---- SUPPORTING INFORMATION ----

Facile Smiles-Type Rearrangement in Radical Cations of *N*-Acyl Arysulfonamides and Analogs

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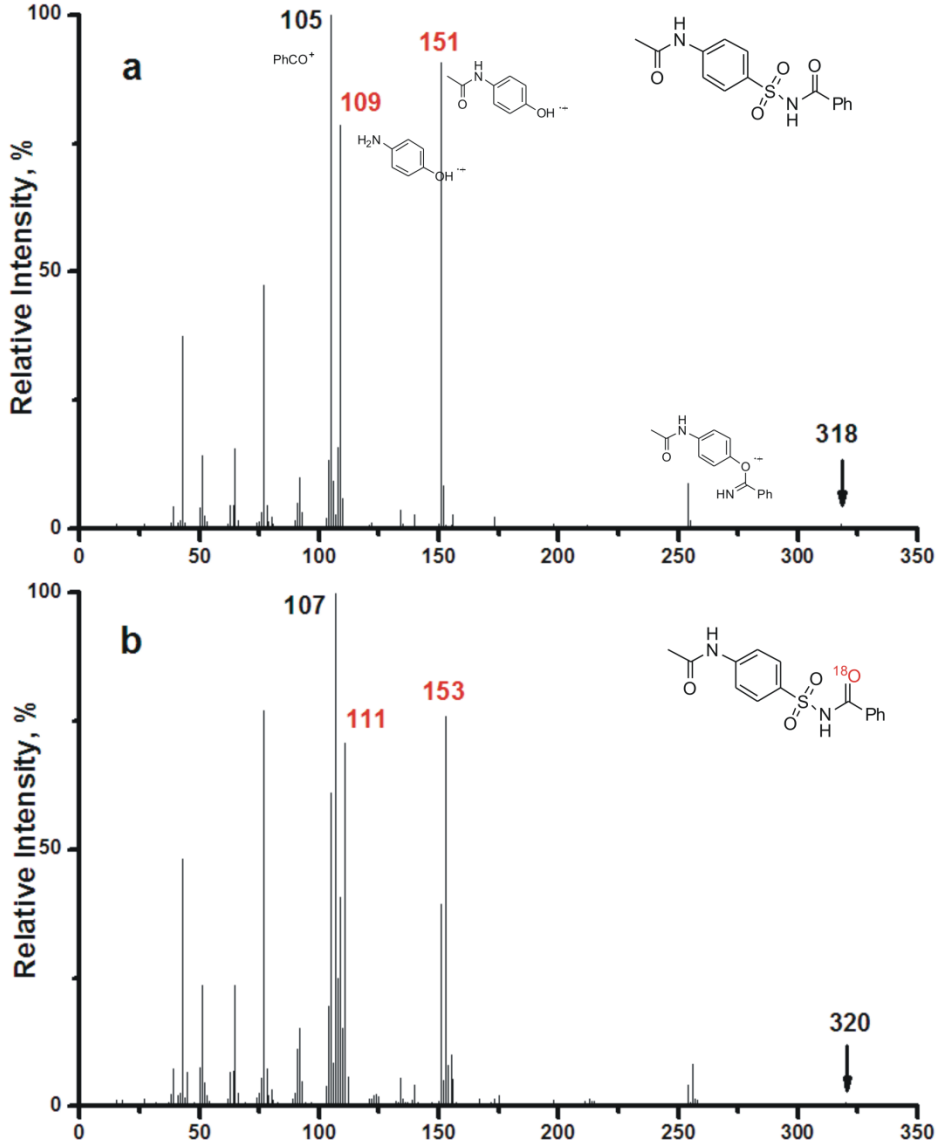


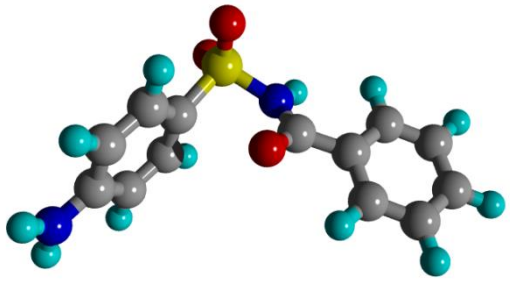
EIMS of pair of isotopologues (70% ^{18}O enrichment in b). The oxygen atom in the major peaks is from the benzoyl group, not the sulfonyl group.

B3LYP/6-31G(d) structures and electronic energies for species in Figure 1a

1a radical cation

E = -1235.644874

$\langle S^2 \rangle$ = 0.765

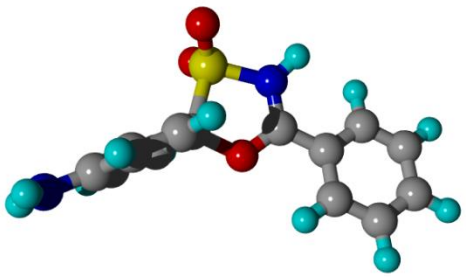


C	-2.924811	-1.736468	-0.260066
C	-4.245604	-2.156003	-0.146694
C	-5.251069	-1.228022	0.140576
C	-4.937260	0.124300	0.310434
C	-3.617105	0.551091	0.204363
C	-2.601390	-0.381062	-0.071146
H	-2.132278	-2.440991	-0.488040
H	-4.494244	-3.203708	-0.284069
H	-6.282668	-1.556604	0.225189
H	-5.722297	0.844863	0.516959
H	-3.395260	1.610691	0.296771
C	-1.182889	0.008579	-0.210123
O	-0.349912	-0.672034	-0.817210
N	-0.762098	1.178298	0.403952
S	0.722604	1.910763	-0.023479
O	1.021207	2.795213	1.095905
O	0.693250	2.371485	-1.402533
C	1.828702	0.484047	0.029789
C	2.105869	-0.134664	1.270544
C	2.533422	0.134822	-1.147278
C	3.053059	-1.125784	1.332605
H	1.579015	0.180538	2.164960
C	3.486713	-0.848787	-1.096308
H	2.297815	0.646548	-2.073612
C	3.764379	-1.505092	0.145857
H	3.283139	-1.616800	2.273588
H	4.034455	-1.137706	-1.988386
N	4.692893	-2.467417	0.203866
H	5.214940	-2.751611	-0.617831
H	4.913515	-2.944017	1.071244
H	-1.361807	1.741376	0.999551

Smiles transition structure from **1a** (radical cation)

E = -1235.621669

$<S^2> = 0.759$

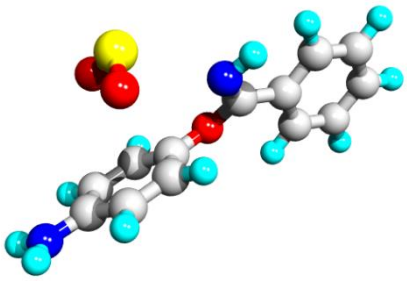


C	-2.735978	-1.646195	-0.000354
C	-4.020150	-2.176538	-0.022164
C	-5.129597	-1.325351	-0.007670
C	-4.960408	0.063463	0.032349
C	-3.682312	0.605818	0.049362
C	-2.560824	-0.248174	0.026746
H	-1.869253	-2.297356	-0.015166
H	-4.158696	-3.252421	-0.050923
H	-6.131246	-1.744410	-0.021656
H	-5.825126	0.718393	0.059260
H	-3.564553	1.683725	0.116746
C	-1.213733	0.293438	0.034344
O	-0.220279	-0.507653	0.336390
N	-0.899362	1.548521	-0.247184
S	0.852010	1.900913	-0.065368
O	1.028782	2.589748	1.204754
O	1.288061	2.463984	-1.334603
C	1.235620	-0.028345	0.099787
C	2.025598	-0.278900	1.298979
C	1.751516	-0.564299	-1.152643
C	3.224977	-0.925189	1.223207
H	1.650445	0.091647	2.246127
C	2.952984	-1.213884	-1.194787
H	1.176956	-0.410651	-2.059795
C	3.734663	-1.409049	-0.018991
H	3.803186	-1.078291	2.130350
H	3.320791	-1.588202	-2.146252
N	4.928524	-2.046107	-0.076463
H	5.313046	-2.369285	-0.953138
H	5.501745	-2.167736	0.746670
H	-1.560225	2.233680	-0.602118

3a…SO_2 complex (radical cation)

E = -1235.674857

$\langle S^2 \rangle$ = 0.760



C	3.256369	-1.325806	0.027615
C	4.623372	-1.585696	0.079548
C	5.536962	-0.530507	0.118791
C	5.082147	0.791297	0.104526
C	3.718205	1.057373	0.058750
C	2.791375	0.000236	0.024874
H	2.550726	-2.148283	-0.004391
H	4.975537	-2.612536	0.087840
H	6.602603	-0.736091	0.154570
H	5.790971	1.613207	0.121289
H	3.379400	2.089127	0.021974
C	1.349487	0.300207	0.008682
O	0.604531	-0.793390	-0.464851
N	0.712977	1.362188	0.292766
S	-1.940029	2.593692	-0.437241
O	-2.431261	2.522542	0.941592
O	-2.305164	1.495001	-1.339688
C	-0.681309	-1.007776	-0.149620
C	-1.413387	-1.763720	-1.105772
C	-1.286947	-0.600579	1.070148
C	-2.733912	-2.046160	-0.890919
H	-0.907750	-2.075484	-2.012984
C	-2.607658	-0.885931	1.290879
H	-0.715466	-0.051406	1.805256
C	-3.371360	-1.592721	0.308430
H	-3.309170	-2.596173	-1.629572
H	-3.087257	-0.565832	2.210692
N	-4.672763	-1.837750	0.515879
H	-5.148179	-1.507734	1.347782
H	-5.237293	-2.326827	-0.168890
H	1.339943	2.093359	0.629749

3a radical cation

E = -687.078595

$<S^2>$ = 0.759

C	3.384016	1.063178	0.320572
C	2.297589	0.240485	-0.024422
C	2.527258	-1.111493	-0.330427
C	3.822763	-1.622084	-0.307552
C	4.896990	-0.797522	0.032017
C	4.674529	0.545260	0.349849
C	0.944751	0.830791	-0.083805
O	-0.026888	-0.188130	0.039868
C	-1.356608	-0.074753	0.022959
C	-2.116444	1.118976	-0.148407
C	-3.486617	1.045461	-0.140681
C	-4.159782	-0.203975	0.037996
C	-3.387346	-1.396856	0.210922
C	-2.023012	-1.326198	0.202008
N	-5.500015	-0.256378	0.043489
N	0.566278	2.030473	-0.212574
H	-4.074878	1.949218	-0.272435
H	-1.599683	2.058210	-0.278866
H	-1.413918	-2.213827	0.333709
H	-3.891004	-2.348983	0.349043
H	-5.997697	-1.130060	0.169003
H	-6.064092	0.576839	-0.076520
H	1.698381	-1.756039	-0.598899
H	3.993520	-2.665236	-0.555268
H	5.905226	-1.200136	0.054337
H	5.505580	1.186129	0.627351
H	3.221183	2.101988	0.594469
H	1.360121	2.660647	-0.327441

SO_2 molecule

E = -548.587464

S	0.000000	0.000000	0.370795
O	0.000000	1.261895	-0.370795
O	0.000000	-1.261895	-0.370795

E-Z transition structure for **3a** (radical cation)

E = -687.046745

$<S^2>$ = 0.757

C	3.385417	1.089172	0.113472
C	2.278962	0.220192	0.147945
C	2.450489	-1.138692	-0.164662
C	3.713078	-1.615336	-0.508135
C	4.807512	-0.748383	-0.541199
C	4.641816	0.604893	-0.229825
C	0.983985	0.808481	0.510131
O	-0.057914	-0.367993	0.564757
C	-1.327620	-0.211555	0.279181
C	-1.837508	0.789491	-0.605902
C	-3.178328	0.840777	-0.882911
C	-4.082847	-0.095107	-0.289165
C	-3.571940	-1.099551	0.591569
C	-2.233347	-1.152688	0.864664
N	-5.397296	-0.034428	-0.562120
N	0.627057	1.922107	0.807922
H	-3.565516	1.587772	-1.570199
H	-1.157281	1.486585	-1.077718
H	-1.823237	-1.902300	1.532817
H	-4.255653	-1.813468	1.041832
H	-6.053164	-0.691919	-0.158623
H	-5.778638	0.666112	-1.185775
H	1.606456	-1.816119	-0.133196
H	3.843156	-2.666159	-0.747659
H	5.790073	-1.126329	-0.808099
H	5.492218	1.279222	-0.254289
H	3.245164	2.136991	0.357848
H	0.333389	2.839631	1.053414

3a_Z radical cation

E = -687.072864

$\langle S^2 \rangle$ = 0.758

C	3.211231	0.666362	-0.675225
C	2.077225	0.338000	0.092033
C	2.001470	-0.914940	0.723587
C	3.043885	-1.828261	0.583210
C	4.162716	-1.500923	-0.184892
C	4.244009	-0.252854	-0.812439
C	1.010096	1.336025	0.207425
O	-0.091532	0.906536	1.060123
C	-1.221094	0.457632	0.527219
C	-1.410981	0.237094	-0.867297
C	-2.614008	-0.239527	-1.319579
C	-3.679002	-0.514345	-0.403834
C	-3.477128	-0.289532	0.995802
C	-2.276707	0.185579	1.446892
N	-4.855279	-0.978414	-0.853547
N	1.003513	2.489248	-0.296456
H	-2.766336	-0.414240	-2.380697
H	-0.606900	0.445838	-1.563540
H	-2.099202	0.367362	2.501483
H	-4.283751	-0.496920	1.692824
H	-5.623046	-1.179380	-0.223669
H	-5.020331	-1.142674	-1.839623
H	1.144667	-1.170572	1.337209
H	2.984916	-2.792708	1.078168
H	4.974310	-2.214673	-0.291319
H	5.116752	0.003142	-1.405192
H	3.264002	1.640034	-1.149993
H	0.179254	3.044795	-0.064024

Transition structure for **3a_Z** to form non-bonded complex

E = -687.044699

$<S^2>$ = 0.761

C	3.274392	0.027465	-1.078855
C	2.471915	0.480518	-0.006699
C	2.279312	-0.304992	1.151710
C	2.909118	-1.538312	1.233786
C	3.711614	-1.988941	0.176778
C	3.891834	-1.212136	-0.973256
C	1.898510	1.762154	-0.087367
O	-0.403433	1.562696	0.226368
C	-1.431795	0.822831	0.108506
C	-1.351487	-0.586618	-0.199794
C	-2.478415	-1.355136	-0.323659
C	-3.772556	-0.781433	-0.148148
C	-3.878813	0.607995	0.158510
C	-2.756153	1.379559	0.281623
N	-4.883918	-1.543458	-0.270385
N	1.774002	2.932135	-0.179136
H	-2.399493	-2.413374	-0.560163
H	-0.368445	-1.024817	-0.337498
H	-2.826344	2.436715	0.516440
H	-4.864755	1.045575	0.293556
H	-5.807302	-1.150851	-0.152669
H	-4.828269	-2.527418	-0.491936
H	1.642214	0.060203	1.949459
H	2.778341	-2.152519	2.118695
H	4.200846	-2.955595	0.251029
H	4.516146	-1.572843	-1.784098
H	3.410115	0.647303	-1.958854
H	0.938967	3.507588	-0.267059

p-aminophenol radical cation

E = -362.568568

$<S^2>$ = 0.759

C	-0.005500	-1.407926	0.000000
C	1.231101	-0.706041	0.000000
C	-1.239973	-0.696988	0.000000
C	1.236013	0.664243	0.000000
H	2.167651	-1.257220	0.000000
C	-1.239646	0.670294	0.000000
H	-2.163349	-1.266174	0.000000
C	0.000000	1.389204	0.000000
H	2.175271	1.209352	0.000000
H	-2.175957	1.220442	0.000000
N	0.004757	2.729847	0.000000
H	-0.856670	3.264506	0.000000
H	0.868630	3.260378	0.000000
O	-0.090652	-2.731831	0.000000
H	0.784378	-3.162288	0.000000

Benzonitrile

E = -324.492216

C	0.000000	1.217349	-0.091486
C	0.000000	1.210891	-1.483885
C	0.000000	0.000000	-2.180722
C	0.000000	-1.210891	-1.483885
C	0.000000	-1.217349	-0.091486
C	0.000000	0.000000	0.610317
H	0.000000	2.152593	0.459163
H	0.000000	2.152036	-2.025928
H	0.000000	0.000000	-3.267120
H	0.000000	-2.152036	-2.025928
H	0.000000	-2.152593	0.459163
C	0.000000	0.000000	2.044923
N	0.000000	0.000000	3.208284

p-aminophenoxyl radical

E = -362.190942

$<S^2>$ = 0.774

C	0.003696	-0.755302	1.232089
C	0.003696	0.616291	1.225911
C	0.000898	1.335370	0.000000
C	0.003696	0.616291	-1.225911
C	0.003696	-0.755302	-1.232089
C	0.002773	-1.527416	0.000000
H	0.007215	1.173174	2.161234
H	0.007215	1.173174	-2.161234
H	0.002056	-1.314141	-2.163027
N	0.039383	2.709109	0.000000
H	-0.199897	3.198034	0.851180
H	-0.199897	3.198034	-0.851180
O	-0.000646	-2.782187	0.000000
H	0.002056	-1.314141	2.163027

N-protonated benzonitrile (cation)

E = -324.819485

C	0.000000	1.237904	-0.156850
C	0.000000	1.220840	-1.543503
C	0.000000	0.000000	-2.231323
C	0.000000	-1.220840	-1.543503
C	0.000000	-1.237904	-0.156850
C	0.000000	0.000000	0.532047
H	0.000000	2.173935	0.391600
H	0.000000	2.156845	-2.091985
H	0.000000	0.000000	-3.317181
H	0.000000	-2.156845	-2.091985
H	0.000000	-2.173935	0.391600
C	0.000000	0.000000	1.932527
N	0.000000	0.000000	3.089395
H	0.000000	0.000000	4.096921

B3LYP/6-31G(d) structures and electronic energies for species in Figure 1b

1b radical cation

E = -1274.953318

$<S^2>$ = 0.762

C	-2.662590	-1.900023	0.214380
C	-3.944035	-2.440263	0.235756
C	-5.047014	-1.633051	-0.057257
C	-4.869616	-0.281850	-0.371436
C	-3.592859	0.272831	-0.373914
C	-2.483397	-0.533304	-0.065851
H	-1.796106	-2.519853	0.418772
H	-4.084231	-3.490664	0.471096
H	-6.046163	-2.058412	-0.049826
H	-5.726111	0.337720	-0.618236
H	-3.459239	1.315292	-0.643720
C	-1.092084	-0.025755	-0.134939
O	-0.203894	-0.740589	-0.637827
N	-0.758361	1.213607	0.355356
C	-1.587105	2.097378	1.195583
H	-0.942425	2.562783	1.942719
H	-2.067514	2.877912	0.600001
H	-2.342458	1.489536	1.692777
S	0.789321	1.844603	-0.152964
O	1.183292	2.769008	0.904386
O	0.700851	2.245587	-1.549713
C	1.848951	0.390829	-0.064225
C	2.181796	-0.152585	1.199893
C	2.535429	-0.007173	-1.238909
C	3.144864	-1.125365	1.284643
H	1.683393	0.205352	2.094384
C	3.504225	-0.972515	-1.161324
H	2.271931	0.452465	-2.184808
C	3.827530	-1.559610	0.102531
H	3.411341	-1.557987	2.244480
H	4.034217	-1.296100	-2.052230
N	4.773260	-2.505958	0.183966
H	5.276431	-2.824314	-0.635853
H	5.026934	-2.930236	1.068256

Smiles transition structure from **1b** (radical cation)

E = -1274.936829

$<S^2>$ = 0.759

C	-2.504896	-1.846430	-0.244978
C	-3.738069	-2.486704	-0.249096
C	-4.899751	-1.771384	0.058718
C	-4.831344	-0.410787	0.373778
C	-3.606084	0.246267	0.363136
C	-2.434099	-0.468537	0.044371
H	-1.598148	-2.395295	-0.473727
H	-3.795617	-3.543990	-0.487060
H	-5.860482	-2.277453	0.061606
H	-5.732169	0.134974	0.635254
H	-3.557627	1.292055	0.645300
C	-1.122682	0.168323	0.060867
O	-0.104474	-0.594361	0.403405
N	-0.856727	1.430562	-0.237519
C	-1.702804	2.444338	-0.880958
H	-2.135605	3.112501	-0.132620
H	-1.063855	3.018708	-1.556411
H	-2.489375	1.951913	-1.454124
S	0.875162	1.816722	0.093751
O	0.942801	2.419514	1.418154
O	1.360030	2.492079	-1.102583
C	1.335427	-0.064033	0.152009
C	2.156496	-0.357180	1.323782
C	1.839035	-0.535554	-1.133966
C	3.346492	-1.012089	1.199898
H	1.801995	-0.019407	2.290813
C	3.031489	-1.196732	-1.222303
H	1.256518	-0.332882	-2.026379
C	3.828585	-1.452439	-0.069122
H	3.940662	-1.204215	2.089207
H	3.382213	-1.530196	-2.195274
N	5.013158	-2.102418	-0.172688
H	5.380995	-2.390138	-1.068501
H	5.599246	-2.261343	0.634721

3b…SO_2 complex (radical cation)

E = -1274.982934

$\langle S^2 \rangle$ = 0.759

C	3.058165	-1.479510	0.362916
C	4.398278	-1.848587	0.429190
C	5.394682	-0.934749	0.075821
C	5.048319	0.350696	-0.345271
C	3.709598	0.732099	-0.399033
C	2.702613	-0.179671	-0.038226
H	2.286883	-2.195425	0.628368
H	4.666192	-2.850388	0.750592
H	6.439480	-1.227277	0.121048
H	5.820007	1.055792	-0.638292
H	3.448196	1.723213	-0.753693
C	1.281849	0.214697	-0.090418
O	0.499616	-0.848985	-0.611491
N	0.671133	1.290076	0.177138
C	1.325472	2.441674	0.782411
H	1.529531	3.193863	0.010785
H	0.623709	2.889744	1.492489
H	2.262382	2.200965	1.295417
S	-1.977546	2.486540	-0.515718
O	-2.273248	2.551324	0.918400
O	-2.551688	1.370067	-1.276897
C	-0.765232	-1.081300	-0.243474
C	-1.534467	-1.827539	-1.179087
C	-1.323954	-0.701488	1.008310
C	-2.843090	-2.121526	-0.913638
H	-1.065368	-2.121922	-2.111413
C	-2.632194	-1.001138	1.279861
H	-0.724804	-0.168504	1.733512
C	-3.433115	-1.693552	0.317988
H	-3.445160	-2.663492	-1.636776
H	-3.072657	-0.707227	2.227751
N	-4.723675	-1.952861	0.575677
H	-5.166147	-1.641801	1.432244
H	-5.312708	-2.432577	-0.094452

3b radical cation

E = -726.387109

$\langle S^2 \rangle$ = 0.759

C	4.216041	-0.277756	0.096644
C	3.410169	0.684465	0.781975
C	2.047211	0.694054	0.634041
C	1.428185	-0.270389	-0.213346
C	2.223108	-1.253912	-0.872487
C	3.583581	-1.257009	-0.733097
N	5.550761	-0.270801	0.240738
N	-0.466644	1.806867	-0.200094
C	-1.344965	2.936118	0.054929
C	-0.862960	0.611074	-0.187074
C	-2.187203	-0.026835	-0.035793
C	-2.323277	-1.204818	0.718401
C	-3.575428	-1.791021	0.878883
C	-4.698822	-1.220804	0.274280
C	-4.567633	-0.062033	-0.492990
C	-3.319156	0.537905	-0.646605
O	0.119299	-0.399608	-0.424162
H	3.889757	1.408612	1.434216
H	1.443205	1.423917	1.151614
H	1.717808	-1.981852	-1.497911
H	4.189796	-1.995126	-1.249901
H	6.138859	-0.949712	-0.227420
H	6.018436	0.414984	0.821160
H	-2.280755	2.674433	0.560944
H	-0.796194	3.665125	0.659473
H	-1.579782	3.426944	-0.897025
H	-1.451855	-1.654440	1.183951
H	-3.675249	-2.695009	1.471937
H	-5.673697	-1.683586	0.395646
H	-5.435973	0.373056	-0.978099
H	-3.220666	1.422830	-1.266367

SO_2 molecule: see p. S6

Transition structure for **3b** dissociating to “complex” (radical cation)

E = -726.366654

$<S^2>$ = 0.757

C	-4.036150	-0.418017	0.426770
C	-2.990351	0.025548	1.294119
C	-1.696808	0.088252	0.851316
C	-1.361718	-0.296704	-0.491487
C	-2.424581	-0.739511	-1.354676
C	-3.715440	-0.800838	-0.912396
N	-5.307079	-0.477155	0.867258
N	0.717782	1.976489	-0.344215
C	0.514914	3.380592	-0.331296
C	1.073276	0.843672	-0.351642
C	2.244548	0.020603	-0.088840
C	2.283470	-1.370040	-0.276586
C	3.455602	-2.068421	0.000812
C	4.586563	-1.393178	0.465566
C	4.551206	-0.008168	0.654321
C	3.387850	0.700284	0.378892
O	-0.158064	-0.297098	-0.962699
H	-3.233571	0.301237	2.316790
H	-0.905593	0.402239	1.522771
H	-2.161301	-1.024233	-2.367840
H	-4.509375	-1.138287	-1.573139
H	-6.058329	-0.799758	0.271376
H	-5.552602	-0.220530	1.814432
H	1.361634	3.886690	-0.807966
H	-0.407804	3.647762	-0.855566
H	0.444505	3.725098	0.706220
H	1.408972	-1.888182	-0.646898
H	3.486558	-3.143184	-0.148818
H	5.496990	-1.945043	0.680186
H	5.429785	0.517619	1.015122
H	3.355445	1.775569	0.524380

Transition structure for CH_3^+ transfer, transforming “complex” to “complex_alt” (radical cation)

E = -726.343256

$<S^2>$ = 0.760

C	-4.945544	-0.564485	1.038478
C	-6.321247	-0.363580	1.062639
C	-6.933234	0.420257	0.079499
C	-6.175083	1.010041	-0.936757
C	-4.798168	0.821264	-0.978772
C	-4.185988	0.031419	0.013368
H	-4.459030	-1.171095	1.795252
H	-6.917067	-0.818203	1.847521
H	-8.008116	0.572072	0.105261
H	-6.658000	1.616455	-1.696221
H	-4.199071	1.272888	-1.762682
C	-2.776028	-0.169338	-0.021889
O	2.125930	-1.393505	-0.383376
N	-1.627260	-0.324809	-0.046399
C	0.203205	-0.758951	-0.182938
H	0.379295	-0.021628	-0.949426
H	-0.001682	-1.778266	-0.465395
H	0.398160	-0.522887	0.850592
C	4.471740	-1.368804	-0.399104
C	5.649320	-0.699706	-0.214712
C	3.195090	-0.720529	-0.198204
C	5.647622	0.670446	0.184771
H	6.599318	-1.204370	-0.370488
C	3.217314	0.664363	0.204535
C	4.400242	1.331276	0.388495
H	2.276598	1.181629	0.363329
H	4.456354	-2.410284	-0.702571
H	4.399786	2.374851	0.692754
N	6.812387	1.332605	0.367178
H	6.830871	2.302153	0.650545
H	7.703801	0.878099	0.226639

“complex_alt” non-bonded radical cation

E = -726.392676

$<S^2>$ = 0.758

C	0.269230	4.257100	1.220706
C	0.269230	5.648791	1.212648
C	0.269261	6.343506	0.000000
C	0.269230	5.648791	-1.212648
C	0.269230	4.257100	-1.220706
C	0.269251	3.558898	0.000000
H	0.269575	3.708564	2.157134
H	0.269583	6.192159	2.152469
H	0.269499	7.429491	0.000000
H	0.269583	6.192159	-2.152469
H	0.269575	3.708564	-2.157134
C	0.270329	2.127211	0.000000
O	2.033741	-2.994208	0.000000
N	0.272480	0.963767	0.000000
C	2.505147	-1.624521	0.000000
H	2.154036	-1.105208	-0.894207
H	3.590564	-1.704499	0.000000
H	2.154036	-1.105208	0.894207
C	0.415056	-4.657367	0.000000
C	-0.890694	-5.058768	0.000000
C	0.741833	-3.265839	0.000000
C	-1.937188	-4.081982	0.000000
H	-1.143535	-6.114955	0.000000
C	-0.290240	-2.283758	0.000000
C	-1.599949	-2.692216	0.000000
H	-0.056862	-1.221543	0.000000
H	1.229563	-5.373660	0.000000
H	-2.395637	-1.952535	0.000000
N	-3.224335	-4.467130	0.000000
H	-3.979381	-3.792370	0.000000
H	-3.485897	-5.445418	0.000000

p-aminoanisole radical cation

E = -401.880534

$\langle S^2 \rangle$ = 0.758

C	0.000000	0.973641	0.000000
C	1.120349	0.095803	0.000000
C	-1.325680	0.439534	0.000000
C	0.919298	-1.261553	0.000000
H	2.129674	0.489221	0.000000
C	-1.527156	-0.911350	0.000000
H	-2.155933	1.137582	0.000000
C	-0.405963	-1.802208	0.000000
H	1.769250	-1.937834	0.000000
H	-2.534077	-1.318072	0.000000
N	-0.594133	-3.130713	0.000000
H	-1.523306	-3.535114	0.000000
H	0.184472	-3.779194	0.000000
O	0.073868	2.291820	0.000000
C	1.348205	2.974572	0.000000
H	1.912280	2.719615	0.901413
H	1.099028	4.033982	0.000000
H	1.912280	2.719615	-0.901413

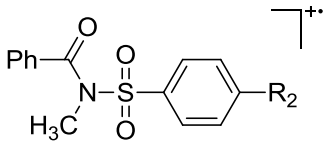
Benzonitrile: see p. S10

p-aminophenoxyl radical: see p. S11

N-methylbenzonitrilium cation
E = -364.153360

C	-1.229723	0.764584	0.000000
C	-1.206593	2.152358	0.000000
C	0.016416	2.834286	0.000000
C	1.231230	2.137902	0.000000
C	1.237938	0.749932	0.000000
C	0.000000	0.066753	0.000000
H	-2.169583	0.222534	0.000000
H	-2.140152	2.705118	0.000000
H	0.022861	3.920096	0.000000
H	2.171274	2.679561	0.000000
H	2.171270	0.196708	0.000000
C	-0.008035	-1.342085	0.000000
N	-0.014571	-2.498756	0.000000
C	-0.020490	-3.929374	0.000000
H	0.490700	-4.285312	0.898034
H	-1.059528	-4.268238	0.000000
H	0.490700	-4.285312	-0.898034

Smiles barrier heights plotted in Figure 3



R_2	$\Delta H_0^{\ddagger}$ (kJ mol^{-1})	σ_p^+
OCH_3	28.6	-0.78
NHAc	30.2	-0.60
CH_3	15.5	-0.31
t-Bu	16.8	-0.26
F	17.2	-0.07
H	15.8	0
Cl	15.6	0.11
CN	13.3	0.66
NO_2	21.2	0.79
Ac	16.8	not avail.
$NHCOCF_3$	22.5	not avail.

Values for σ_p^+ are from: C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165-195.

B3LYP/6-31G(d) structures and electronic energies for species in Figure 3

Labeling as in Scheme 1

$R_1 = CH_3$, $R_2 = NH_2$ (radical cation)
This is **1b**; see p. S12

Smiles transition structure for $R_1 = CH_3$, $R_2 = NH_2$ (radical cation)
See p. S13

$R_1 = CH_3$, $R_2 = OCH_3$ (radical cation)
E = -1334.108074
$\langle S^2 \rangle = 0.758$

C	-2.647040	-2.079276	0.324828
C	-3.835040	-2.801913	0.340248
C	-5.026923	-2.193914	-0.064861
C	-5.033968	-0.858488	-0.484269
C	-3.854812	-0.120210	-0.484008
C	-2.657740	-0.725698	-0.062140
H	-1.711584	-2.543693	0.617748
H	-3.832458	-3.839645	0.658382
H	-5.952111	-2.762415	-0.062363
H	-5.958870	-0.395665	-0.813766
H	-3.860479	0.906846	-0.833859
C	-1.358292	-0.017493	-0.119644
O	-0.364320	-0.638412	-0.562518
N	-1.217078	1.272921	0.296097
C	-2.201352	2.089052	1.029687
H	-1.662973	2.693229	1.761699
H	-2.751085	2.748153	0.352993
H	-2.891287	1.420828	1.544673
S	0.274255	2.074563	-0.177718
O	0.506834	3.069080	0.861610
O	0.185537	2.417392	-1.589322
C	1.473072	0.743534	0.002124
C	1.830494	0.299309	1.298653
C	2.231222	0.373211	-1.139237
C	2.891251	-0.558149	1.439597
H	1.276514	0.641817	2.166048
C	3.300370	-0.479699	-1.001689
H	1.944633	0.762308	-2.109957
C	3.640813	-0.962729	0.291299
H	3.202944	-0.930923	2.409331
H	3.874815	-0.772547	-1.871916
O	4.642177	-1.783580	0.544787
C	5.503238	-2.268059	-0.511021
H	6.225820	-2.910375	-0.011311
H	4.921690	-2.843998	-1.236010
H	6.012317	-1.430083	-0.994725

Smiles transition structure for $R_1 = CH_3$, $R_2 = OCH_3$ (radical cation)

E = -1334.096733

$\langle S^2 \rangle = 0.763$

C	-2.546102	-2.026362	0.283233
C	-3.690380	-2.814433	0.278584
C	-4.920935	-2.259825	-0.087843
C	-5.011248	-0.912688	-0.452020
C	-3.877652	-0.108027	-0.432740
C	-2.637088	-0.660927	-0.055846
H	-1.586173	-2.449654	0.557404
H	-3.624833	-3.861755	0.555268
H	-5.811406	-2.881186	-0.097782
H	-5.963958	-0.492759	-0.758114
H	-3.949549	0.925585	-0.752469
C	-1.412329	0.129826	-0.064114
O	-0.299981	-0.499260	-0.356688
N	-1.313903	1.427593	0.203490
C	-2.298963	2.345817	0.792777
H	-1.760045	3.011198	1.471636
H	-2.787672	2.935925	0.013922
H	-3.035322	1.770578	1.354903
S	0.340586	2.030772	-0.122013
O	0.711988	2.825048	1.038584
O	0.360612	2.556302	-1.478388
C	1.069667	0.286965	-0.073305
C	1.564712	-0.082800	1.252236
C	1.961598	0.044422	-1.204962
C	2.772187	-0.697518	1.392447
H	0.953188	0.142232	2.119417
C	3.174482	-0.568155	-1.029699
H	1.633416	0.362810	-2.187677
C	3.604588	-0.962166	0.264191
H	3.138575	-0.985479	2.372504
H	3.804846	-0.737311	-1.894892
O	4.760538	-1.564783	0.539534
C	5.692207	-1.866703	-0.513542
H	6.533134	-2.352638	-0.021132
H	5.241851	-2.548287	-1.241917
H	6.028166	-0.947773	-1.004001

$R_1 = CH_3$, R_2 = NHAc (radical cation)
E = -1427.593232
$\langle S^2 \rangle = 0.760$

C	2.789867	2.374531	0.029866
C	3.851478	3.272782	0.027467
C	5.160561	2.805595	-0.122535
C	5.410794	1.436664	-0.268958
C	4.357111	0.528001	-0.246823
C	3.041121	0.994215	-0.080759
H	1.767402	2.724448	0.123436
H	3.660541	4.336151	0.132368
H	5.987826	3.508947	-0.134714
H	6.426952	1.079655	-0.403970
H	4.554061	-0.529637	-0.387771
C	1.871691	0.086028	-0.138114
O	0.859511	0.444804	-0.775148
N	1.873162	-1.129647	0.492910
C	2.856483	-1.627631	1.472256
H	2.319361	-2.182207	2.243379
H	3.589566	-2.286616	0.999962
H	3.359089	-0.771573	1.921795
S	0.623274	-2.252582	-0.001218
O	0.412211	-3.110825	1.158419
O	0.960269	-2.778216	-1.315885
C	-0.806889	-1.173655	-0.188911
C	-1.406087	-0.602359	0.956739
C	-1.464901	-1.146943	-1.441443
C	-2.614143	0.045738	0.852767
H	-0.916205	-0.681950	1.921423
C	-2.671320	-0.507137	-1.548202
H	-0.999627	-1.620885	-2.298376
C	-3.280157	0.113935	-0.409651
H	-3.055099	0.481309	1.736490
H	-3.182785	-0.470541	-2.505882
N	-4.476317	0.725563	-0.623425
H	-4.821192	0.692627	-1.582077
C	-5.443510	1.447300	0.166777
O	-6.401248	1.848358	-0.451113
C	-5.234447	1.654904	1.641189
H	-4.326266	2.234603	1.838593
H	-5.170321	0.700208	2.174180
H	-6.095459	2.210604	2.014073

Smiles transition structure for $R_1 = CH_3$, $R_2 = NHAc$ (radical cation)
E = -1427.581436
$\langle S^2 \rangle = 0.762$

C	-2.826158	-2.217238	-0.314524
C	-3.857566	-3.148022	-0.301457
C	-5.138738	-2.767462	0.110713
C	-5.392667	-1.452466	0.513030
C	-4.374228	-0.506417	0.486533
C	-3.083736	-0.883504	0.063088
H	-1.827681	-2.505113	-0.624292
H	-3.664427	-4.171206	-0.607246
H	-5.940315	-3.499800	0.126685
H	-6.382606	-1.167759	0.854564
H	-4.570713	0.500883	0.836330
C	-1.972150	0.059804	0.060569
O	-0.778792	-0.425671	0.302876
N	-2.052058	1.366035	-0.171396
C	-3.167334	2.162501	-0.703463
H	-3.706690	2.657496	0.107487
H	-2.741421	2.914712	-1.371864
H	-3.836936	1.511993	-1.267045
S	-0.481593	2.173155	0.121276
O	-0.487866	2.674589	1.486877
O	-0.250364	3.028069	-1.032908
C	0.468843	0.542647	0.016604
C	1.410634	0.393492	1.121108
C	0.989355	0.273651	-1.320067
C	2.688686	-0.044097	0.915305
H	1.066964	0.643787	2.118118
C	2.266708	-0.168838	-1.490303
H	0.344063	0.433962	-2.176975
C	3.165584	-0.354370	-0.392135
H	3.336430	-0.136213	1.774666
H	2.620865	-0.373065	-2.497500
N	4.426851	-0.801934	-0.697211
H	4.609520	-0.949091	-1.687228
C	5.605990	-1.139688	0.026532
O	6.546596	-1.512739	-0.641595
C	5.640542	-1.029268	1.528938
H	5.493572	0.005747	1.856691
H	4.876752	-1.659449	1.997026
H	6.625395	-1.364395	1.855603

$R_1 = CH_3$, $R_2 = CH_3$ (radical cation)
E = -1258.890271
$\langle S^2 \rangle = 0.759$

C	2.577566	-1.888276	-0.326941
C	3.836110	-2.478632	-0.332127
C	4.952436	-1.743356	0.077711
C	4.815169	-0.410692	0.491545
C	3.564964	0.196591	0.485015
C	2.444311	-0.536742	0.052633
H	1.699204	-2.450849	-0.624063
H	3.947773	-3.511796	-0.644894
H	5.933254	-2.209229	0.084249
H	5.684865	0.149480	0.819957
H	3.455611	1.220033	0.828570
C	1.079918	0.035475	0.099777
O	0.186418	-0.696238	0.603637
N	0.779730	1.270664	-0.354063
C	1.657284	2.171589	-1.121880
H	1.051421	2.663354	-1.884876
H	2.106170	2.927739	-0.472911
H	2.435331	1.576971	-1.600695
S	-0.807619	1.915284	0.112896
O	-1.174661	2.795624	-0.986828
O	-0.713421	2.367398	1.491807
C	-1.810918	0.422538	0.061385
C	-2.131990	-0.152642	-1.191413
C	-2.476625	0.025597	1.248630
C	-3.069631	-1.161301	-1.234467
H	-1.653794	0.204987	-2.097303
C	-3.415475	-0.982287	1.178480
H	-2.227658	0.509748	2.186383
C	-3.732311	-1.599218	-0.055222
H	-3.324139	-1.620434	-2.185162
H	-3.924985	-1.305991	2.080794
C	-4.776048	-2.668515	-0.132515
H	-4.941284	-3.150541	0.834308
H	-5.734113	-2.228143	-0.448451
H	-4.519114	-3.429562	-0.876392

Smiles transition structure for $R_1 = CH_3$, $R_2 = CH_3$ (radical cation)
E = -1258.884210
$<S^2> = 0.770$

C	2.449662	-1.897253	-0.239551
C	3.672908	-2.556419	-0.235663
C	4.843233	-1.857936	0.078101
C	4.793854	-0.495666	0.390327
C	3.578954	0.180369	0.370915
C	2.399072	-0.517831	0.045619
H	1.535159	-2.431895	-0.471523
H	3.715997	-3.614883	-0.471394
H	5.796215	-2.378358	0.087535
H	5.701548	0.036693	0.655697
H	3.544465	1.227725	0.649761
C	1.090988	0.132978	0.062628
O	0.071187	-0.579285	0.431729
N	0.854624	1.403199	-0.279137
C	1.731728	2.373419	-0.952399
H	1.114449	2.950153	-1.645124
H	2.192935	3.046762	-0.226058
H	2.496684	1.833002	-1.510617
S	-0.807685	1.897478	0.105371
O	-1.285460	2.637313	-1.051474
O	-0.813413	2.442494	1.452771
C	-1.462655	0.162997	0.127582
C	-1.913223	-0.332408	-1.161228
C	-2.271033	-0.139782	1.296749
C	-2.993114	-1.173563	-1.228434
H	-1.378814	-0.035433	-2.057300
C	-3.345990	-0.977120	1.180208
H	-1.987536	0.297755	2.247187
C	-3.737843	-1.532212	-0.072337
H	-3.304173	-1.558613	-2.195203
H	-3.929690	-1.213203	2.065609
C	-4.931302	-2.431139	-0.162615
H	-4.908703	-3.198900	0.619746
H	-5.855164	-1.854914	-0.008140
H	-5.002730	-2.922720	-1.135777

$R_1 = CH_3$, R_2 = *tert*-Bu (radical cation)
E = -1376.829672
$\langle S^2 \rangle = 0.759$

C	2.828286	2.248497	0.298085
C	3.900945	3.133003	0.297943
C	5.169078	2.690919	-0.090565
C	5.370319	1.359260	-0.477134
C	4.309417	0.460634	-0.463649
C	3.036830	0.900386	-0.055404
H	1.834878	2.580967	0.579021
H	3.749309	4.167058	0.590464
H	6.003671	3.385513	-0.100963
H	6.354573	1.026114	-0.790716
H	4.461855	-0.563818	-0.787061
C	1.856438	0.008638	-0.097784
O	0.802361	0.484755	-0.596415
N	1.876584	-1.262140	0.364070
C	2.948889	-1.911822	1.137941
H	2.482163	-2.550065	1.890272
H	3.586074	-2.520940	0.491846
H	3.540933	-1.140332	1.630388
S	0.504382	-2.282897	-0.099793
O	0.354052	-3.214957	1.008940
O	0.714652	-2.716064	-1.472246
C	-0.837783	-1.084369	-0.072561
C	-1.288004	-0.571912	1.168212
C	-1.604284	-0.915109	-1.252422
C	-2.458714	0.155793	1.206319
H	-0.722103	-0.760421	2.074709
C	-2.772458	-0.191719	-1.185793
H	-1.253948	-1.347463	-2.183023
C	-3.237913	0.371746	0.037191
H	-2.795015	0.552417	2.155977
H	-3.353703	-0.056667	-2.090845
C	-4.540089	1.159376	0.057410
C	-4.888389	1.707306	1.453967
C	-4.418376	2.355235	-0.928646
C	-5.691680	0.224470	-0.411109
H	-5.034330	0.906784	2.187642
H	-4.121965	2.393901	1.830732
H	-5.825778	2.268286	1.396857
H	-4.225652	2.033740	-1.956594
H	-5.360242	2.913511	-0.927103
H	-3.617458	3.038400	-0.626934
H	-6.630959	0.787199	-0.401583
H	-5.539293	-0.150149	-1.427719
H	-5.802797	-0.634562	0.258584

Smiles transition structure for $R_1 = CH_3$, R_2 = *tert*-Bu (radical cation)
E = -1376.823260
$\langle S^2 \rangle = 0.770$

C	-2.767249	-2.205411	0.226083
C	-3.807043	-3.127267	0.223887
C	-5.109094	-2.712825	-0.074055
C	-5.375769	-1.372811	-0.371910
C	-4.347694	-0.436650	-0.353790
C	-3.036314	-0.848787	-0.044739
H	-1.752410	-2.518375	0.445425
H	-3.604314	-4.169509	0.448443
H	-5.917633	-3.437605	-0.082486
H	-6.383669	-1.060110	-0.625123
H	-4.556419	0.593437	-0.620915
C	-1.912202	0.084739	-0.063407
O	-0.758863	-0.372625	-0.445843
N	-1.969536	1.371892	0.288559
C	-3.036793	2.111236	0.979277
H	-2.559363	2.800356	1.679792
H	-3.640069	2.676052	0.264579
H	-3.659623	1.405845	1.530032
S	-0.461100	2.231609	-0.095764
O	-0.153787	3.045152	1.069661
O	-0.590068	2.783757	-1.434302
C	0.561625	0.682848	-0.146689
C	1.131633	0.291660	1.129887
C	1.413100	0.590012	-1.320051
C	2.383461	-0.266416	1.183311
H	0.549642	0.439527	2.033488
C	2.657911	0.037021	-1.215286
H	1.029475	0.955441	-2.265801
C	3.194939	-0.427353	0.025998
H	2.765521	-0.570281	2.150329
H	3.263176	-0.033351	-2.112537
C	4.591103	-1.038280	0.068959
C	4.995895	-1.489911	1.484625
C	4.629249	-2.270803	-0.874517
C	5.615730	0.018957	-0.426208
H	5.030523	-0.652594	2.190582
H	4.319812	-2.255517	1.881918
H	5.998398	-1.926882	1.452447
H	4.398743	-2.009675	-1.912193
H	5.633821	-2.706301	-0.859121
H	3.921098	-3.041092	-0.550603
H	6.620201	-0.416900	-0.407169
H	5.416605	0.344677	-1.452128
H	5.617659	0.903828	0.218988

$R_1 = CH_3$, $R_2 = F$ (radical cation)
E = -1318.798045
$\langle S^2 \rangle = 0.758$

C	2.607290	-1.834018	-0.367564
C	3.878269	-2.396109	-0.372505
C	4.971685	-1.648308	0.075460
C	4.799600	-0.329950	0.526469
C	3.537264	0.249757	0.521250
C	2.440185	-0.495122	0.048032
H	1.745353	-2.406505	-0.692397
H	4.017601	-3.416919	-0.713170
H	5.962472	-2.092525	0.083730
H	5.653198	0.238861	0.881112
H	3.399545	1.260620	0.891019
C	1.062560	0.046212	0.094886
O	0.198137	-0.716843	0.602288
N	0.729836	1.272663	-0.352367
C	1.593070	2.199497	-1.106536
H	0.984581	2.678126	-1.875689
H	2.013586	2.964153	-0.448629
H	2.392435	1.627113	-1.577457
S	-0.876254	1.884667	0.111144
O	-1.252180	2.758826	-0.989650
O	-0.792264	2.333610	1.491280
C	-1.853181	0.377122	0.054176
C	-2.169255	-0.191254	-1.202777
C	-2.486654	-0.050944	1.248518
C	-3.070194	-1.233971	-1.256322
H	-1.718447	0.197392	-2.109770
C	-3.392800	-1.089396	1.191878
H	-2.241890	0.435172	2.186260
C	-3.666839	-1.669749	-0.056842
H	-3.346875	-1.710087	-2.190624
H	-3.898175	-1.460859	2.076480
F	-4.531969	-2.665024	-0.115854

Smiles transition structure for $R_1 = CH_3$, $R_2 = F$ (radical cation)
E = -1318.791368
$\langle S^2 \rangle = 0.770$

C	2.459468	-1.859069	-0.248087
C	3.693949	-2.496486	-0.242708
C	4.850553	-1.779014	0.079438
C	4.776283	-0.419330	0.398813
C	3.550147	0.235548	0.378137
C	2.383564	-0.481737	0.044153
H	1.555981	-2.408938	-0.487391
H	3.756646	-3.552690	-0.483934
H	5.812467	-2.282684	0.089894
H	5.673502	0.127181	0.670838
H	3.496588	1.280408	0.663140
C	1.065639	0.145452	0.058812
O	0.055301	-0.590369	0.415080
N	0.806191	1.413863	-0.272083
C	1.669031	2.408038	-0.930547
H	1.045171	2.979307	-1.621867
H	2.112324	3.082499	-0.194287
H	2.447385	1.887350	-1.488933
S	-0.866168	1.874542	0.104665
O	-1.355748	2.603206	-1.053695
O	-0.893055	2.413361	1.453826
C	-1.484573	0.125467	0.120607
C	-1.930168	-0.368539	-1.174164
C	-2.281424	-0.196620	1.295906
C	-2.979766	-1.245009	-1.249347
H	-1.412755	-0.043584	-2.070111
C	-3.330867	-1.069748	1.193576
H	-2.007657	0.252077	2.243785
C	-3.666473	-1.601949	-0.069287
H	-3.314897	-1.648719	-2.198892
H	-3.924693	-1.345053	2.058741
F	-4.680986	-2.445387	-0.156060

$R_1 = CH_3$, $R_2 = H$ (radical cation)
E = -1219.565295
$\langle S^2 \rangle = 0.759$

C	2.645639	-1.573929	-0.453407
C	3.986639	-1.922102	-0.546233
C	4.967548	-1.027471	-0.104145
C	4.610953	0.227891	0.426235
C	3.276310	0.594818	0.511967
C	2.291123	-0.293300	0.034935
H	1.867541	-2.262849	-0.763413
H	4.269999	-2.890698	-0.944672
H	6.015700	-1.305993	-0.158036
H	5.382832	0.910071	0.767999
H	2.994516	1.553733	0.935029
C	0.842809	0.022280	0.168032
O	0.226765	-0.857627	0.819659
N	0.270920	1.129792	-0.320246
C	0.941704	2.127908	-1.173110
H	0.241450	2.441615	-1.948044
H	1.242054	3.000053	-0.586958
H	1.815377	1.667571	-1.635496
S	-1.403660	1.533479	0.221939
O	-1.856760	2.467189	-0.797241
O	-1.303342	1.869201	1.632483
C	-2.244072	-0.032886	0.035972
C	-2.762387	-0.382571	-1.209605
C	-2.406564	-0.849064	1.178579
C	-3.442813	-1.595292	-1.319981
H	-2.656056	0.280764	-2.061133
C	-3.087397	-2.062668	1.043213
H	-2.037033	-0.513335	2.140175
C	-3.598971	-2.433184	-0.196829
H	-3.865749	-1.889042	-2.275583
H	-3.226606	-2.699335	1.910553
H	-4.138339	-3.369450	-0.302679

Smiles transition structure for $R_1 = CH_3$, $R_2 = H$ (radical cation)
E = -1219.559394
$\langle S^2 \rangle = 0.775$

C	2.494062	-1.628141	-0.278790
C	3.814332	-2.061347	-0.268798
C	4.837811	-1.177537	0.088095
C	4.544040	0.144720	0.436892
C	3.229398	0.596729	0.412119
C	2.196831	-0.288481	0.043281
H	1.691837	-2.308013	-0.543770
H	4.047290	-3.087837	-0.532926
H	5.867506	-1.521927	0.102682
H	5.339586	0.820114	0.734704
H	3.005710	1.612697	0.718570
C	0.793113	0.119931	0.056280
O	-0.083617	-0.766271	0.405167
N	0.341250	1.336352	-0.270463
C	1.046214	2.454475	-0.917944
H	0.352183	2.919990	-1.621431
H	1.365338	3.190907	-0.176730
H	1.906714	2.062407	-1.460505
S	-1.377666	1.544768	0.112699
O	-1.965356	2.223020	-1.030628
O	-1.478110	2.046287	1.472731
C	-1.761733	-0.262185	0.092842
C	-2.093947	-0.809869	-1.208453
C	-2.492723	-0.724066	1.257415
C	-2.984778	-1.850741	-1.294843
H	-1.625483	-0.393272	-2.093658
C	-3.381034	-1.762576	1.127836
H	-2.302633	-0.244655	2.210893
C	-3.627402	-2.346452	-0.136102
H	-3.216581	-2.280406	-2.264199
H	-3.912525	-2.125744	2.001595
H	-4.333485	-3.166075	-0.222311

$R_1 = CH_3$, R_2 = Cl (radical cation)
E = -1679.159155
$\langle S^2 \rangle$ = 0.758

C	2.60828	-2.05572	-0.33229
C	3.78941	-2.78797	-0.34029
C	4.98299	-2.18758	0.07236
C	5.00119	-0.84735	0.49010
C	3.83059	-0.09929	0.48690
C	2.63319	-0.69684	0.04996
H	1.66991	-2.51154	-0.62867
H	3.78066	-3.82630	-0.65551
H	5.90337	-2.76369	0.07898
H	5.93089	-0.39303	0.81759
H	3.84053	0.92970	0.83126
C	1.34165	0.02673	0.10424
O	0.38708	-0.59867	0.63310
N	1.17344	1.28145	-0.36267
C	2.14463	2.07151	-1.14080
H	1.59697	2.62044	-1.90863
H	2.67607	2.77903	-0.49936
H	2.85079	1.38899	-1.61405
S	-0.32541	2.11185	0.10966
O	-0.58605	3.02622	-0.99224
O	-0.17225	2.54979	1.48753
C	-1.51011	0.75799	0.06519
C	-1.90343	0.22773	-1.18356
C	-2.19733	0.43548	1.25947
C	-2.94502	-0.67616	-1.22791
H	-1.40264	0.53704	-2.09497
C	-3.24294	-0.46400	1.21028
H	-1.88742	0.88865	2.19458
C	-3.61139	-1.02404	-0.02982
H	-3.27101	-1.10654	-2.16830
H	-3.78342	-0.73876	2.10913
Cl	-4.91016	-2.14503	-0.09459

Smiles transition structure for $R_1 = CH_3$, $R_2 = Cl$ (radical cation)
E = -1679.153254
$\langle S^2 \rangle = 0.769$

C	2.48647	-2.05821	-0.24050
C	3.62905	-2.84882	-0.23332
C	4.86902	-2.28345	0.08115
C	4.97058	-0.92329	0.39071
C	3.83831	-0.11675	0.36830
C	2.58869	-0.68081	0.04175
H	1.51889	-2.48916	-0.47296
H	3.55501	-3.90601	-0.46693
H	5.75850	-2.90616	0.09344
H	5.93133	-0.49442	0.65670
H	3.91961	0.92824	0.64627
C	1.36007	0.10981	0.05821
O	0.26978	-0.48271	0.43187
N	1.26663	1.39865	-0.28937
C	2.24806	2.26088	-0.96764
H	1.70120	2.89656	-1.66780
H	2.77889	2.88464	-0.24469
H	2.94941	1.63324	-1.51780
S	-0.32025	2.08700	0.09903
O	-0.71409	2.87315	-1.05842
O	-0.26035	2.62920	1.44587
C	-1.18727	0.45298	0.13096
C	-1.69713	0.00312	-1.15068
C	-2.00564	0.24635	1.31122
C	-2.85000	-0.73335	-1.20963
H	-1.15073	0.24868	-2.05485
C	-3.15793	-0.48764	1.22601
H	-1.67303	0.66780	2.25295
C	-3.58418	-0.99965	-0.02566
H	-3.22345	-1.09470	-2.16178
H	-3.76158	-0.66573	2.10939
Cl	-5.02693	-1.92292	-0.11592

$R_1 = CH_3$, $R_2 = CN$ (radical cation)
E = -1311.794380
$\langle S^2 \rangle = 0.759$

C	2.57769	-2.00625	-0.40864
C	3.77453	-2.70720	-0.46140
C	4.95341	-2.09844	-0.01603
C	4.94222	-0.77652	0.47627
C	3.75675	-0.05962	0.52260
C	2.57601	-0.66152	0.04119
H	1.64675	-2.46703	-0.72020
H	3.79131	-3.72755	-0.82973
H	5.88766	-2.65150	-0.03686
H	5.86532	-0.31956	0.81838
H	3.73895	0.95155	0.91631
C	1.26394	0.03224	0.13737
O	0.42133	-0.63531	0.78464
N	1.00966	1.24353	-0.37272
C	1.92777	2.02761	-1.21874
H	1.34354	2.50349	-2.00743
H	2.43465	2.79732	-0.63128
H	2.65892	1.35207	-1.66432
S	-0.50513	2.06899	0.14730
O	-0.74470	3.01791	-0.92839
O	-0.31070	2.45660	1.53401
C	-1.70726	0.73955	0.06524
C	-2.19789	0.34758	-1.18816
C	-2.22182	0.22277	1.27124
C	-3.19713	-0.61116	-1.23713
H	-1.82085	0.80108	-2.09854
C	-3.22647	-0.73265	1.21457
H	-1.83357	0.57491	2.22004
C	-3.71150	-1.15781	-0.03523
H	-3.60299	-0.93660	-2.18892
H	-3.64083	-1.14932	2.12588
C	-4.73980	-2.14788	-0.10238
N	-5.57208	-2.95930	-0.16254

Smiles transition structure for $R_1 = CH_3$, $R_2 = CN$ (radical cation)
E = -1311.789539
$\langle S^2 \rangle = 0.777$

C	2.41172	-2.05615	-0.24950
C	3.56985	-2.82372	-0.23724
C	4.79523	-2.23508	0.09158
C	4.86713	-0.87443	0.40967
C	3.71940	-0.09054	0.38289
C	2.48492	-0.67827	0.04059
H	1.45479	-2.50480	-0.49246
H	3.51931	-3.88077	-0.47755
H	5.69698	-2.83975	0.10821
H	5.81724	-0.42804	0.68490
H	3.77651	0.95482	0.66591
C	1.23834	0.08732	0.05823
O	0.17180	-0.51909	0.45430
N	1.12190	1.37196	-0.31065
C	2.09214	2.23230	-1.00941
H	1.53793	2.84852	-1.72083
H	2.61979	2.87520	-0.30111
H	2.79749	1.59939	-1.54824
S	-0.45044	2.06804	0.10199
O	-0.84525	2.87500	-1.04024
O	-0.37923	2.58356	1.45812
C	-1.36131	0.47042	0.11898
C	-1.82550	-0.01293	-1.15950
C	-2.15837	0.23594	1.29954
C	-2.93239	-0.81743	-1.21739
H	-1.28754	0.25846	-2.06133
C	-3.26525	-0.56669	1.21974
H	-1.84914	0.68597	2.23610
C	-3.66194	-1.11976	-0.03134
H	-3.27816	-1.20955	-2.16786
H	-3.85913	-0.77200	2.10392
C	-4.80506	-1.95712	-0.10339
N	-5.74064	-2.65124	-0.16356

$R_1 = CH_3$, $R_2 = NO_2$ (radical cation)
E = -1424.049290
$\langle S^2 \rangle = 0.760$

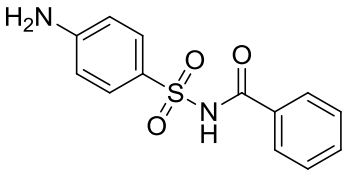
C	2.73941	-2.09339	-0.45121
C	3.88042	-2.87079	-0.57617
C	5.11669	-2.35600	-0.16262
C	5.21976	-1.05020	0.36888
C	4.09169	-0.25764	0.48953
C	2.85415	-0.76171	0.03055
H	1.76502	-2.48003	-0.72948
H	3.81278	-3.87908	-0.97075
H	6.00784	-2.97241	-0.23478
H	6.18683	-0.67012	0.68222
H	4.15629	0.74077	0.91020
C	1.60276	0.03256	0.19227
O	0.83123	-0.56527	0.97973
N	1.36460	1.21276	-0.37634
C	2.25793	1.86580	-1.35174
H	1.64533	2.31771	-2.13232
H	2.85345	2.64412	-0.86842
H	2.91210	1.11262	-1.79347
S	-0.04661	2.20035	0.22164
O	-0.17173	3.21524	-0.81114
O	0.24611	2.49151	1.61396
C	-1.40318	1.04108	0.11290
C	-2.07328	0.90135	-1.10396
C	-1.78167	0.34234	1.27122
C	-3.14363	0.01200	-1.17321
H	-1.78188	1.48537	-1.97001
C	-2.85439	-0.54858	1.19341
H	-1.26812	0.51429	2.20944
C	-3.50486	-0.69837	-0.02463
H	-3.70375	-0.13339	-2.08910
H	-3.18990	-1.10891	2.05753
N	-4.64018	-1.65277	-0.11220
O	-4.94726	-2.24551	0.91496
O	-5.17485	-1.77688	-1.20862

Smiles transition structure for $R_1 = CH_3$, $R_2 = NO_2$ (radical cation)
E = -1424.041094
$<S^2> = 0.777$

C	2.51333	-2.16544	-0.22006
C	3.59612	-3.03562	-0.19750
C	4.86998	-2.55813	0.12752
C	5.06675	-1.20606	0.43117
C	3.99626	-0.32044	0.39447
C	2.71330	-0.79655	0.05535
H	1.51978	-2.52704	-0.46109
H	3.44919	-4.08601	-0.42697
H	5.71242	-3.24277	0.15227
H	6.05387	-0.84604	0.70257
H	4.14870	0.71860	0.66555
C	1.54372	0.08096	0.06237
O	0.42949	-0.42356	0.47599
N	1.54056	1.36280	-0.32769
C	2.58207	2.12067	-1.04282
H	2.08296	2.76945	-1.76594
H	3.16508	2.72782	-0.34650
H	3.22810	1.41766	-1.56917
S	0.03818	2.20584	0.07907
O	-0.28465	3.02915	-1.07328
O	0.16048	2.72823	1.42837
C	-1.01085	0.69597	0.11851
C	-1.50820	0.22834	-1.15418
C	-1.82498	0.54795	1.30250
C	-2.67960	-0.48753	-1.20057
H	-0.94699	0.43705	-2.05852
C	-2.99819	-0.16358	1.23123
H	-1.47987	0.98457	2.23286
C	-3.40460	-0.68672	-0.01009
H	-3.07028	-0.88229	-2.13093
H	-3.62511	-0.31574	2.10183
N	-4.66636	-1.45893	-0.07462
O	-5.32827	-1.52012	0.95497
O	-4.93942	-1.97603	-1.15258

B3LYP/6-31G(d) structures and electronic energies for species in Table 1

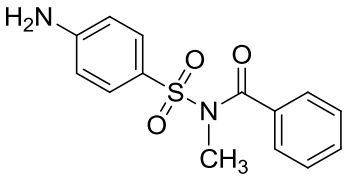
Molecule in row 1 (Sulfabenzamide)



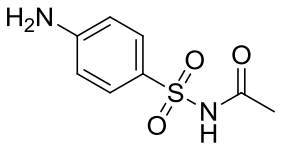
This is **1a.**
See p. S3 for the radical cation.
See p. S4 for the Smiles transition structure.

Molecule in row 2 (N-methyl sulfabenzamide)

This is **1b.**
See p. S12 for the radical cation.
See p. S13 for the Smiles transition structure.



Molecule in row 3 (Sulfacetamide; Cetazin)



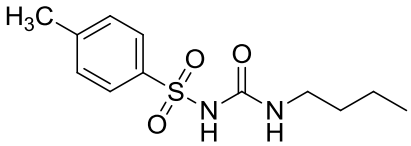
Radical cation
Energy = -1043.902564
$<S^2> = 0.767$

C	2.00276	1.40321	-0.05640
N	2.14948	0.15526	0.53433
S	1.23693	-1.19157	-0.01338
O	1.36470	-2.17390	1.05479
O	1.54544	-1.49256	-1.40225
C	-0.43102	-0.49570	0.01618
C	-1.02622	-0.17717	1.25771
C	-1.15466	-0.42616	-1.19858
C	-2.33113	0.24762	1.28808
H	-0.45718	-0.27805	2.17583
C	-2.46076	-0.01053	-1.18160
H	-0.65817	-0.69336	-2.12470
C	-3.07626	0.34236	0.06368
H	-2.81307	0.49926	2.22826
H	-3.03446	0.05797	-2.10106
N	-4.34818	0.75304	0.09028
H	-4.90092	0.82659	-0.75764
H	-4.81000	1.00534	0.95781
O	1.00210	1.64237	-0.72086
C	3.11368	2.39420	0.18569
H	3.49496	2.33537	1.21009
H	3.94127	2.17788	-0.50067
H	2.74372	3.39995	-0.01685
H	2.97768	-0.09820	1.06878

Smiles transition structure (radical cation)
Energy = -1043.875562
$<S^2> = 0.758$

C	2.15463	1.12495	-0.00008
O	0.88649	1.41260	-0.00025
N	2.51066	-0.13630	0.00013
S	1.08805	-1.27805	0.00006
O	1.11802	-1.97008	1.27901
O	1.11819	-1.97011	-1.27888
C	-0.17980	0.25892	-0.00008
C	-0.93434	0.29049	1.24109
C	-0.93443	0.29018	-1.24120
C	-2.30018	0.29358	1.22568
H	-0.39215	0.27972	2.18002
C	-2.30027	0.29327	-1.22569
H	-0.39231	0.27920	-2.18017
C	-3.03040	0.29075	0.00002
H	-2.84131	0.29830	2.16781
H	-2.84147	0.29774	-2.16778
N	-4.38291	0.28760	0.00007
H	-4.91178	0.27308	-0.86118
H	-4.91172	0.27330	0.86137
H	3.47994	-0.44723	0.00034
C	3.11196	2.26724	-0.00003
H	2.92694	2.88745	-0.88358
H	2.92747	2.88689	0.88403
H	4.14877	1.92562	-0.00042

Molecule in row 4 (Tolbutamide)



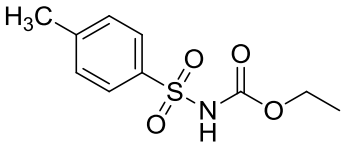
Radical cation
Energy = -1201.141642
$<S^2> = 0.759$

C	-1.06225	0.20947	-0.09446
O	-0.19598	-0.52796	-0.64202
N	-0.63265	1.37560	0.51074
S	0.88934	2.01729	0.01434
O	1.30647	2.87014	1.11587
O	0.82576	2.48738	-1.36021
C	1.81401	0.46154	0.01596
C	2.02813	-0.21938	1.24639
C	2.54991	0.12429	-1.15269
C	2.92413	-1.26143	1.28022
H	1.49449	0.09272	2.13795
C	3.44282	-0.91897	-1.09458
H	2.38275	0.68804	-2.06376
C	3.64931	-1.64094	0.11501
H	3.09931	-1.79624	2.20864
H	4.00846	-1.19727	-1.97864
H	-1.26298	2.03672	0.95749
N	-2.35486	-0.11570	-0.03614
H	-3.02448	0.58497	0.25865
C	-2.88789	-1.37937	-0.58537
H	-3.15089	-1.22760	-1.63975
H	-2.06152	-2.09397	-0.55563
C	4.60065	-2.79013	0.15340
H	4.96780	-2.98740	1.16403
H	4.08650	-3.70206	-0.19061
H	5.44901	-2.63577	-0.52077
C	-4.09114	-1.89752	0.21221
H	-3.85468	-1.85430	1.28405
H	-4.18926	-2.96173	-0.03442
C	-5.44297	-1.21647	-0.06899
H	-5.69513	-1.34347	-1.13007
H	-6.20816	-1.76695	0.49064
C	-5.54137	0.27030	0.30105
H	-4.95233	0.90917	-0.37233
H	-6.57424	0.62249	0.21899
H	-5.22162	0.45183	1.33603

Smiles transition structure (radical cation)
Energy = -1201.134947
$<S^2> = 0.771$

C	1.09296	0.38774	0.05425
O	0.13079	-0.39505	0.44480
N	0.71803	1.58646	-0.45779
S	-0.93873	1.99641	-0.03480
O	-1.52777	2.64140	-1.19313
O	-0.95281	2.59119	1.29214
C	-1.41420	0.18899	0.08023
C	-1.81053	-0.39485	-1.19463
C	-2.23508	-0.10730	1.24636
C	-2.85742	-1.27590	-1.24779
H	-1.26198	-0.12062	-2.08949
C	-3.27448	-0.98873	1.14187
H	-1.99065	0.38097	2.18295
C	-3.61816	-1.61083	-0.09440
H	-3.12840	-1.71690	-2.20267
H	-3.86843	-1.21063	2.02423
H	1.37093	2.33398	-0.67577
N	2.35068	-0.00325	0.13149
H	3.07505	0.65815	-0.12537
C	2.79394	-1.33533	0.61137
H	3.07587	-1.24184	1.66671
H	1.92259	-1.98988	0.55538
C	-4.77653	-2.55563	-0.17141
H	-4.73735	-3.29739	0.63526
H	-5.72335	-2.01011	-0.04793
H	-4.81529	-3.08038	-1.12897
C	3.95303	-1.89463	-0.22369
H	3.99877	-2.96726	-0.00003
H	3.69609	-1.81660	-1.28867
C	5.34442	-1.29002	0.04112
H	6.06560	-1.87074	-0.54538
H	5.61277	-1.45080	1.09351
C	5.51854	0.19577	-0.30680
H	5.17260	0.41764	-1.32519
H	4.99987	0.85847	0.40162
H	6.57340	0.48276	-0.25868

Molecule in row 5 (O-ethyl-tosylcarbamate)



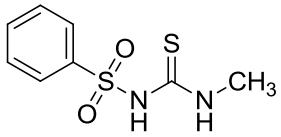
Radical cation
Energy = -1142.373203
$<S^2> = 0.759$

C	1.74110	-0.13079	-0.03478
O	0.85455	-0.80569	0.51408
N	1.44921	1.09854	-0.58094
S	0.06126	1.93081	0.00924
O	-0.29407	2.87744	-1.03444
O	0.25047	2.32065	1.39724
C	-1.09237	0.53066	-0.00194
C	-1.47316	-0.04829	-1.24308
C	-1.77893	0.22216	1.20772
C	-2.49692	-0.96147	-1.25517
H	-0.96467	0.24217	-2.15647
C	-2.80198	-0.69504	1.17461
H	-1.47188	0.70950	2.12676
C	-3.18656	-1.31239	-0.04851
H	-2.80855	-1.41880	-2.18961
H	-3.33217	-0.95208	2.08615
H	2.19513	1.67870	-0.96112
C	3.38329	-1.83908	0.28516
H	3.22642	-1.85022	1.36602
H	2.71406	-2.56577	-0.18177
C	-4.28630	-2.31487	-0.09136
H	-4.98629	-2.09446	-0.90774
H	-3.87177	-3.31155	-0.31187
H	-4.83505	-2.37530	0.85044
C	4.83143	-2.03578	-0.10119
H	5.47035	-1.27817	0.36127
H	5.15951	-3.01994	0.24892
H	4.96152	-1.99739	-1.18648
O	2.98668	-0.49742	-0.19868

Smiles transition structure (radical cation)
Energy = -1142.361413
$<S^2> = 0.773$

C	1.82943	0.12343	-0.10359
O	0.81299	-0.62702	0.20597
N	1.59998	1.39802	-0.39678
S	-0.06985	1.88864	0.01545
O	-0.61093	2.58759	-1.13376
O	-0.04337	2.45289	1.35393
C	-0.61533	0.03511	0.06719
C	-1.21490	-0.37967	-1.20262
C	-1.37262	-0.24516	1.28752
C	-2.44019	-0.98671	-1.21889
H	-0.67704	-0.17450	-2.12244
C	-2.59552	-0.85132	1.21304
H	-0.94592	0.06297	2.23554
C	-3.17635	-1.24396	-0.02757
H	-2.86738	-1.27894	-2.17397
H	-3.14374	-1.03870	2.13209
H	2.35106	2.06318	-0.56783
C	3.27131	-1.79856	0.14570
H	2.90425	-1.98445	1.15674
H	2.67652	-2.36424	-0.57403
C	-4.53305	-1.87461	-0.07641
H	-4.72217	-2.49376	0.80625
H	-5.31302	-1.09836	-0.09539
H	-4.66479	-2.48666	-0.97327
C	4.75708	-2.02054	-0.00023
H	4.96983	-3.07499	0.20479
H	5.09595	-1.79429	-1.01485
H	5.32163	-1.41323	0.71241
O	3.02548	-0.34801	-0.13872

Molecule in row 6 (N-phenylsulfonyl-N’-methylthiourea)



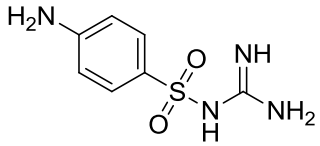
Radical cation
Energy = -1366.850831
$<S^2> = 0.756$

C	1.89726	-0.13170	-0.22135
N	1.22950	1.00495	-0.52079
S	-0.23013	1.64840	0.26873
O	-0.52514	2.77922	-0.59315
O	0.04721	1.75693	1.68940
C	-1.37858	0.30632	0.00164
C	-2.01547	0.17955	-1.22869
C	-1.61893	-0.58458	1.07163
C	-2.90267	-0.88659	-1.40532
H	-1.83565	0.89604	-2.02329
C	-2.50402	-1.65428	0.86540
H	-1.19539	-0.38427	2.04989
C	-3.13707	-1.80212	-0.36537
H	-3.41691	-1.00255	-2.35425
H	-2.71127	-2.34177	1.67904
H	1.67540	1.72041	-1.09389
H	-3.83301	-2.62064	-0.52063
N	3.15643	-0.26911	-0.62851
H	3.61791	0.54699	-1.01698
C	3.97231	-1.47984	-0.46538
H	4.87110	-1.36235	-1.07123
H	4.25789	-1.61889	0.58167
H	3.41857	-2.35446	-0.81808
S	1.12990	-1.43585	0.62799

Smiles transition structure (radical cation)
Energy = -1366.834315
$<S^2>$ = 0.781

C	1.97733	0.00755	-0.17922
N	1.43658	1.16772	-0.54860
S	-0.22257	1.55263	0.06137
O	-0.83879	2.30939	-1.01645
O	-0.07518	2.07348	1.41284
C	-0.76558	-0.40091	0.11207
C	-1.26920	-0.77047	-1.21488
C	-1.69751	-0.54951	1.23886
C	-2.58402	-1.12579	-1.38578
H	-0.58959	-0.73086	-2.05979
C	-3.00368	-0.90739	1.01412
H	-1.33676	-0.32444	2.23668
C	-3.47151	-1.19194	-0.28854
H	-2.93967	-1.37451	-2.38093
H	-3.68294	-0.98151	1.85780
H	1.96699	1.91872	-0.98689
H	-4.50686	-1.47533	-0.44388
N	3.26223	-0.27499	-0.33549
H	3.87020	0.47404	-0.65111
C	3.90018	-1.55933	-0.00401
H	4.89589	-1.56039	-0.44740
H	3.98825	-1.68157	1.07967
H	3.32407	-2.38567	-0.42776
S	0.90473	-1.19038	0.53146

Molecule in row 7 (Sulfaguanidine)



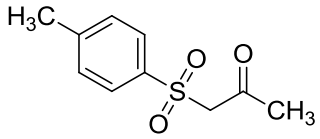
Radical cation
Energy = -1040.061860
$<S^2> = 0.764$

C	-2.13336	1.36400	0.08748
N	-2.21977	0.10470	-0.51222
S	-1.21516	-1.16383	-0.02590
O	-1.26674	-2.10493	-1.13869
O	-1.50795	-1.54598	1.34559
C	0.42446	-0.39684	-0.00635
C	0.99638	0.05758	-1.22085
C	1.20166	-0.50689	1.17456
C	2.31337	0.43418	-1.25073
H	0.39463	0.09609	-2.12247
C	2.52107	-0.13904	1.15470
H	0.73247	-0.88094	2.07766
C	3.10761	0.34276	-0.06002
H	2.77027	0.78500	-2.17146
H	3.13209	-0.21511	2.04938
N	4.39759	0.69893	-0.08824
H	4.98468	0.63306	0.73568
H	4.83971	1.03214	-0.93747
N	-1.03482	1.64890	0.69088
H	-1.04703	2.49938	1.25056
N	-3.23389	2.15013	-0.11641
H	-3.22861	3.07563	0.29241
H	-4.14300	1.70384	-0.14041
H	-2.74612	-0.05373	-1.36539

Smiles transition structure (radical cation)
Energy = -1040.057078
$<S^2> = 0.758$

C	2.06719	1.30539	-0.17208
N	2.44142	0.06659	0.28419
S	1.23291	-1.17602	0.10516
O	1.20718	-1.86824	1.38566
O	1.45265	-1.85788	-1.15793
C	-0.25522	-0.08349	-0.08474
C	-0.88934	0.32987	1.14194
C	-1.10279	-0.43359	-1.19799
C	-2.23950	0.54312	1.19059
H	-0.28270	0.47899	2.02875
C	-2.45176	-0.22418	-1.13575
H	-0.64293	-0.85000	-2.08694
C	-3.06150	0.28223	0.05263
H	-2.70123	0.87850	2.11509
H	-3.07661	-0.47348	-1.98889
N	-4.39260	0.48721	0.10627
H	-4.99325	0.26218	-0.67575
H	-4.84609	0.79908	0.95474
N	0.86226	1.35994	-0.67183
H	0.48180	2.21441	-1.06416
N	2.94064	2.32482	-0.04275
H	2.69779	3.23807	-0.40333
H	3.93072	2.12713	0.03588
H	3.06285	-0.03551	1.08160

Molecule in row 8 (tosylacetone)



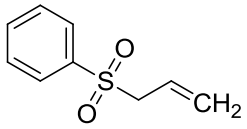
Radical cation
Energy = -1011.779458
$<S^2> = 0.758$

C	-1.98037	1.44975	-0.13804
S	-1.28492	-1.20903	0.06794
O	-1.26988	-2.37020	-0.81895
O	-1.66440	-1.28165	1.47905
C	0.37985	-0.45738	0.01332
C	1.03746	-0.28333	-1.23554
C	1.07267	-0.28689	1.24255
C	2.35479	0.10536	-1.24448
H	0.50985	-0.47834	-2.16387
C	2.39144	0.10075	1.21582
H	0.54405	-0.46287	2.17351
C	3.06610	0.31202	-0.02202
H	2.87643	0.24382	-2.18671
H	2.93558	0.24497	2.14421
O	-0.81409	1.68433	0.15981
C	-3.06446	2.47543	0.02619
H	-3.66594	2.54518	-0.88758
H	-3.73365	2.14149	0.83118
H	-2.63840	3.44635	0.28172
C	4.50395	0.69885	-0.04670
H	5.12108	-0.21137	-0.13607
H	4.74452	1.32366	-0.91264
H	4.81138	1.20483	0.87235
C	-2.33365	0.08780	-0.70360
H	-2.15591	0.08500	-1.78570
H	-3.37003	-0.21224	-0.52176

Smiles transition structure (radical cation)
Energy = -1011.755087
$<S^2> = 0.773$

C	2.21174	-1.02291	-0.25429
S	1.02547	1.27635	0.10018
O	0.50274	2.35861	-0.72497
O	1.51763	1.46475	1.46585
C	-0.15504	-0.45887	0.03167
C	-0.87472	-0.49757	-1.22555
C	-0.91521	-0.54985	1.25907
C	-2.24001	-0.37058	-1.21964
H	-0.32788	-0.57461	-2.16001
C	-2.28187	-0.42527	1.21530
H	-0.37939	-0.63230	2.19856
C	-2.98812	-0.31164	-0.01118
H	-2.76821	-0.34048	-2.16831
H	-2.83973	-0.42736	2.14725
O	1.02917	-1.40355	0.07803
C	3.33367	-1.91541	0.10108
H	3.98068	-2.07816	-0.76946
H	3.95140	-1.40464	0.85671
H	2.97693	-2.86598	0.50045
C	-4.47586	-0.13885	-0.03636
H	-4.73376	0.92943	-0.08740
H	-4.92294	-0.61741	-0.91340
H	-4.94608	-0.54274	0.86471
C	2.35871	0.30521	-0.85507
H	2.00826	0.35147	-1.89176
H	3.35712	0.73716	-0.76179

Molecule in row 9 (Phenylallylsulfone)



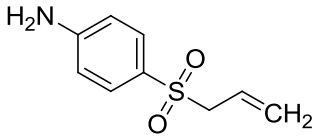
Radical cation
Energy = -897.206959
$<S^2> = 0.756$

C	-1.45021	1.95014	-0.34710
S	-1.32953	-0.73550	0.21626
O	-1.64854	-1.98146	-0.47779
O	-1.74566	-0.43302	1.58967
C	0.46297	-0.47435	0.15420
C	1.24324	-1.28491	-0.64923
C	1.01216	0.56157	0.94002
C	2.62665	-1.01668	-0.71596
H	0.79802	-2.08388	-1.23326
C	2.39485	0.83207	0.83554
H	0.41248	1.05004	1.70056
C	3.19240	0.04027	0.01784
H	3.25140	-1.61760	-1.37002
H	2.83346	1.61293	1.44859
C	-1.98641	0.69354	-0.87739
H	-1.65068	0.43474	-1.88418
H	-3.06952	0.58296	-0.77774
H	4.26065	0.22283	-0.04196
H	-1.97411	2.40383	0.49151
C	-0.29014	2.51851	-0.80124
H	0.25317	2.10722	-1.64764
H	0.07815	3.44989	-0.38108

Smiles transition structure (radical cation)
Energy = -897.187967
$<S^2> = 0.770$

C	1.49357	1.88227	-0.29617
S	1.32532	-0.68184	0.22550
O	1.49798	-0.72792	1.67511
O	1.46425	-1.84875	-0.64021
C	-0.40487	0.05631	-0.07497
C	-1.09303	0.50699	1.11175
C	-1.17803	-0.59474	-1.10356
C	-2.46855	0.45452	1.17962
H	-0.51040	0.89239	1.94267
C	-2.55259	-0.63355	-1.01974
H	-0.65859	-1.04555	-1.94401
C	-3.20172	-0.10753	0.11618
H	-2.98506	0.82160	2.06052
H	-3.13404	-1.09909	-1.80892
C	2.40260	0.74752	-0.44506
H	3.31112	0.76957	0.15787
H	2.61246	0.45881	-1.47959
C	0.23835	1.75999	-0.93707
H	0.23534	1.36468	-1.95063
H	-0.54249	2.48950	-0.74099
H	1.63886	2.60170	0.50589
H	-4.28454	-0.16147	0.18409

Molecule in row 10 (*p*-Aminophenylallylsulfone)



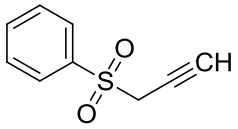
Radical cation
Energy = -952.602290
$\langle S^2 \rangle$ = 0.770

C	-2.21647	1.81452	-0.12851
S	-1.56984	-0.85116	0.19906
O	-1.67695	-2.11164	-0.54347
O	-1.87354	-0.74170	1.63029
C	0.20592	-0.38916	0.07320
C	0.97467	-0.92449	-0.98401
C	0.80024	0.34776	1.12452
C	2.32372	-0.66566	-1.03943
H	0.49356	-1.54440	-1.73363
C	2.14715	0.61560	1.08782
H	0.18469	0.68129	1.95282
C	2.93702	0.11419	-0.00005
H	2.93502	-1.05268	-1.84973
H	2.62476	1.19222	1.87475
C	-2.47702	0.45852	-0.70548
H	-2.18285	0.36661	-1.75524
H	-3.52227	0.14106	-0.60277
H	-2.61523	1.99664	0.86689
C	-1.55059	2.77341	-0.78019
H	-1.16332	2.62626	-1.78625
H	-1.40520	3.75638	-0.34213
N	4.25025	0.35944	-0.04111
H	4.71584	0.89401	0.68599
H	4.83685	0.00372	-0.78974

Smiles transition structure (radical cation)
Energy = -952.578818
$<S^2> = 0.774$

C	1.97661	1.84554	-0.26368
S	1.64286	-0.70906	0.23724
O	1.78732	-0.74679	1.69336
O	1.73504	-1.90497	-0.59987
C	-0.03289	0.10162	-0.09925
C	-0.74890	0.53281	1.08063
C	-0.80877	-0.52182	-1.14664
C	-2.11061	0.50148	1.13683
H	-0.17975	0.89265	1.93164
C	-2.17089	-0.55233	-1.10038
H	-0.28624	-0.96892	-1.98676
C	-2.86481	-0.03428	0.04251
H	-2.63373	0.85569	2.02036
H	-2.73982	-1.00326	-1.90834
C	2.80266	0.64431	-0.42679
H	3.71282	0.59441	0.17226
H	2.99325	0.35441	-1.46436
C	0.73472	1.82082	-0.91718
H	0.70340	1.42946	-1.93171
H	-0.00612	2.58887	-0.71175
H	2.15233	2.51346	0.57518
N	-4.19822	-0.07322	0.09593
H	-4.70716	0.25949	0.90611
H	-4.74870	-0.47354	-0.65424

Molecule in row 11 (Phenylpropargylsulfone)



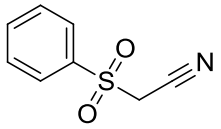
Radical cation
Energy = -895.940752
$\langle S^2 \rangle$ = 0.758

S	-1.39012	-0.62894	0.23452
O	-1.77509	-1.88064	-0.41054
O	-1.73076	-0.27657	1.61629
C	0.41390	-0.44967	0.13091
C	1.14837	-1.31730	-0.64885
C	1.02323	0.57577	0.89991
C	2.54320	-1.10750	-0.73445
H	0.66426	-2.11016	-1.20998
C	2.41627	0.78891	0.77579
H	0.44670	1.10316	1.65268
C	3.16722	-0.05650	-0.02531
H	3.13562	-1.74344	-1.38583
H	2.89315	1.56459	1.36624
C	-2.01733	0.78637	-0.86674
H	-2.05853	0.37833	-1.88123
H	-3.02595	0.98323	-0.48693
H	4.24283	0.06993	-0.09756
C	-1.12646	1.90176	-0.73699
C	-0.29677	2.78611	-0.60022
H	0.36075	3.62739	-0.51992

Smiles transition structure (radical cation)
Energy = -895.925599
$<S^2> = 0.768$

S	1.39628	-0.61083	0.00005
O	1.61982	-1.25793	1.28929
O	1.61985	-1.25814	-1.28908
C	-0.38131	-0.00485	0.00000
C	-1.09478	-0.11610	1.24411
C	-1.09477	-0.11635	-1.24409
C	-2.47361	-0.15285	1.23043
H	-0.53485	-0.15320	2.17290
C	-2.47359	-0.15310	-1.23042
H	-0.53482	-0.15362	-2.17287
C	-3.16395	-0.16821	0.00001
H	-3.02678	-0.20164	2.16274
H	-3.02676	-0.20208	-2.16272
C	2.38423	1.06751	-0.00009
H	2.99322	1.06553	0.90784
H	2.99317	1.06540	-0.90805
H	-4.24901	-0.22043	0.00001
C	1.27522	1.96065	-0.00014
C	0.02640	2.03556	-0.00017
H	-0.89504	2.58827	-0.00023

Molecule in row 12 (Phenylcyanomethylsulfone)



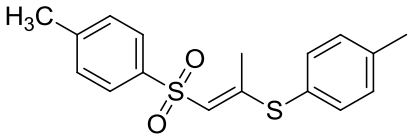
Radical cation
Energy = -912.019885
$<S^2> = 0.761$

S	-1.37411	-0.63468	0.24294
O	-1.71251	-1.91734	-0.36131
O	-1.66576	-0.27050	1.63287
C	0.43314	-0.40321	0.10588
C	1.18354	-1.29860	-0.61439
C	1.04532	0.65782	0.84318
C	2.58615	-1.07293	-0.70033
H	0.71762	-2.12553	-1.14166
C	2.44084	0.89612	0.71186
H	0.46024	1.22370	1.56102
C	3.20448	0.02156	-0.03293
H	3.18686	-1.72239	-1.33152
H	2.89162	1.72379	1.24926
C	-2.08252	0.71429	-0.85048
H	-2.13259	0.31947	-1.86955
H	-3.09008	0.89730	-0.46106
H	4.27913	0.15241	-0.11124
C	-1.21821	1.87083	-0.74701
N	-0.40822	2.69623	-0.60708

Smiles transition structure (radical cation)
Energy = -911.986195
$<S^2> = 0.774$

S	1.30738	-0.69546	0.00007
O	1.43374	-1.37048	1.28327
O	1.43378	-1.37068	-1.28302
C	-0.41578	0.35210	-0.00005
C	-1.13693	0.18062	1.24899
C	-1.13694	0.18030	-1.24904
C	-2.48114	-0.09347	1.23267
H	-0.59264	0.26969	2.18348
C	-2.48115	-0.09378	-1.23264
H	-0.59265	0.26913	-2.18355
C	-3.16425	-0.22520	0.00004
H	-3.02147	-0.21840	2.16542
H	-3.02149	-0.21895	-2.16535
C	2.53960	0.89789	-0.00004
H	3.13684	0.84249	0.91326
H	3.13692	0.84228	-0.91328
H	-4.22871	-0.44031	0.00007
C	1.48545	1.84652	-0.00019
N	0.29597	1.92012	-0.00023

Molecule in row 13 (*E*-1-tosyl-2-(*p*-tolylthio)propene)



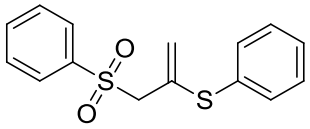
Radical cation
Energy = -1605.131280
$<S^2> = 0.760$

C	-0.64333	1.96257	-0.45804
S	1.40793	0.93889	1.20438
O	0.82368	0.20716	2.34064
O	1.90683	2.31034	1.34055
C	2.65575	-0.06721	0.43539
C	2.64455	-1.45115	0.64402
C	3.64136	0.54551	-0.34921
C	3.63191	-2.22656	0.04474
H	1.89373	-1.90185	1.28476
C	4.61688	-0.24992	-0.93841
H	3.65036	1.62321	-0.47355
C	4.63118	-1.64366	-0.75265
H	3.63733	-3.30080	0.20678
H	5.38879	0.21595	-1.54478
C	0.04169	0.90032	0.02221
H	-0.26633	-0.12097	-0.18026
S	-2.10567	1.66305	-1.43515
C	-2.97964	0.33853	-0.71568
C	-3.91959	-0.30299	-1.56743
C	-2.88567	-0.04654	0.64785
C	-4.71244	-1.31698	-1.07120
H	-4.00255	-0.00277	-2.60790
C	-3.69357	-1.06254	1.12123
H	-2.20661	0.46160	1.32267
C	-4.61828	-1.72522	0.28145
H	-5.42208	-1.81087	-1.72838
H	-3.63161	-1.34275	2.16857
C	5.71804	-2.48663	-1.36766
H	6.62027	-2.46420	-0.74235
H	5.41236	-3.53228	-1.46457
H	6.00218	-2.11497	-2.35729
C	-5.47478	-2.83787	0.80376
H	-5.02025	-3.80830	0.55484
H	-5.58018	-2.79554	1.89095
H	-6.46997	-2.82760	0.34803
C	-0.31322	3.42747	-0.35592
H	-0.97816	3.91236	0.36909
H	0.71565	3.57182	-0.02925
H	-0.46842	3.92402	-1.32137

Smiles transition structure (radical cation)
Energy = -1605.087652
$<S^2> = 0.778$

C	-0.24799	2.32750	-0.79417
S	1.46565	1.47554	1.13199
O	0.68660	1.12266	2.33152
O	2.86353	1.91201	1.20740
C	1.25381	-0.12908	-0.32468
C	1.01464	-1.33765	0.42910
C	2.43516	-0.08545	-1.16277
C	1.99723	-2.29962	0.50440
H	0.09914	-1.44038	0.99949
C	3.38665	-1.07142	-1.05818
H	2.59693	0.76344	-1.82060
C	3.21192	-2.19658	-0.21434
H	1.82707	-3.17001	1.13207
H	4.29305	-0.98970	-1.65166
C	0.53315	2.70594	0.21321
H	0.65117	3.73790	0.53508
S	-0.25305	0.55889	-1.25783
C	-1.75541	-0.09765	-0.54451
C	-2.48004	-0.96287	-1.37458
C	-2.20221	0.22636	0.74533
C	-3.66989	-1.50954	-0.89929
H	-2.12939	-1.20017	-2.37457
C	-3.39391	-0.33335	1.19059
H	-1.63301	0.88370	1.39388
C	-4.14705	-1.20726	0.38399
H	-4.23771	-2.17703	-1.54067
H	-3.74844	-0.08697	2.18767
C	4.28370	-3.23914	-0.08608
H	5.02360	-2.93607	0.66846
H	3.87479	-4.20362	0.22865
H	4.82511	-3.37834	-1.02733
C	-5.42835	-1.80751	0.90110
H	-5.21897	-2.54693	1.68427
H	-6.07223	-1.04154	1.34660
H	-5.98905	-2.30931	0.10842
C	-1.11564	3.18920	-1.66197
H	-1.05380	4.22960	-1.33253
H	-0.80215	3.13380	-2.71087
H	-2.16342	2.87201	-1.60718

Molecule in row 14 (3-phenylsulfonyl-2-(phenylthio)propene)



Radical cation
Energy = -1526.489481
$<S^2> = 0.768$

C	-0.21527	1.33379	-0.61536
S	0.99162	-1.14961	-0.01600
O	1.03896	-2.43526	-0.71613
O	0.32797	-0.99660	1.29253
C	2.63674	-0.46092	0.10122
C	3.57343	-0.78565	-0.88518
C	2.95181	0.36776	1.18387
C	4.85535	-0.24494	-0.78910
H	3.31241	-1.46548	-1.69008
C	4.24124	0.89644	1.26457
H	2.21428	0.56041	1.95548
C	5.18514	0.59483	0.27986
H	5.59992	-0.49057	-1.53990
H	4.51089	1.53020	2.10379
C	0.06392	-0.01605	-1.18384
H	0.68392	0.06717	-2.08046
H	-0.83550	-0.58492	-1.43080
H	6.18808	1.00486	0.35159
C	0.71908	2.33087	-0.62708
H	1.68286	2.17267	-1.10044
H	0.53647	3.30843	-0.18984
S	-1.74059	1.84977	0.08286
C	-2.95216	0.58337	0.08602
C	-4.25872	1.04425	-0.21668
C	-2.72643	-0.75818	0.47182
C	-5.31479	0.14635	-0.19722
H	-4.42548	2.08224	-0.48827
C	-3.80240	-1.63521	0.49249
H	-1.74721	-1.07888	0.81086
C	-5.08911	-1.19403	0.15014
H	-6.31406	0.48451	-0.45138
H	-3.64392	-2.66371	0.80070
H	-5.92152	-1.89070	0.17467

Smiles transition structure, C-attack (radical cation)
Energy = -1526.460836
$<S^2> = 0.767$

C	0.14676	-0.73028	-1.04268
S	-1.01345	1.46120	-0.17120
O	-1.65498	2.60278	-0.81793
O	-0.38351	1.55383	1.15006
C	-2.24727	0.02345	-0.07579
C	-3.48115	0.24070	-0.78776
C	-2.31699	-0.62677	1.20733
C	-4.65548	-0.32167	-0.33452
H	-3.46889	0.84053	-1.69283
C	-3.50352	-1.18100	1.64359
H	-1.42053	-0.68565	1.81550
C	-4.67297	-1.04209	0.87512
H	-5.57414	-0.18152	-0.89517
H	-3.53833	-1.70374	2.59410
C	0.27081	0.70835	-1.33969
H	-0.06863	0.96564	-2.34738
H	1.22930	1.17579	-1.11339
H	-5.60552	-1.46765	1.23318
C	-1.18013	-1.22198	-1.21780
H	-1.65744	-0.95082	-2.15586
H	-1.43643	-2.21994	-0.87047
S	1.26962	-1.69123	-0.17319
C	2.74716	-0.70537	0.06752
C	3.90989	-1.12921	-0.59040
C	2.76587	0.36909	0.96958
C	5.10350	-0.44689	-0.35783
H	3.88304	-1.97345	-1.27239
C	3.96934	1.04107	1.18405
H	1.86542	0.67549	1.49145
C	5.13260	0.63573	0.52460
H	6.00877	-0.76299	-0.86668
H	3.99629	1.87639	1.87696
H	6.06580	1.16081	0.70418

Smiles transition structure, S-attack (radical cation)
Energy = -1526.440003
$<S^2> = 0.781$

C	-0.12451	-2.02916	-0.93440
S	1.75672	-1.16870	0.78483
O	3.21236	-1.15480	0.94214
O	0.82916	-1.35577	1.91439
C	1.07697	0.59665	-0.30496
C	2.11224	0.95844	-1.24777
C	0.71087	1.56031	0.70491
C	2.86392	2.09539	-1.03881
H	2.33025	0.30759	-2.08980
C	1.48571	2.68876	0.87981
H	-0.11139	1.34591	1.37684
C	2.57100	2.96645	0.02744
H	3.67585	2.32700	-1.72121
H	1.24407	3.37359	1.68692
C	1.27643	-2.36112	-0.53890
H	2.01145	-2.23906	-1.34167
H	1.34981	-3.37046	-0.12460
H	3.16428	3.86229	0.17613
C	-1.13065	-2.88247	-1.11503
H	-0.96770	-3.94780	-0.97613
H	-2.12972	-2.56955	-1.40082
S	-0.40157	-0.24174	-1.22941
C	-1.92121	0.15460	-0.36923
C	-2.78772	1.00998	-1.06276
C	-2.22153	-0.34024	0.90823
C	-3.99090	1.37402	-0.45756
H	-2.53526	1.37619	-2.05324
C	-3.42937	0.03733	1.49043
H	-1.53115	-0.99218	1.43322
C	-4.30919	0.88907	0.81224
H	-4.67725	2.03044	-0.98277
H	-3.68214	-0.33369	2.47877
H	-5.24807	1.17322	1.27756