505961	1.289986
19	6	0	-4.304861	1.247856	0.742907
20	6	0	-4.894465	-0.834803	1.873483
21	1	0	-3.616398	-2.554562	1.488912
22	6	0	-5.136295	0.521220	1.604923
23	1	0	-4.483006	2.296203	0.526948
24	1	0	-5.558843	-1.370953	2.544393
25	1	0	-5.983069	1.013483	2.073595
26	7	0	1.337850	0.048615	-1.020577
27	7	0	-1.337818	-0.048816	-1.020546
28	8	0	2.091433	-2.169391	-1.274572
29	8	0	1.254210	2.297810	-0.343971
30	8	0	-2.091414	2.169126	-1.274985
31	8	0	-1.254302	-2.297922	-0.343635

## N,N'-Thiobisphthalimide Radical Anion

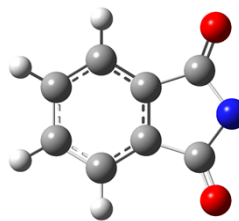
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2	6	0	3.072103	-0.707260	0.307213
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4	6	0	4.948274	-0.708400	1.800277
5	6	0	4.948030	0.709415	1.800230
6	6	0	4.013755	1.424221	1.052233
7	6	0	1.998509	1.192517	-0.565382
8	6	0	1.998804	-1.192679	-0.565167
9	1	0	4.006150	-2.509720	1.042918
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11	1	0	5.687388	1.242435	2.392478
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24	1	0	-5.687536	-1.241383	2.392841
25	1	0	-5.687674	1.242176	2.392192
26	7	0	1.348274	-0.000204	-1.046014
27	7	0	-1.348272	-0.000256	-1.046010
28	8	0	1.700001	-2.339237	-0.868914
29	8	0	1.699318	2.338945	-0.869198
30	8	0	-1.699871	2.338856	-0.869756
31	8	0	-1.699445	-2.339325	-0.868350

## Phthalimide Radical

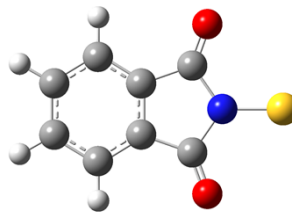
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5	6	0	-2.526477	-0.704131	0.000275
6	6	0	-1.330816	-1.428821	0.000179
7	6	0	1.279222	-1.147151	-0.000137
8	6	0	1.279373	1.146992	-0.000199
9	1	0	-1.320503	2.514014	-0.000003
10	1	0	-3.474786	1.233143	0.000298
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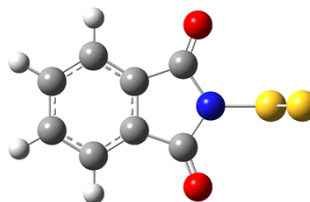
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Total Energy: -910.66099863 a.u.



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3	6	0	-1.976405	1.425559	0.000202
4	6	0	-3.175076	0.702022	0.000293
5	6	0	-3.175074	-0.702025	0.000360
6	6	0	-1.976400	-1.425558	0.000335
7	6	0	0.611179	-1.188620	0.000244
8	6	0	0.611173	1.188625	0.000136
9	1	0	-1.964312	2.510467	0.000147
10	1	0	-4.121804	1.233514	0.000308
11	1	0	-4.121800	-1.233519	0.000423
12	1	0	-1.964302	-2.510466	0.000381
13	7	0	1.436801	-0.000003	-0.000146
14	8	0	1.025873	-2.321460	0.000010
15	8	0	1.025875	2.321450	-0.000208
16	16	0	3.104384	0.000003	-0.000683

## PhthalimideSS Radical



Total Energy: -1308.86531101 a.u.

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3	6	0	-2.556113	1.425801	0.141733
4	6	0	-3.739401	0.701577	0.339964
5	6	0	-3.739495	-0.701159	0.340130
6	6	0	-2.556308	-1.425590	0.142062
7	6	0	0.002318	-1.182363	-0.283903
8	6	0	0.002510	1.182126	-0.283987
9	1	0	-2.544777	2.510767	0.140148
10	1	0	-4.672810	1.233564	0.496602
11	1	0	-4.672980	-1.232983	0.496881
12	1	0	-2.545127	-2.510558	0.140684
13	16	0	2.499957	-0.000328	-0.710573
14	16	0	3.397124	0.000368	1.052553
15	8	0	0.422295	-2.315688	-0.339747
16	8	0	0.422630	2.315372	-0.340112
17	7	0	0.785858	-0.000186	-0.435404

**References**

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