Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supplementary Data

Diagnostic fragmentations of adducts formed between carbanions and carbon disulfide in the gas phase. A joint experimental and theoretical study.

Micheal J. Maclean, Scott Walker, Tianfang Wang,
Peter C.H. Eichinger, and John H. Bowie.*

Department of Chemistry, The University of Adelaide, South Australia, 5005.

Table 1

Reaction Pathway for the CS_2 Addition to the Singlet Phenyl Anion. Anion Geometries and Energies. Carbon-Sulfur Skeleton Only.

Level of theory used - UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p).

Relative energies in kJ mol^{-1} with respect to a+CS_2 (0 kJ mol^{-1}).

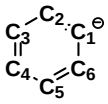
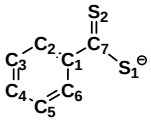
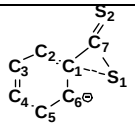
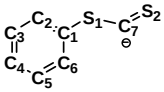
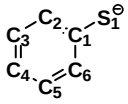
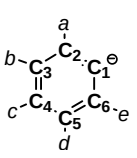
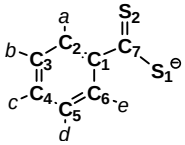
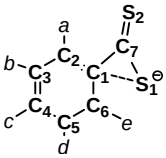
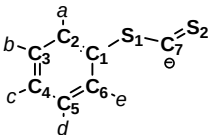
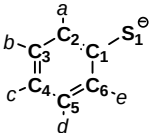
	 **A**	 **B**	 **TSB/C**	 **C**	 **D**
State	$^1A_1$	^1A	^1A	$^1A'$	$^1A'$
Symmetry	C_{2V}	C_1	C_1	C_S	C_S
Energy (Hartrees)	-230.85327 [-1064.1525]	-1064.26773	-1064.14790	-1064.19111	-628.60034 [-1064.17814]
Energy Relative to a+CS_2	0 [**A**+CS_2]	-303	+12	-101	-68 [**D**+CS]
Gibbs Free Energy	-230.8801 [-1064.19975]	-1064.30188	-1064.181691	-1064.22630	-628.63016 [-1064.22854]
Free Energy Relative to a+CS_2	0 [**A**+CS_2]	-268	+47	-70	-76 [**D**+CS]
Bond Lengths (Å)					
C_1S_1	-	-	3.019	1.791	1.750
C_1C_2	1.421	1.407	1.440	1.405	1.424
C_1C_7	-	1.512	1.491	-	-
C_2C_3	1.407	1.396	1.388	1.396	1.395
C_3C_4	1.402	1.400	1.405	1.401	1.403
C_4C_5	1.401	1.398	1.405	1.399	1.403
C_5C_6	1.407	1.397	1.387	1.397	1.394
C_6C_1	1.422	1.408	1.441	1.407	1.424
C_7S_1	-	1.706	1.937	1.823	-
C_7S_2	-	1.705	1.654	1.682	-
Bond Angles (°)					
$S_1C_7S_2$	-	125.5	104.4	112.4	-
$S_1C_1C_2$	-	-	-	123.0	122.4
$S_1C_1C_6$	-	-	-	118.4	122.3
$S_1C_7C_1$	-	117.2	75.6	-	-
$S_2C_7C_1$	-	117.2	180.0	-	-
$C_1C_2C_3$	125.0	121.3	120.9	120.3	122.3
$C_2C_3C_4$	119.9	120.4	121.7	121.0	121.0
$C_3C_4C_5$	118.2	119.0	117.5	118.9	118.0
$C_4C_5C_6$	119.9	120.5	121.8	120.5	121.0
$C_5C_6C_1$	124.9	121.2	120.8	120.8	122.3
$C_6C_1C_2$	112.0	117.6	115.1	118.6	115.3
$C_7C_1C_2$	-	121.2	120.0	-	-
$C_7S_1C_1$	-	-	56.7	103.4	-
Dihedral Angle (°)					
$C_1C_2C_3C_4$	0.0	1.5	-7.2	0.0	0.0
$S_1C_1C_2C_3$	-	-	-118.6	180.0	180.0
$C_2C_3C_4C_5$	0.0	-0.8	-2.6	0.0	-0.316
$S_2C_7S_1C_1$	-	-	180.0	-	-

Table 1(a)

Reaction Pathway for the CS_2 Addition to the Singlet Phenyl Anion. Anion Geometries and Energies. C-H Only.

Level of theory used - UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p).

Relative energies in kJ mol^{-1} with respect to a+CS_2 (0 kJ mol^{-1}).

	 **A**	 **B**	 **TSB/C**	 **C**	 **D**
State	$^1A_1$	^1A	^1A	$^1A'$	$^1A'$
Symmetry	C_{2V}	C_1	C_1	C_S	C_S
Energy (Hartrees)	-230.85327 [-1064.1525]	-1064.26773	-1064.14790	-1064.19111	-628.60034 [-1064.17814]
Energy Relative to a+CS_2	0 [**A**+CS_2]	-303	+12	-101	-68 [**D**+CS]
Gibbs Free Energy	-230.8801 [-1064.19975]	-1064.30188	-1064.181691	-1064.22630	-628.63016 [-1064.22854]
Free Energy Relative to a+CS_2	0 [**A**+CS_2]	-268	+47	-70	-76 [**D**+CS]
Bond Lengths (Å)					
C_2a*	1.097	1.085	1.087	1.086	1.087
C_3b	1.094	1.088	1.089	1.088	1.090
C_4c	1.090	1.087	1.087	1.087	1.088
C_5d	1.094	1.089	1.090	1.089	1.090
C_6e	1.097	1.084	1.086	1.088	1.087
Bond Angles (°)					
aC_2C_1	118.9	118.1	118.4	117.5	117.8
aC_2C_3	116.1	120.6	120.3	122.2	119.9
bC_3C_4	119.6	120.0	119.7	119.7	119.8
cC_4C_5	120.9	120.5	121.2	120.5	121.1
dC_5C_6	120.4	119.5	118.5	119.4	119.8
eC_6C_1	119.0	118.1	118.4	119.2	117.8
Dihedral Angle (°)					
a$C_2C_3C_4$	180.0	-178.1	-179.0	180.0	180.0
c$C_4C_3C_2$	180.0	179.2	-179.6	180.0	180.0
c$C_4C_5C_6$	180.0	179.3	179.6	180.0	180.0
e$C_6C_5C_4$	180.0	-178.1	180.0	-179.0	-

*** Individual Hydrogens have been designated letters a - e**

S_1=C=S_2; State $^1A_1$, Symmetry C_{2V}, Energy (Hartrees) -833.29923, Gibbs Free Energy -833.31965, S_1=C 1.563Å, C=S_2 1.563Å, S_1=C=S_2 179.7°

C=S; State ^{1}SG, Symmetry C_{*V}, Energy (Hartrees) -435.5778, Gibbs Free Energy -435.59838, C=S 1.544Å

Table 2

Reaction Pathway for the Collision Induced Dissociation of the Singlet $PhCOS^-$ Anion. Anion Geometries and Energies. Carbon-Sulfur-Oxygen Skeleton Only.

Level of theory used - UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p).

Relative energies in kJ mol^{-1} with respect to A (0 kJ mol^{-1}).

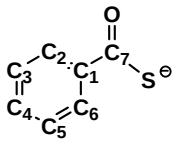
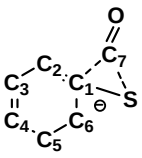
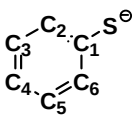
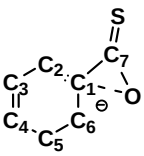
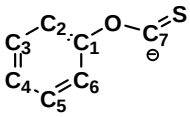
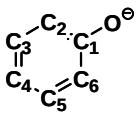
	 A	 TS A/B	 B	 TS A/C	 C	 D
State	^1A	^1A	$^1A'$	^1A	$^1A'$	$^1A'$
Symmetry	C_1	C_1	C_S	C_1	C_S	C_S
Energy (Hartrees)	-741.66644	-741.55247	-628.60034 [-741.64111]	-741.55040	-741.57485	-305.97915 [-741.55695]
Energy Relative to A	0	+299	+67 [**B**+CO]	+305	+241	+288 [**E**+CS]
Gibbs Free Energy	-741.69969	-741.58543	-628.63016 [-741.69007]	-741.58300	-741.60937	-306.00803 [-741.60641]
Free Energy Relative to A	0	+300	+25 [**B**+CO]	+306	+237	+245 [**E**+CS]
Bond Lengths (Å)						
C_1S	-	1.865	1.750	-	-	-
C_1C_2	1.403	1.427	1.424	1.443	1.407	1.448
C_1C_7	1.537	1.686	-	1.537	-	-
C_2C_3	1.398	1.401	1.395	1.389	1.395	1.392
C_3C_4	1.400	1.394	1.403	1.406	1.401	1.407
C_4C_5	1.399	1.415	1.403	1.406	1.400	1.407
C_5C_6	1.399	1.383	1.394	1.389	1.396	1.392
C_6C_1	1.405	1.437	1.424	1.442	1.408	1.449
C_7S	1.738	2.033	-	1.686	1.682	-
C_7O	1.244	1.187	-	1.342	1.434	-
C_1O	-	-	-	1.633	1.362	1.275
Bond Angles (°)						
SC_7O	125.7	127.0	-	111.3	109.0	-
SC_1C_2	-	118.5	122.4	-	-	-
SC_1C_6	-	119.8	122.3	-	-	-
SC_7C_1	118.4	-	-	180.0	-	-
OC_7C_1	115.9	143.1	-	68.7	-	-
$C_1C_2C_3$	120.9	121.9	122.3	120.6	120.5	122.6
$C_2C_3C_4$	120.4	121.2	121.0	122.2	120.6	121.7
$C_3C_4C_5$	119.3	118.0	118.0	117.4	118.7	117.5
$C_4C_5C_6$	120.2	121.3	121.0	122.2	121.5	121.7
$C_5C_6C_1$	121.1	122.0	122.3	120.6	119.6	122.6
$C_6C_1C_2$	118.2	115.3	115.3	116.0	119.1	113.9
$C_7C_1C_2$	123.4	-	-	120.9	-	-
C_7SC_1	-	-	-	-	-	-
OC_1C_2	-	-	-	115.4	115.9	123.1
C_7OC_1	-	-	-	61.3	118.5	-
Dihedral Angle (°)						
$C_1C_2C_3C_4$	0.0	2.8	0.0	5.2	0.0	0.0
$C_2C_3C_4C_5$	0.0	0.8	-0.316	1.8	0.0	0.0
$OC_1C_2C_3$	-	-	-	127.8	180.0	-179.0
SC_7OC_1	-	-	-	180.0	-179.0	-

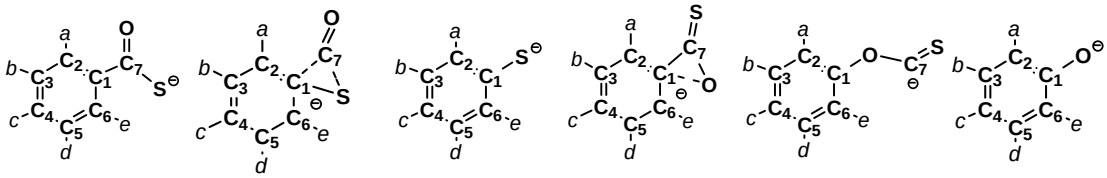
Table 2(a)

Reaction Pathway for the Collision Induced Dissociation of the Singlet $PhCOS^-$ Anion. Anion Geometries and Energies.

C-H Only.

Level of theory used - UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p).

Relative energies in kJ mol^{-1} with respect to A (0 kJ mol^{-1}).



	A	TS A/B	B	TS A/D	D	E
State	^1A	^1A	$^1A'$	^1A	$^1A'$	$^1A'$
Symmetry	C_1	C_1	C_S	C_1	C_S	C_S
Energy (Hartrees)	-741.66644	-741.55247	-628.60034 [-741.64111]	-741.55040	-741.57485	-305.97915 [-741.55695]
Energy Relative to A	0	+299	+67 [**B**+CO]	+305	+241	+288 [**E**+CS]
Gibbs Free Energy	-741.69969	-741.58543	-628.63016 [-741.69007]	-741.58300	-741.60937	-306.00803 [-741.60641]
Free Energy Relative to A	0	+300	+25 [**B**+CO]	+306	+237	+245 [**E**+CS]
Bond Lengths (Å)						
C_2a*	1.086	1.087	1.087	1.085	1.085	1.089
C_3b	1.088	1.090	1.090	1.091	1.089	1.092
C_4c	1.088	1.088	1.088	1.086	1.087	1.087
C_5d	1.089	1.090	1.090	1.090	1.089	1.092
C_6e	1.085	1.086	1.087	1.086	1.082	1.089
Bond Angles (°)						
aC_2C_1	117.6	118.1	117.8	118.7	118.1	116.9
aC_2C_3	121.5	119.9	119.9	120.6	121.4	120.5
bC_3C_4	119.9	119.9	119.8	119.5	120.0	119.2
cC_4C_5	120.3	120.8	121.1	121.3	120.7	121.3
dC_5C_6	119.9	119.0	119.8	118.3	118.9	119.0
eC_6C_1	117.5	117.9	117.8	118.7	117.9	116.9
Dihedral Angle (°)						
a$C_2C_3C_4$	-179.0	-178.0	180.0	-178.4	180.0	180.0
c$C_4C_3C_2$	180.0	178.3	180.0	179.1	180.0	-179.0
c$C_4C_5C_6$	180.0	-178.9	180.0	-179.0	180.0	180.0
e$C_6C_5C_4$	180.0	178.5	-	178.3	-179.0	180.0

*** Individual Hydrogens have been designated letters a - e**

C=O; State ^{1}SG, Symmetry C_{*v}, Energy (Hartrees) -113.04077, Gibbs Free Energy -113.05991, C=O 1.138Å

C=S; State ^{1}SG, Symmetry C_{*v}, Energy (Hartrees) -435.57780, Gibbs Free Energy -435.59838, C=S 1.544Å

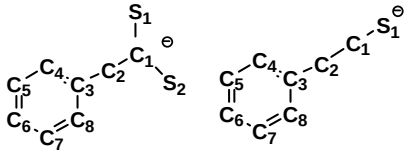
Table 3

Possible Reaction Pathway for the CS_2 Addition to the Singlet Benzyl Anion. Anion Geometries and Energies.

Carbon and Sulfur Skeleton Only.

Level of theory used - UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p).

Relative energies in kJ mol^{-1} with respect to A (0 kJ mol^{-1}).



	A	B
State	^{1}A	^{1}A'
Symmetry	C_1	C_1
Energy (Hartrees)	-1103.43726	-704.55370 [-1103.37578]
Energy Relative to A	0	+161 [**B**+H_2S]
Gibbs Free Energy	-1103.47418	-704.58712 [-1103.42847]
Free Energy Relative to A	0	+120 [**B**+H_2S]
Bond Lengths (Å)		
C_1S_1	1.699	1.656
C_1S_2	1.700	-
C_1C_2	1.549	1.240
C_2C_3	1.516	1.409
C_3C_4	1.404	1.425
C_4C_5	1.397	1.393
C_5C_6	1.399	1.402
C_6C_7	1.399	1.403
C_7C_8	1.398	1.393
C_8C_3	1.404	1.425
Bond Angles (°)		
$S_1C_1S_2$	127.3	-
$S_1C_1C_2$	116.4	180.0
$S_2C_1C_2$	116.3	-
$C_1C_2C_3$	112.9	180.0
$C_2C_3C_4$	121.0	121.9
$C_3C_4C_5$	121.0	121.7
$C_4C_5C_6$	120.3	121.0
$C_5C_6C_7$	119.3	118.4
$C_6C_7C_8$	120.3	121.0
$C_7C_8C_3$	121.0	121.7
$C_8C_3C_2$	120.9	121.9
$C_8C_3C_4$	118.2	116.2
Dihedral Angle (°)		
$C_1C_2C_3C_4$	89.7	0.0
$S_1C_1C_2C_3$	-89.6	180.0
$C_1C_2C_3C_8$	-89.8	0.0
$C_2C_3C_4C_5$	-179.7	-179.0

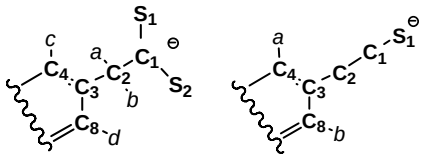
Table 3(a)

Possible Reaction Pathway for the CS_2 Addition to the Singlet Benzyl Anion. Anion Geometries and Energies.

C-H Only.

Level of theory used - UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p).

Relative energies in kJ mol^{-1} with respect to A (0 kJ mol^{-1}).



	A	B
State	^{1}A	^{1}A'
Symmetry	C_1	C_1
Energy (Hartrees)	-1103.43726	-704.55370 [-1103.37578]
Energy Relative to A	0	+161 [**B**+H_2S]
Gibbs Free Energy	-1103.47418	-704.58712 [-1103.42847]
Free Energy Relative to A	0	+120 [**B**+H_2S]
Bond Lengths (Å)		
C_2a	1.095	-
C_2b	1.094	-
C_4a	-	1.087
C_4c	1.087	-
C_8b	-	1.086
C_8d	1.086	-
Bond Angles (°)		
aC_2b	108.9	-
aC_2C_1	108.4	-
aC_2C_3	109.0	-
aC_4C_3	-	118.1
bC_2C_1	108.5	-
bC_2C_3	109.0	-
bC_8C_3	-	118.2
cC_4C_3	118.7	-
dC_8C_3	118.7	-
Dihedral Angle (°)		
a$C_4C_3C_8$	-	180.0
b$C_2C_3C_8$	30.9	-
d$C_8C_3C_4$	-178.4	-

H_1-S-H_2; State ^{1}A', Symmetry C_S, Energy (Hartrees) -398.82208, Gibbs Free Energy -398.84135, H_1-S 1.348 Å, H_2-S 1.348 Å, Angle H_1-S-H_2 92.7°

Table 4

Reaction Pathway for the Interconversion of the Singlet Anion *o*-$CH_3(C_6H_4)^-$ to Singlet $PhCH_2^-$.

Anion Geometries and Energies.

Carbon Skeleton Only.

Level of theory used - UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p).

Relative energies in kJ mol^{-1} with respect to A (0 kJ mol^{-1}).

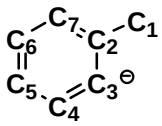
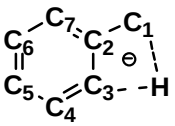
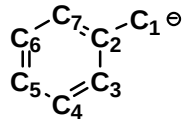
			
	A	**TS A/B**	**B**
State	$^1A'$	^1A	^1A
Symmetry	C_S	C_1	C_1
Energy (Hartrees)	-270.03120	-269.96265	-270.05125
Energy Relative to A	0	+180	-53
Gibbs Free Energy	-270.06021	-269.99218	-270.08051
Free Energy Relative to A	0	+179	-53
Bond Lengths (Å)			
C_1C_2	1.526	1.509	1.395
C_2C_3	1.422	1.423	1.451
C_3C_4	1.420	1.404	1.386
C_4C_5	1.405	1.412	1.412
C_5C_6	1.401	1.399	1.413
C_6C_7	1.401	1.408	1.386
C_7C_2	1.409	1.403	1.450
Bond Angles (°)			
$C_1C_2C_3$	119.3	105.3	123.2
$C_2C_3C_4$	113.3	118.5	122.8
$C_3C_4C_5$	124.9	120.6	122.1
$C_4C_5C_6$	119.4	120.0	116.7
$C_5C_6C_7$	118.5	120.4	122.1
$C_6C_7C_2$	120.8	119.3	122.8
$C_7C_2C_1$	117.5	133.5	123.2
$C_7C_2C_3$	123.2	121.1	113.6
Dihedral Angle (°)			
$C_1C_2C_3C_4$	-179.0	178.7	-179.0
$C_1C_2C_7C_6$	180.0	-175.4	180.0
$C_2C_3C_4C_5$	0.0	-3.0	0.0
$C_2C_7C_6C_5$	0.0	-1.7	0.0

Table 4(a)

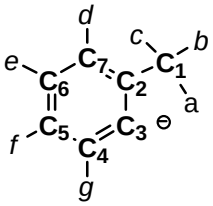
Reaction Pathway for the Interconversion of the Singlet Anion *o*-$CH_3(C_6H_4)^-$ to Singlet $PhCH_2^-$.

Anion Geometries and Energies.

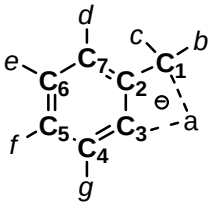
C-H Only.

Level of theory used - UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p).

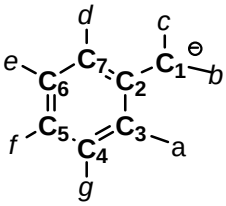
Relative energies in kJ mol^{-1} with respect to A (0 kJ mol^{-1}).



A



TS A/B



B

	A	TS A/B	B
State	$^1A'$	^1A	^1A
Symmetry	C_S	C_1	C_1
Energy (Hartrees)	-270.03120	-269.96265	-270.05125
Energy Relative to A	0	+180	-53
Gibbs Free Energy	-270.06021	-269.99218	-270.08051
Free Energy Relative to A	0	+179	-53
Bond Lengths (Å)			
C_1a	1.102	1.537	-
C_1b	1.102	1.105	1.087
C_1c	1.093	1.104	1.087
C_3a	-	1.421	1.090
C_4g	1.097	1.093	1.091
C_5f	1.094	1.092	1.087
C_6e	1.090	1.091	1.092
C_7d	1.095	1.091	1.090
Bond Angles (°)			
aC_1C_2	112.2	72.2	-
aC_1b	106.7	132.2	-
aC_1c	108.3	110.4	-
bC_1C_2	112.2	115.5	121.3
bC_1c	108.3	108.6	117.5
cC_1C_2	108.9	113.0	121.2
dC_7C_6	118.8	119.5	119.2
eC_6C_5	121.0	119.7	119.3
fC_5C_4	120.8	120.4	121.6
gC_4C_3	118.8	120.9	118.6
Dihedral Angle (°)			
a$C_1C_2C_3$	-119.9	-3.2	-
b$C_1C_2C_3$	119.9	-132.2	-179.0

*** Individual Hydrogens have been designated letters a - g**

Table 5

Reaction Pathway for the Interconversion of the Singlet Anion $PhCH_2CH_2^-$. Anion Geometries and Energies. Carbon Skeleton Only.

Level of theory used - UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p).

Relative energies in kJ mol^{-1} with respect to A (0 kJ mol^{-1}).

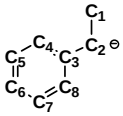
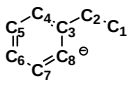
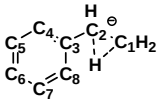
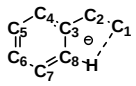
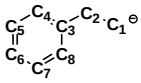
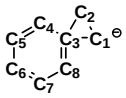
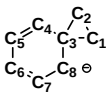
	 D	 C	 TS A/D	 TS A/C	 A	 TS A/B	 B
State	^{1}A	^{1}A	^{1}A	^{1}A	^{1}A	^{1}A	^{1}A
Symmetry	C_1	C_1	C_1	C_1	C_1	C_1	C_1
Energy (Hartrees)	-309.22336	-309.20572	-309.12837	-309.16471	-309.18370	-309.17008	-309.17799
Energy Relative to A	-104	-58	+144	+50	0	+36	+13
Gibbs Free Energy	-309.25480	-309.23759	-309.15998	-309.19645	-309.21513	-309.20086	-309.20928
Free Energy Relative to A	-104	-59	+145	+49	0	+38	+15
Bond Lengths (Å)							
C_1C_2	1.504	1.539	1.564	1.534	1.514	1.503	1.519
C_2C_3	1.392	1.525	1.430	1.555	1.529	1.475	1.517
C_1C_3	-	-	-	-	-	1.902	1.555
C_3C_4	1.453	1.408	1.433	1.399	1.404	1.458	1.499
C_4C_5	1.390	1.403	1.386	1.403	1.399	1.384	1.379
C_5C_6	1.407	1.398	1.414	1.402	1.402	1.415	1.420
C_6C_7	1.417	1.408	1.402	1.406	1.399	1.415	1.420
C_7C_8	1.383	1.416	1.396	1.402	1.402	1.383	1.378
C_8C_3	1.452	1.424	1.435	1.402	1.402	1.458	1.499
Bond Angles (°)							
$C_1C_2C_3$	123.3	112.6	123.7	109.3	116.2	79.4	61.6
$C_2C_3C_4$	123.4	118.2	121.8	124.4	121.0	121.7	119.2
$C_3C_4C_5$	122.3	120.6	122.4	119.8	121.6	121.0	121.3
$C_4C_5C_6$	122.3	118.4	121.1	119.6	119.9	122.0	123.1
$C_5C_6C_7$	116.9	119.6	117.7	119.6	119.1	117.1	116.6
$C_6C_7C_8$	121.9	124.7	121.9	121.6	120.5	122.0	123.1
$C_7C_8C_3$	122.8	113.4	121.4	117.8	121.0	121.0	121.3
$C_8C_3C_2$	122.8	118.5	122.7	114.0	121.2	121.7	119.2
$C_8C_3C_4$	113.8	123.3	115.5	121.6	117.8	114.2	112.3
Dihedral Angle (°)							
$C_1C_2C_3C_4$	0.0	-105.2	-173.7	-179.0	177.4	-99.5	-108.0
$C_1C_2C_3C_8$	180.0	73.9	7.6	0.0	-3.364	99.5	108.1
$C_2C_3C_4C_5$	-179.0	178.8	-177.3	180.0	-179.2	-179.0	-162.2
$C_2C_3C_8C_7$	180.0	-178.6	176.6	-179.0	-179.6	179.7	162.2

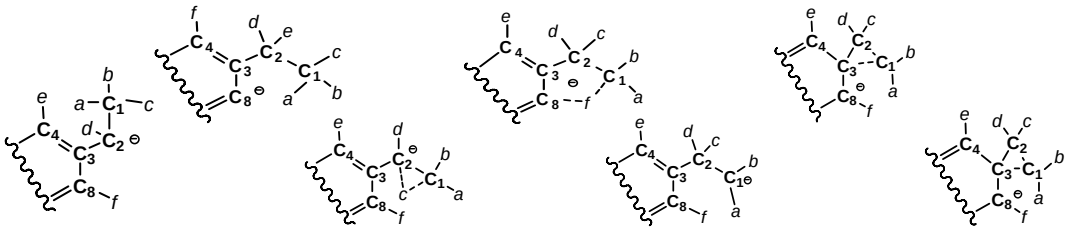
Table 5(a)

Reaction Pathway for the Interconversion of the Singlet Anion $PhCH^{-}CH_3$. Anion Geometries and Energies.

C-H Only.

Level of theory used - UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p).

Relative energies in kJ mol^{-1} with respect to A (0 kJ mol^{-1}).

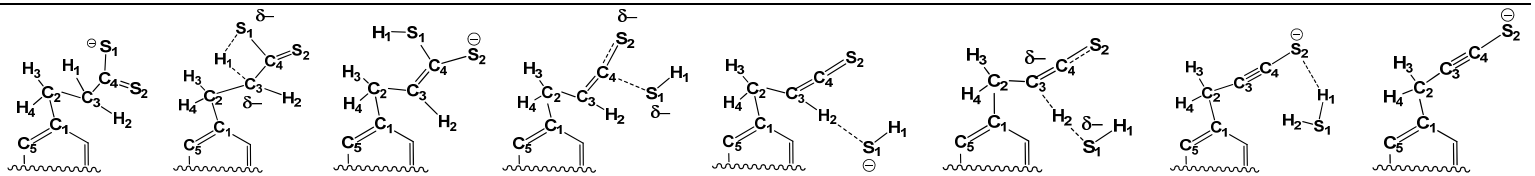


	D	C	TS A/D	TS A/C	A	TS A/B	B
State	^{1}A	^{1}A	^{1}A	^{1}A	^{1}A	^{1}A	^{1}A
Symmetry	C_1	C_1	C_1	C_1	C_1	C_1	C_1
Energy (Hartrees)	-309.22336	-309.20572	-309.12837	-309.16471	-309.18370	-309.17008	-309.17799
Energy Relative to A	-104	-58	+144	+50	0	+36	+13
Gibbs Free Energy	-309.25480	-309.23759	-309.15998	-309.19645	-309.21513	-309.20086	-309.20928
Free Energy Relative to A	-104	-59	+145	+49	0	+38	+15
Bond Lengths (Å)							
C_1a	1.110	1.098	1.089	1.100	1.100	1.086	1.092
C_1b	1.109	1.100	1.095	1.099	1.103	1.085	1.092
C_1c	1.098	1.095	1.401	-	-	-	-
C_1f	-	-	-	1.528	-	-	-
C_2c	-	-	1.220	1.104	1.104	1.098	1.091
C_2d	1.089	1.103	1.092	1.104	1.126	1.098	1.091
C_2e	-	1.097	-	-	-	-	-
C_4e	1.088	-	1.090	1.094	1.091	1.090	1.090
C_4f	-	1.095	-	-	-	-	-
C_8f	1.090	-	1.085	1.361	1.088	1.090	1.090
Bond Angles (°)							
aC_1b	105.0	108.1	115.2	109.1	109.2	118.3	114.8
aC_1c	106.4	107.9	112.5	-	-	-	-
aC_1C_2	113.8	110.9	112.1	113.1	111.5	120.1	118.3
bC_1c	106.4	108.9	131.5	-	-	-	-
bC_1C_2	113.9	111.9	116.7	113.1	112.9	120.1	118.3
cC_1C_2	110.8	108.9	48.2	-	-	-	-
cC_2C_1	-	-	58.9	113.1	-	120.1	-
cC_2C_3	-	-	112.2	108.0	-	113.9	-
cC_2d	-	-	115.4	105.1	103.4	109.8	113.5
dC_2C_1	117.8	109.2	116.6	113.2	117.4	116.8	118.4
dC_2C_3	118.8	110.8	116.1	107.9	103.4	115.7	117.8
eC_2C_3	-	108.3	-	-	-	-	-
eC_4C_3	118.8	-	118.3	120.5	118.8	118.7	118.1
fC_8C_3	117.9	-	119.0	95.3	116.6	118.7	118.1
fC_4C_3	-	120.4	-	-	-	-	-
Dihedral Angle (°)							
a$C_1C_2C_3$	60.2	63.0	161.6	-117.7	-166.0	-97.0	106.9
d$C_2C_3C_8$	0.0	-163.5	165.4	123.5	126.7	-145.7	-1.0
e$C_4C_3C_8$	180.0	-	-178.6	180.0	-179.0	166.8	166.9
f$C_8C_3C_4$	-179.0	-	178.6	180.0	-178.0	-166.8	-166.9

Table 6

Reaction Pathway for the Dissociation of the Singlet $PhCH_2CH_2CS_2^-$ Anion. Energies and Selected Geometries of Anion Minima and Transition States.

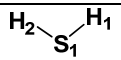
Level of theory used – UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p). Relative energies in kJ mol^{-1} with respect to A (0 kJ mol^{-1})



	A	TS A/B	B	TS B/C	C	TS C/D	D	E
State	^1A	^1A	^1A	^1A	^1A	^1A	^1A	^1A
Symmetry	C_1	C_1	C_1	C_1	C_1	C_1	C_1	C_1
Energy (Hartree)	-1142.61346	-1142.52437	-1142.58933	-1142.54184	-1142.55548	-1142.54932	-1142.55202	-743.71570 [-1142.53778]
Energy Relative to A	0	234	63	188	152	168	161	199 **[E+F]**
Gibbs Free Energy (Hartree)	-1142.64983	-1142.56038	-1142.62546	-1142.58123	-1142.59489	-1142.58866	-1142.59341	-1142.591365
Gibbs Free Energy Relative to A	0	235	64	180	144	161	148	154 **[E+F]**
Bond Length (Å)								
C_1C_2	1.511	1.519	1.520	1.526	1.521	1.524	1.532	1.532
C_2C_3	1.550	1.533	1.508	1.516	1.523	1.488	1.459	1.457
C_3C_4	1.535	1.452	1.363	1.317	1.297	1.258	1.230	1.233
C_4S_1	1.702	1.809	1.828	3.382	—	—	—	—
C_4S_2	1.703	1.679	1.739	1.586	1.596	1.639	1.678	1.674
C_3H_1	1.095	1.605	—	—	—	—	—	—
C_3H_2	1.095	1.097	1.090	1.091	1.137	1.626	—	—
S_1H_1	2.787	1.578	1.359	1.354	1.353	1.348	1.347	—
S_1H_2	—	—	—	2.643	2.246	1.498	1.397	—
C_2H_3	1.096	1.105	1.101	1.100	1.097	1.102	1.104	
C_2H_4	1.096	1.098	1.099	1.098	1.095	1.100	1.104	

Table 6 Continued.

Bond Angle (°)								
$C_1C_2C_3$	113.0	113.9	114.2	115.3	113.8	113.6	116.4	116.4
$C_2C_3C_4$	111.1	119.4	123.2	122.1	126.5	146.6	178.3	179.3
$C_3C_4S_1$	116.4	105.6	118.6	79.5	—	—	—	—
$C_3C_4S_2$	116.4	127.9	129.0	168.9	177.8	173.5	179.4	179.9
$H_1C_3C_4$	109.6	73.8	—	—	—	—	—	—
$H_2C_3C_4$	109.6	113.6	120.2	116.9	120.1	109.4	66.2	—
$H_3C_2C_1$	110.0	107.7	108.3	108.0	109.0	108.0	107.0	106.6
$H_4C_2C_1$	110.0	108.9	108.8	108.5	109.2	108.7	107.0	106.6
Dihedral Angle (°)								
$C_3C_2C_1C_5$	-89.4	-127.1	-124.6	-162.8	114.9	109.8	179.6	179.9
$C_4C_3C_2C_1$	180.0	-165.2	-107.0	-118.0	120.1	-79.5	—	-141.9
$S_1C_4C_3C_2$	88.9	71.2	-179.5	175.7	-177.0	-179.6	—	—
$S_2C_4C_3C_2$	-88.8	-117.8	0.9	-3.4	175.1	-177.4	—	136.9
$H_1C_3C_4S_1$	-31.3	-16.9	-0.6	-19.2	13.5	5.1	-0.4	—
$H_2C_3C_4S_1$	-150.8	-155.8	1.6	-4.6	1.5	-0.4	3.5	—
$H_3C_2C_1C_5$	31.4	-3.7	-0.7	-40.5	-126.2	-128.3	-56.2	-55.4
$H_4C_2C_1C_5$	149.8	110.7	115.7	73.9	-8.8	-13.6	55.4	55.7

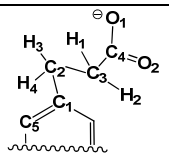
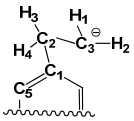


[F]; State ^{1}A', Symmetry C_S, Energy (Hartree) -398.82208, Gibbs Free Energy (Hartree) -398.84201, H_1S_1 1.348 Å, H_2S_1 1.348 Å, ∠$H_1S_1H_2$ 92.7°.

Table 7

Energies and Selected Geometries of Stationary Points on the Potential Energy Surface of Dissociation of the Singlet $PhCH_2CH_2CO_2^-$ Anion.

Level of theory used – UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p). Relative energies in kJ mol^{-1} with respect to A (0 kJ mol^{-1})

		
	A	**B**
State	^1A	^1A
Symmetry	C_1	C_1
Energy (Hartree)	-497.40907	-309.18830 [-497.31026]
Energy Relative to A	0	+259 **[B+C]**
GibbsFree Energy (Hartree)	-497.44402	-309.21764 [-497.35621]
GibbsFree Energy Relative to A	0	+231 **[B+C]**
Bond Length (Å)		
C_1C_2	1.510	1.517
C_2C_3	1.541	1.530
C_3C_4	1.571	—
C_4O_1	1.261	—
C_4O_2	1.259	—
C_3H_1	1.096	1.103
C_3H_2	1.100	1.102
C_2H_3	1.097	1.103
C_2H_4	1.095	1.103
Bond Angle (°)		
$C_1C_2C_3$	113.7	113.3
$C_2C_3C_4$	113.8	—
$C_3C_4O_1$	116.1	—
$C_3C_4O_2$	114.8	—
$H_1C_3C_2$	111.1	111.2
$H_2C_3C_4$	107.0	—
$H_3C_2C_1$	109.5	108.1
$H_4C_2C_1$	110.9	108.1
Dihedral Angle (°)		
$C_3C_2C_1C_5$	-93.3	-88.7
$C_4C_3C_2C_1$	-171.8	—
$O_1C_4C_3C_2$	27.9	—
$O_2C_4C_3C_2$	-153.8	—
$H_1C_3C_2O_1$	64.8	60.6
$H_2C_3C_2O_1$	-52.3	-60.5
H3C2C1C5	28.7	34.0
H4C2C1C5	145.8	148.7

$O_1{=}C_4{=}O_2$ [C]; State $^1A'$, Symmetry C_S, Energy (Hartree) -188.12196, Gibbs Free Energy (Hartree) -188.13857, O_1C_4 1.563 Å, O_2C_4 1.563 Å, $\angle H_1S_1H_2$ 180.0°.