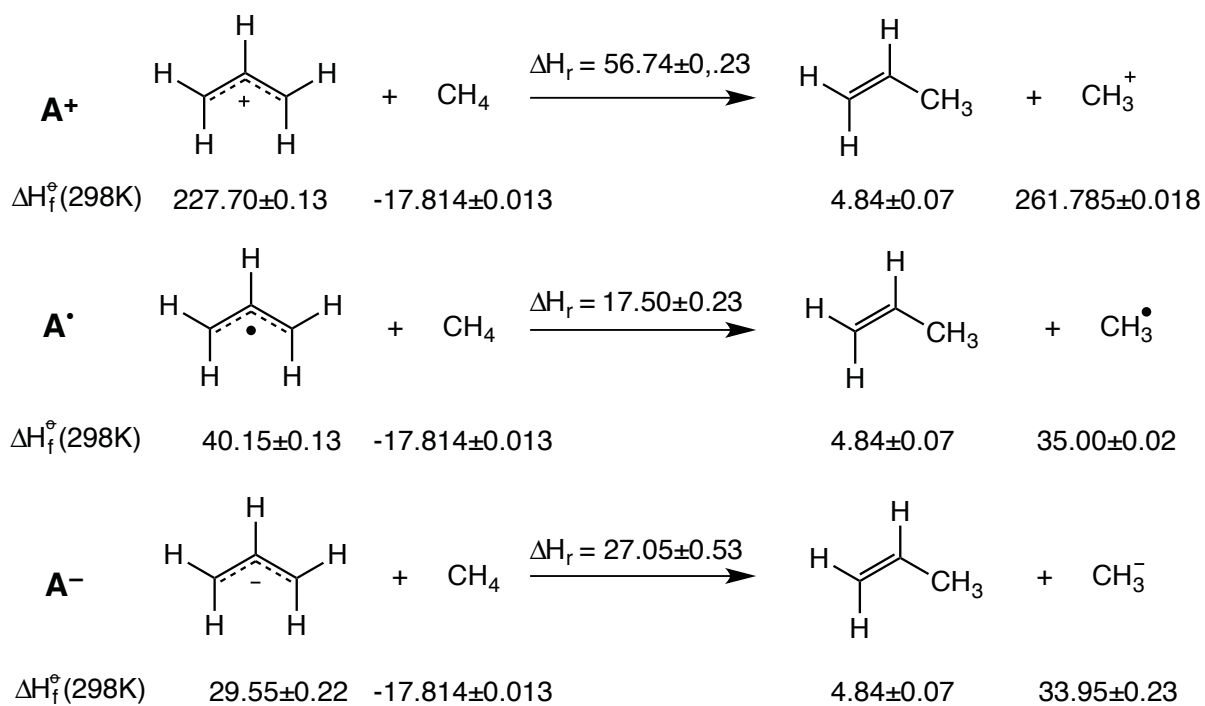


Variations in Rotational Barriers of Allyl and Benzyl Cations, Anions, and Radicals

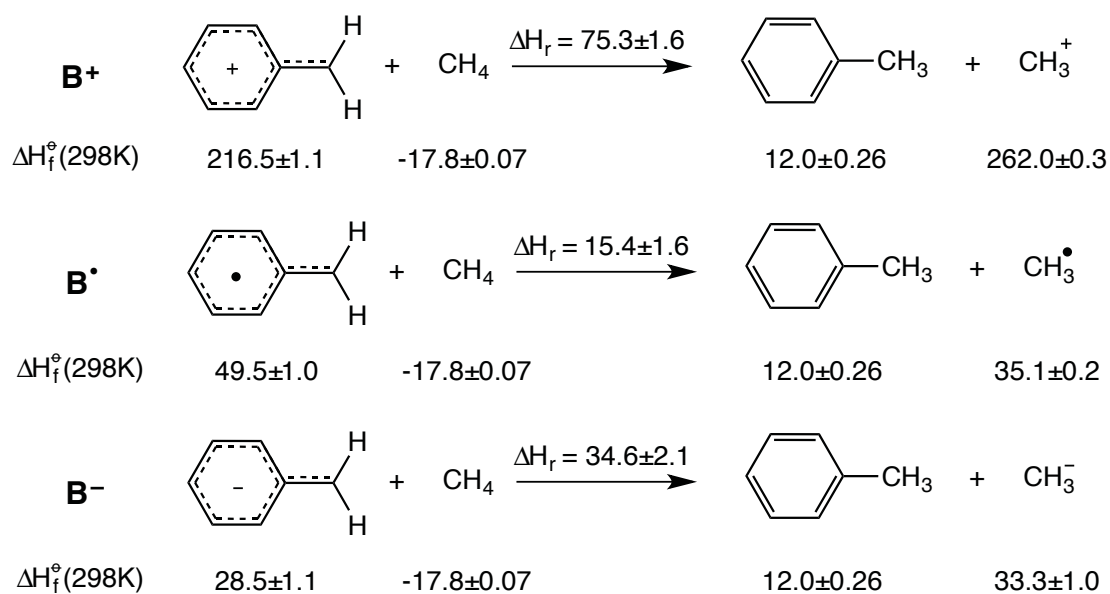
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Supporting Information

Scheme S1: Experimental thermochemical data for the allyl species	S2
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Scheme S1: Thermochemical data for the allyl species from the Active Thermochemical Tables (Ref. 14 in the paper)



Scheme S2: Thermochemical data for the benzyl species. All the data were taken from the NIST Webbook (Ref 15 in the paper)

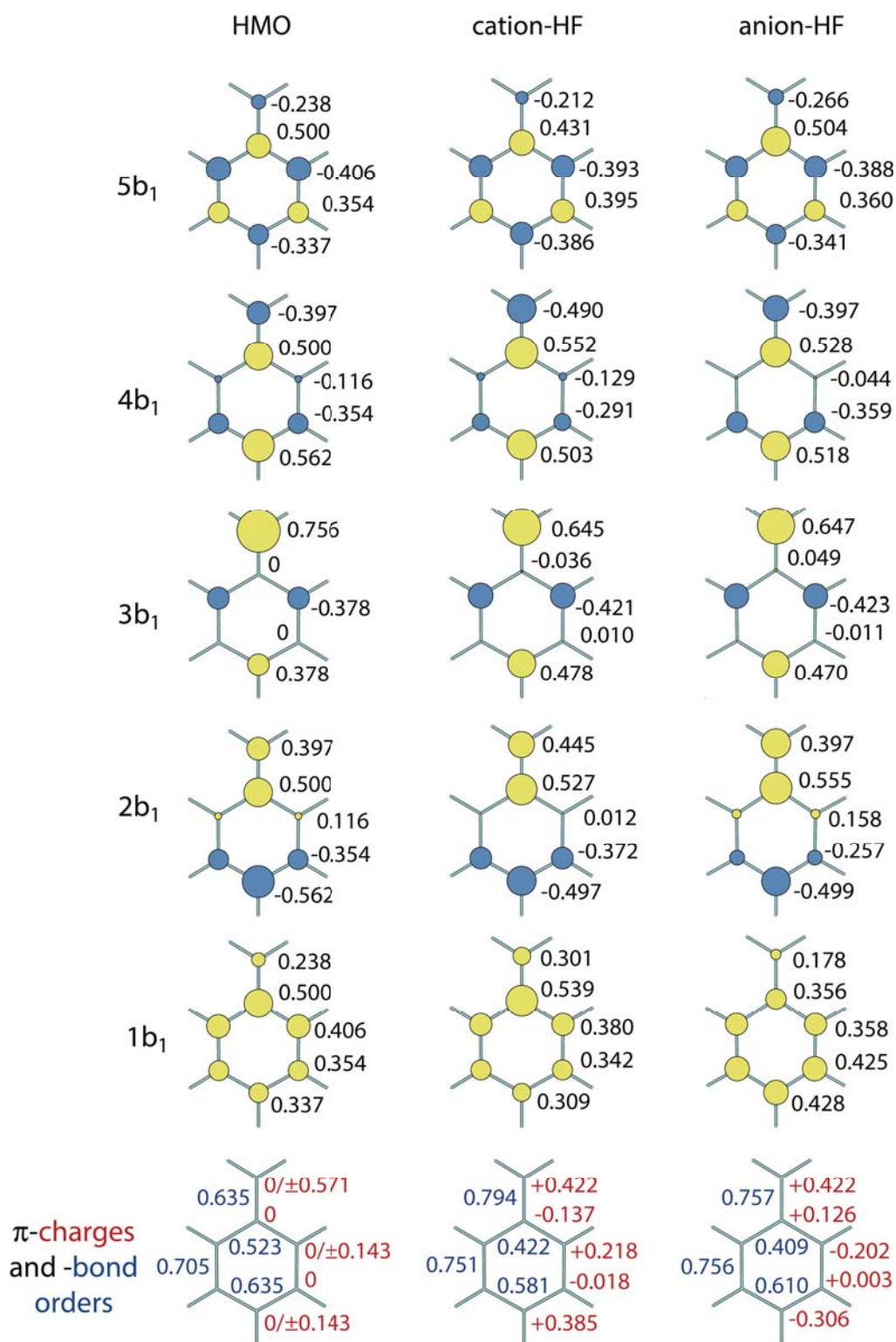


Figure S1: b₁- π -molecular orbitals (with coefficients) obtained from calculations at the HMO level (left column), and at the HF/STO-3G level for the benzyl cation (central column) and the benzyl anion (right column). The HF-MOs were normalized to 1. At the bottom the π -charges and -bond orders are listed which were calculated according to HMO theory for the different set of MOs. The MOs shown on the right in Figures 5 and 6 are drawn a bit exaggerated, compared to the "true" HF MOs, to better illustrate the effects of the mixing.

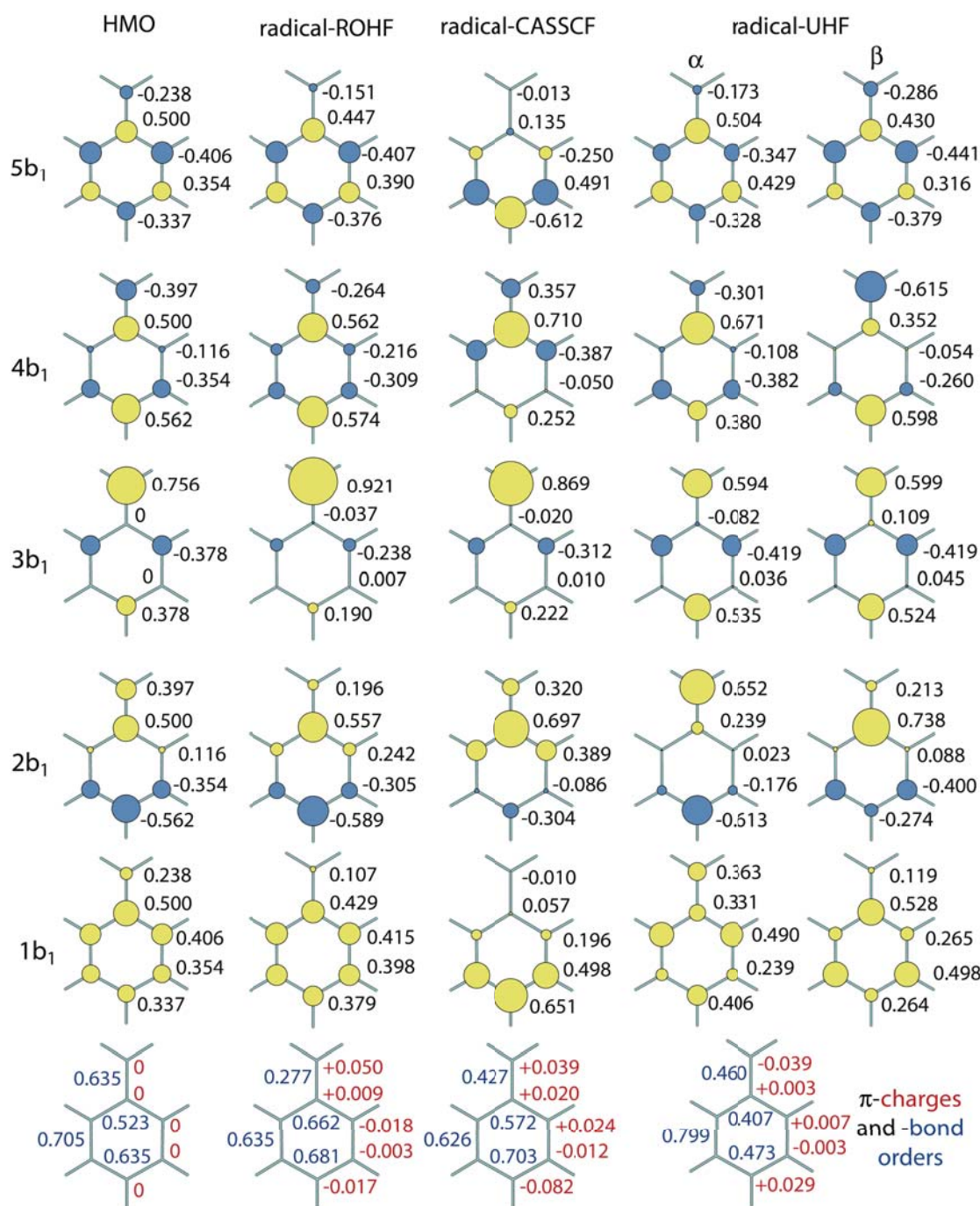


Figure S1: b₁-π-molecular orbitals (with coefficients) obtained from calculations at the HMO level (leftmost column), and, for the radical at three different levels. At the bottom the π-charges and -bond orders are listed which were calculated according to HMO theory for the different set of MOs. The transfer of spin from the ring to the exocyclic carbon is very well illustrated by the change of the shape of the 3b₁ MO between HMO and ROHF which results from mixing of the 3b₁ with the 2b₁ MO with a positive sign and with the 4b₁-MO with a negative sign. The mixing of the 3b₁ with the 2b₁ and with the 1b₁MO with a negative sign decreases the coefficient at the exocyclic carbon in the latter two MOs, and hence decreases the *ipso-exo* π-bond order. Similar effects can be seen at the CASSCF level, although the rotations among the occupied MOs distort the picture. In the UHF orbitals the 3b₁ MO seems to indicate transfer of spin from the exocyclic MOP to the ring, but the very pronounced spin polarization, which is very clearly visible (also in the a₂-MOs which are not shown), over emphasizes this effect.

Results of Pariser-Parr-Pople (PPP) Calculations on the Rotational Barriers in the Allyl Cation, Radical, and Anion

Due to the zero-differential overlap (ZDO) approximation in PPP theory, the J and K -integrals in equations 1 – 3 of the manuscript can be broken down into contributions from γ_{11} (repulsion energy between two electrons in the same 2p-AO), γ_{12} (repulsion energy between two electrons in neighboring 2p-AOs), and γ_{13} (repulsion energy between two electrons in 2p-AOs that are separated by two bonds). We assume that γ_{11} is the same at planar (pl) and in the twisted (tw) geometries, but the two-center integrals can be different at these two geometries.. At a twisted geometry, one has to distinguish the situation where two p-AOs are parallel (i.e. in the π -bond) from that where the two p-AOs are perpendicular. We denote the latter type of Coulomb repulsion energies by the superscript tw ($\gamma_{12}^{tw}, \gamma_{13}^{tw}$).

Using the Hückel MOs for planar and twisted allyl and the ZDO approximation, the J and K -integrals over MOs in eqns. 1 – 3 can be broken down into electron repulsion integrals between AOs in the planar and twisted geometries as follows:

$$J_{11}^{pl} = (3 \cdot \gamma_{11} + 4 \cdot \gamma_{12}^{pl} + \gamma_{13}^{pl}) / 8 ; \quad J_{11}^{tw} = (4 \cdot \gamma_{11} + 4 \cdot \gamma_{12}^{tw}) / 8 \quad (4)$$

$$J_{12}^{pl} = (2 \cdot \gamma_{11} + 4 \cdot \gamma_{12}^{pl} + 2 \cdot \gamma_{13}^{pl}) / 8 \quad J_{12}^{tw} = (4 \cdot \gamma_{12}^{tw} + 4 \cdot \gamma_{13}^{tw}) / 8 \quad (5)$$

$$K_{12}^{pl} = (2 \cdot \gamma_{11} - 2 \cdot \gamma_{13}^{pl}) / 8 ; \quad K_{12}^{tw} = 0 \quad (6)$$

$$J_{22}^{pl} = (4 \cdot \gamma_{11} + 4 \cdot \gamma_{13}^{pl}) / 8 ; \quad J_{22}^{tw} = \gamma_{11} \quad (7)$$

In order to keep the evaluations of the J and K integrals in eqns. 4 – 7 as simple as possible, we calculated all of these γ s at the geometries of the planar and twisted allyl cation (where the twisted CH_2 group is planar). We used the minimal STO-3G basis set, which assures, for example, that γ_{11} is the same in the anion, cation and radical. Perhaps surprisingly, but happily, the Hartree-Fock (HF)/STO-3G rotational barriers (calculated at the structures of planar \mathbf{A}^+ and \mathbf{A}^- and at the HF/STO-3G transition states for rotation, are in reasonable agreement with those from the above W1BD calculations (34.4 and 25.3 for \mathbf{A}^+ and \mathbf{A}^- from HF/STO-3G vs. 32.8 and 20.8 kcal/mol from W1BD).

For \mathbf{A}^\bullet things are a bit more complicated. The unrestricted (U)HF procedure overestimates the stabilizing effect of spin polarization in the planar radical and thus overestimates its barrier to rotation; whereas, the restricted open-shell (RO)HF method underestimates the barrier, largely due to the penchant of this method to localize the unpaired electron on one of the two CH_2 groups.¹ In fact, ROHF calculations with small basis sets find that the optimized geometry of even the planar allyl radical to consist of a $\bullet\text{CH}_2$ group attached to a localized ethene moiety by a C-C single bond.²

Fortunately, it is possible to sail safely between the Scylla of UHF and the Charybdis of ROHF¹ by performing a small CASSCF calculation, for which configurations are generated by distributing 3 electrons among the 3 π MOs. A (3/3)CASSCF/STO-3G calculation gives a

rotational barrier for \mathbf{A}^\bullet of 13.7 kcal/mol, which is very close to the value of 14.7 kcal/mol computed at the W1BD level.

It is certainly worth noting that an analogous (2/3)CASSCF calculation for \mathbf{A}^+ and (4/3)CASSCF for \mathbf{A}^- with the STO-3G basis set gives barriers (31.3 and 21.7 kcal/mol, respectively) that are even closer to the W1BD barriers (32.8 and 20.8 kcal/mol, respectively). This agreement shows that these calculated barriers depend very little on the level of sophistication of the methods that are used to compute them and thus instills a degree of confidence in our simple model calculations with the STO-3G basis set.

The STO-3G values for the γ s are listed in the top row of Table S-1. These values allow us to compute the J s and K s in equations 4-7 above. These Coulomb and exchange integrals are given in the second row of Table S-1. The differences between the J s and K s that are needed to compute the changes in the electron repulsion terms on twisting, using eqns. 1 – 3, are provided in the third row, while the differences in electron repulsion between the planar and the twisted forms are listed in the bottom row of Table S-1.

Table S-1: STO-3G values of the electron repulsion integrals (in kcal/mol) between AOs (first row) and between MOs (second row), in the planar (pl) and twisted (tw) allyl systems, calculated at the CAS(2,3)/3-21G geometry of the allyl cation. The third row gives the differences between the J s and K s in the planar and twisted geometries.

integral	γ_{11}	γ_{12}^{pl}	γ_{13}^{pl}	γ_{12}^{tw}	γ_{12}^{tw}	γ_{13}^{tw}		
value	422.2	212.9	133.1	221.8	196.9	128.3		
integral	J_{11}^{pl}	J_{11}^{tw}	J_{12}^{pl}	J_{12}^{tw}	K_{12}^{pl}	K_{12}^{tw}	J_{22}^{pl}	J_{22}^{tw}
value	281.4	317.5	245.3	162.6	72.3	0	277.6	422.2
difference	$J_{11}^{tw} - J_{11}^{pl}$		$J_{12}^{tw} - J_{12}^{pl}$		$K_{12}^{tw} - K_{12}^{pl}$		$J_{22}^{tw} - J_{22}^{pl}$	
value	36.1		-82.6		-72.3		144.6	
Δ_{elrep}^a	cation		radical		anion			
value	36.1		-56.8		-5.2			

^a difference in electron repulsion between the planar and the twisted form, see eq. 1-3

Due to the approximations that we made, the values of the numbers in the last row of Table S-1 are not even close to being quantitatively correct; but this simple model has the virtue of revealing why the allyl cation is calculated to have a higher barrier to rotation than the anion and why the anion has a higher barrier than the radical. The Coulombic repulsion (J_{11}) between the pair of electrons in the bonding MO is higher in the more localized ethylenic bonding π MO in the twisted geometry; and this tends to favor the planar geometry for \mathbf{A}^+ , \mathbf{A}^\bullet , and \mathbf{A}^- . In \mathbf{A}^\bullet the Coulombic repulsion between this pair of electrons and the electron in

the NBMO ($2J_{12} - K_{12}$) is far smaller in the twisted geometry, where the unpaired electron is localized on the twisted CH_2 group. This localization favors the twisted geometry not only in A^\bullet but also in A^- . However, in A^- both nonbonding electrons become localized in the AO on the twisted carbon; and their mutual Coulombic repulsion destabilizes the twisted geometry.

In order to examine the consequences of the approximations we made in our PPP-type calculations, there are mainly two types of possible errors to assess critically: (a) the differences in geometries between the cation, the radical, and the anion, and (b) the fact that the bonding and nonbonding MOs for the three species are not the same.

Concerning the geometries, the effect of the relaxation from the cation geometry on the rotational barrier is relatively small in the radical (2.2 kcal/mol at the planar, 4.8 kcal/mol at the twisted geometry), but much more pronounced in the anion (7.8 kcal/mol at the planar, 31.7 kcal/mol at the twisted geometry). At the planar geometry the stabilization is mainly due to the opening of the angle which decreases the 1,3-antibonding interaction in the NBMO; whereas, at the twisted geometry, the strong pyramidalization of the rotated CH_2^- group is primarily responsible for the even stronger stabilization.

While the effect of the changing angle could easily be accommodated in our above simple model (but would not change much), the consequences of pyramidalization on the PPP-type electron repulsion integrals is more difficult to model, because, instead of simple p-AOs, sp hybrids are involved, which cannot readily be dealt with in the PPP-approximation. However, we can assume that this pyramidalization decreases the repulsion between the pair of nonbonding and the pair of π -bonding electrons at the twisted geometry, because the main lobe points away from the π -bond, i.e. $\Delta_{\text{elrep}}(\text{A}^-)$ should be more negative than indicated in Table 2.

Obviously, allowing the AOs to shrink or expand as a function of the charge of the system will affect the electron repulsion integrals quite profoundly. However, the fact that the rotational barriers are quite insensitive to the basis set¹⁶ indicates that the planar and the twisted structure are similarly affected by this orbital relaxation, so the Δ_{elrep} should not change greatly as a consequence of it.

To account properly for all the above factors, we have computed the J s and K s directly in the basis of the SCF MOs, and we augmented the basis set to 6-311++G**, to allow for optimal orbital relaxation as the charge of the allyl system changes. By this approach the hyperconjugation in the twisted structures, which is quite pronounced (as can be seen from the SCF MOs shown in Figure S-1 of the Supporting Information), is also taken into account. Table S-2 shows the values we obtained for these integrals calculated at the SCF level.

Of course the Δ_{elrep} values change from those computed at the frozen geometries of the planar and twisted allyl cation with the STO-3G basis set. However, the order of these Δ_{elrep} values is still the same. Electron repulsion increases the barrier to CH_2 group rotation in the

cation, increases the barrier in the anion, but by less than in the cation, and decreases the barrier for the radical.

Table S-2: Values of the J - and K -integrals for \mathbf{A}^+ , \mathbf{A}^\bullet , and \mathbf{A}^- , calculated in the basis of the SCF MOs with the 6-311++G** basis set at the CAS(x,3)/3-21G-optimized geometries (x=2,3, or 4 electrons, respectively).

	J_{11}^{pl}	J_{11}^{tw}	J_{12}^{pl}	J_{12}^{tw}	K_{12}^{pl}	K_{12}^{tw}	J_{22}^{pl}	J_{22}^{tw}	Δ_{elrep}
\mathbf{A}^+	259.7	272.3	–	–	–	–	–	–	12.6
\mathbf{A}^\bullet	246.3	260.9	212.0	159.2	58.7	1.1	–	–	-33.5
\mathbf{A}^-	234.5	236.9	198.0	151.5	56.8	2.1	198.4	277.4	4.8

Even with the correct geometries and a big basis set, the values of Δ_{elrep} in Table S-2 focus on a small fraction of the total electron repulsion energies. In addition, there are other terms that contribute to the total energies (expectation values from the core hamiltonian, nuclear repulsion), which also change on twisting. Therefore, it is not to be expected that the Δ_{elrep} values in Table S-2 should reproduce exactly the differences in rotational barriers for the allyl cation, radical, and anion in Table 1 of the text. Nevertheless, the energies in Table S-2 allow us to explain qualitatively the origin of the differences between the rotational barriers in the allyl cation, radical, and anion in Table 1.

References

1. Bally, T.; Borden, W. T., *Rev. Comput. Chem.* **2007**, *13*, 1.
2. For a discussion, see: Davidson, E. R.; Borden, W. T., *J. Phys. Chem.* **1983**, *87*, 4783.

Total energies, thermal corrections, and cartesian coordinates of all stationary points located in this study.

1. planar allyl cation

=====
HF/STO-3G (C2v)

State=1-A1\HF=-114.8095268

Potential energy minimum

	X	Y	Z
6	0.000000	1.191981	-0.210808
6	0.000000	0.000000	0.493192
6	0.000000	-1.191981	-0.210808
1	0.000000	2.164291	0.305367
1	0.000000	1.218067	-1.310583
1	0.000000	0.000000	1.577570
1	0.000000	-2.164291	0.305367
1	0.000000	-1.218067	-1.310583

=====
CAS(2,3)/STO-3G (C2v)

State=1-A1\HF=-114.8447245

Potential energy minimum

	X	Y	Z
6	0.000000	1.203689	-0.212722
6	0.000000	0.000000	0.495972
6	0.000000	-1.203689	-0.212722
1	0.000000	2.171697	0.305916
1	0.000000	1.222661	-1.310165
1	0.000000	0.000000	1.585328
1	0.000000	-2.171697	0.305916
1	0.000000	-1.222661	-1.310165

=====
HF/3-21G (C2v)

State=1-A1\HF=-115.542137

Potential energy minimum

	X	Y	Z
6	0.000000	1.182332	-0.208313
6	0.000000	0.000000	0.484380
6	0.000000	-1.182332	-0.208313
1	0.000000	2.126975	0.302405
1	0.000000	1.209567	-1.283153
1	0.000000	0.000000	1.554969
1	0.000000	-2.126975	0.302405
1	0.000000	-1.209567	-1.283153

=====
CAS(2,3)/3-21G (C2v)

State=1-A1\HF=-115.5693337

Potential energy minimum

	X	Y	Z
6	0.000000	1.188906	-0.208825
6	0.000000	0.000000	0.485107
6	0.000000	-1.188906	-0.208825
1	0.000000	2.132593	0.302355
1	0.000000	1.213408	-1.283076

1	0.000000	0.000000	1.556696
1	0.000000	-2.132593	0.302355
1	0.000000	-1.213408	-1.283076

=====
HF/6-31G* (C2v)

State=1-A1\HF=-116.1932137

Potential energy minimum

	X	Y	Z
6	0.000000	1.178011	-0.211234
6	0.000000	0.000000	0.494724
6	0.000000	-1.178011	-0.211234
1	0.000000	2.131793	0.286125
1	0.000000	1.189964	-1.286928
1	0.000000	0.000000	1.568064
1	0.000000	-2.131793	0.286125
1	0.000000	-1.189964	-1.286928

=====
CAS(2,3)/6-31G* (C2v)

State=1-A1\HF=-116.2227009

Potential energy minimum

single-point energy with the 6-311++G** basis:

HF=-116.2511931

	X	Y	Z
6	0.000000	1.186608	-0.210450
6	0.000000	0.000000	0.490818
6	0.000000	-1.186608	-0.210450
1	0.000000	2.136372	0.293542
1	0.000000	1.201496	-1.285892
1	0.000000	0.000000	1.565192
1	0.000000	-2.136372	0.293542
1	0.000000	-1.201496	-1.285892

=====
B3LYP/6-31G(2df,p) (C1) (from G4 calculation)

State=1-A\E(RB3LYP)=-116.982152165

potential energy minimum

G4-energy:-116.861132 (enthalpy:-116.860188)

	X	Y	Z
6	1.187458	-0.211150	-0.000008
6	0.000000	0.494846	-0.000006
1	2.152403	0.291880	-0.000020
1	1.196126	-1.299589	0.000009
1	0.000001	1.580142	-0.000020
6	-1.187459	-0.211150	0.000014
1	-1.196123	-1.299589	0.000023
1	-2.152403	0.291880	0.000008

=====
B3LYP/cc-pVTZ+d (C1) (from W1BD calculation)

State=1-A\E(RB3LYP)=-117.013549598

potential energy minimum

W1BD-energy:-116.912513 (enthalpy:-116.911569)

	X	Y	Z
6	1.184679	-0.210400	-0.000007
6	-0.000001	0.492169	-0.000006
1	2.144835	0.293886	-0.000020

1	1.193474	-1.295164	0.000009
1	0.000002	1.574353	-0.000020
6	-1.184679	-0.210401	0.000013
1	-1.193468	-1.295164	0.000023
1	-2.144835	0.293886	0.000009

=====
B3LYP/6-311++G** (C1)

State=1-A\E(RB3LYP) = -117.001552484
Potential energy minimum

	X	Y	Z
6	1.188756	-0.210721	-0.000007
6	-0.000011	0.492247	-0.000006
1	2.149737	0.297291	-0.000019
1	1.201926	-1.298085	0.000005
1	0.000022	1.576804	-0.000018
6	-1.188758	-0.210731	0.000012
1	-1.201888	-1.298091	0.000029
1	-2.149722	0.297310	0.000005

2. twisted allyl cation

=====
HF/STO-3G (Cs)

State=1-A'\HF=-114.7546392
first oder saddle point

	X	Y	Z
6	-1.244762	0.021888	0.000000
6	0.000000	0.439393	0.000000
6	1.217433	-0.419066	0.000000
1	-1.526182	-1.028916	0.000000
1	-2.055802	0.746676	0.000000
1	0.299644	1.492271	0.000000
1	1.723158	-0.731663	0.948157
1	1.723158	-0.731663	-0.948157

=====
CAS(2,3)/STO-3G (Cs)

State=1-A1\HF=-114.8447245
first oder saddle point

	X	Y	Z
6	-1.268517	-0.012711	0.000000
6	0.000000	0.437215	0.000000
6	1.237073	-0.391749	0.000000
1	-1.521806	-1.068167	0.000000
1	-2.084174	0.702859	0.000000
1	0.271086	1.499888	0.000000
1	1.761777	-0.665554	0.950248
1	1.761777	-0.665554	-0.950248

=====
HF/3-21G (Cs)

State=1-A'\HF=-115.4878209
first oder saddle point

	X	Y	Z
6	-1.241287	-0.030039	0.000000
6	0.000000	0.407761	0.000000
6	1.220514	-0.351885	0.000000
1	-1.496335	-1.071677	0.000000

1	-2.052811	0.668642	0.000000
1	0.236366	1.473588	0.000000
1	1.718709	-0.612788	0.922519
1	1.718709	-0.612788	-0.922519

=====
CAS(2,3)/3-21G (Cs)

State=1-A'\HF=-115.51708731out
first oder saddle point
single-point energy with the 6-311++G** basis:
HF=-116.2511931

	X	Y	Z
6	-1.246060	-0.063509	0.000000
6	0.000000	0.423265	0.000000
6	1.228141	-0.328159	0.000000
1	-1.463372	-1.113119	0.000000
1	-2.076672	0.611615	0.000000
1	0.202809	1.494214	0.000000
1	1.722375	-0.591147	0.923291
1	1.722375	-0.591147	-0.923291

=====
HF/6-31G* (Cs)

State=1-A'\HF=-116.1389889
first oder saddle point

	X	Y	Z
6	-1.241877	-0.025842	0.000000
6	0.000000	0.416074	0.000000
6	1.218755	-0.360178	0.000000
1	-1.493662	-1.070332	0.000000
1	-2.053930	0.675106	0.000000
1	0.248985	1.477562	0.000000
1	1.718670	-0.631331	0.919900
1	1.718670	-0.631331	-0.919900

=====
CAS(2,3)/6-31G* (Cs)

State=1-A'\HF=-116.1673194
first oder saddle point
single-point energy with the 6-311++G** basis:
HF=-116.1967493:q!

	X	Y	Z
6	-1.248603	-0.057078	0.000000
6	0.000000	0.427501	0.000000
6	1.227306	-0.336313	0.000000
1	-1.467309	-1.108296	0.000000
1	-2.076956	0.623617	0.000000
1	0.220841	1.493768	0.000000
1	1.725602	-0.606876	0.920367
1	1.725602	-0.606876	-0.920367

=====
B3LYP/6-31G(2df,p) (C1) (from G4 calculation)

State=1-A\E(RB3LYP)=-116.923658577
second oder saddle point (a minor negative

frequency comes from the fixed C-C-C angle)
G4-energy:-116.809958 (enthalpy:-116.809013)

	X	Y	Z
6	-1.207292	-0.161242	-0.000002
6	0.058472	0.490119	0.000019
1	-1.726025	-0.429463	-0.930278
1	-1.726141	-0.429490	0.930198
1	0.059187	1.588928	-0.000009
6	1.166189	-0.263714	0.000000
1	1.153927	-1.347404	0.000032
1	2.134843	0.226449	-0.000043

=====
B3LYP/cc-pVTZ+d (C1) (from W1BD calculation)

State=1-A\E(RB3LYP)=-116.955847422
second order saddle point (a minor negative
frequency comes from the fixed C-C-C angle)
W1BD-energy:-116.861049 (enthalpy:-116.860105)

	X	Y	Z
6	-1.204707	-0.160919	-0.000002
6	0.057804	0.487461	0.000017
1	-1.719741	-0.425788	-0.928587
1	-1.719844	-0.425813	0.928515
1	0.061974	1.584394	-0.000008
6	1.163390	-0.262666	0.000000
1	1.150315	-1.343339	0.000029
1	2.128377	0.227291	-0.000038

=====
B3LYP/6-311++G** (C1)

State=1-A\E(RB3LYP) = -116.943563554
First order saddle point

	X	Y	Z
6	-1.207766	-0.161942	-0.000003
6	0.058106	0.489889	0.000019
1	-1.723569	-0.427581	-0.931018
1	-1.723685	-0.427611	0.930937
1	0.060824	1.588891	-0.000008
6	1.166053	-0.263680	0.000000
1	1.154946	-1.346788	0.000032
1	2.133120	0.227487	-0.000044

3. planar allyl radical

=====
UHF/STO-3G (C2v)

State=2-A2\HF=-115.0542911\S2=1.101186?
Potential energy minimum

	X	Y	Z
6	0.000000	1.240947	-0.201886
6	0.000000	0.000000	0.457930
6	0.000000	-1.240947	-0.201886
1	0.000000	2.171378	0.348054
1	0.000000	1.301571	-1.281704
1	0.000000	0.000000	1.542344
1	0.000000	-2.171378	0.348054
1	0.000000	-1.301571	-1.281704

ROHF/STO-3G (C2V symmetry enforced)

\State=2-A2\HF=-115.0118088
Potential energy minimum(!)
 X Y Z
6 0.000000 1.211185 -0.196226
6 0.000000 0.000000 0.446226
6 0.000000 -1.211185 -0.196226
1 0.000000 2.144230 0.348418
1 0.000000 1.274557 -1.275136
1 0.000000 0.000000 1.530792
1 0.000000 -2.144230 0.348418
1 0.000000 -1.274557 -1.275136

=====
ROHF/STO-3G (Cs symmetry enforced)

State=2-A"\HF=-115.0212741
first order saddle point (-> pyramidal. CH2)
 X Y Z
6 1.220700 -0.356127 0.000000
6 0.000000 0.453777 0.000000
6 -1.220501 -0.044215 0.000000
1 2.196073 0.106288 0.000000
1 1.163738 -1.434302 0.000000
1 0.139736 1.529366 0.000000
1 -2.097156 0.588007 0.000000
1 -1.403582 -1.109965 0.000000

=====
ROHF/STO-3G (no symmetry enforced)

State=2-A\HF=-115.0212743
potential energy minimum
 X Y Z
6 1.258313 0.184681 -0.008545
6 -0.062551 -0.449456 -0.000431
6 -1.202792 0.211864 0.001095
1 2.159955 -0.407704 0.027683
1 1.350219 1.260281 0.015408
1 -0.072283 -1.534085 0.000249
1 -2.158115 -0.293720 0.003742
1 -1.237599 1.292694 0.000204

=====
CAS(2,3)/STO-3G (C2v)

State=2-A2\HF=-115.0748693
Potential energy minimum
 X Y Z
6 0.000000 1.237225 -0.200605
6 0.000000 0.000000 0.454362
6 0.000000 -1.237225 -0.200605
1 0.000000 2.165958 0.350546
1 0.000000 1.300247 -1.279153
1 0.000000 0.000000 1.538296
1 0.000000 -2.165958 0.350546
1 0.000000 -1.300247 -1.279153

=====
UHF/3-21G (C2v)

State=2-A2\HF=-115.8230401\S2=0.974684

Potential energy minimum

	X	Y	Z
6	0.000000	1.227626	-0.198661
6	0.000000	0.000000	0.450220
6	0.000000	-1.227626	-0.198661
1	0.000000	2.149339	0.349250
1	0.000000	1.289221	-1.270853
1	0.000000	0.000000	1.525816
1	0.000000	-2.149339	0.349250
1	0.000000	-1.289221	-1.270853

=====
ROHF/3-21G (C2V symmetry enforced)

State=2-A2\HF=-115.7977668

(no frequency calculation possible)

	X	Y	Z
6	0.000000	1.211195	-0.195527
6	0.000000	0.000000	0.443652
6	0.000000	-1.211195	-0.195527
1	0.000000	2.133673	0.349330
1	0.000000	1.274154	-1.266822
1	0.000000	0.000000	1.519398
1	0.000000	-2.133673	0.349330
1	0.000000	-1.274154	-1.266822

=====
ROHF/3-21G (Cs symmtery enforced)

State=2-A"\HF=-115.8005791

Potential energy minimum

	X	Y	Z
6	1.217707	-0.308615	0.000000
6	0.000000	0.448746	0.000000
6	-1.217222	-0.087474	0.000000
1	2.172060	0.176327	0.000000
1	1.193925	-1.380410	0.000000
1	0.096690	1.519793	0.000000
1	-2.100982	0.519831	0.000000
1	-1.364601	-1.151484	0.000000

=====
CAS(2,3)/3-21G (C2v)

State=2-A2\HF=-115.8402426

Potential energy minimum

	X	Y	Z
6	0.000000	1.228022	-0.198329
6	0.000000	0.000000	0.449128
6	0.000000	-1.228022	-0.198329
1	0.000000	2.148602	0.350020
1	0.000000	1.290890	-1.269710
1	0.000000	0.000000	1.524561
1	0.000000	-2.148602	0.350020
1	0.000000	-1.290890	-1.269710


```

=====
UHF/6-31G* (C2v)
-----
State=2-A2\HF=-116.4680999\S2=0.972865
Potential energy minimum
      X           Y           Z
6      0.000000    1.230851   -0.198289
6      0.000000    0.000000    0.448532
6      0.000000   -1.230851   -0.198289
1      0.000000    2.152790    0.352839
1      0.000000    1.296108   -1.271968
1      0.000000    0.000000    1.526538
1      0.000000   -2.152790    0.352839
1      0.000000   -1.296108   -1.271968

```

```

=====
ROHF/6-31G* (C2v)
-----
State=2-A2\HF=-116.4428501
frequency calculation not possible
      X           Y           Z
6      0.000000    1.213822   -0.195689
6      0.000000    0.000000    0.443461
6      0.000000   -1.213822   -0.195689
1      0.000000    2.137332    0.351540
1      0.000000    1.277010   -1.268665
1      0.000000    0.000000    1.521745
1      0.000000   -2.137332    0.351540
1      0.000000   -1.277010   -1.268665

```

```

=====
ROHF/6-31G* (Cs)
-----
State=2-A"\HF=-116.4457928
frequency calculation not possible
      X           Y           Z
6      1.220634   -0.306995    0.000000
6      0.000000    0.446577    0.000000
6     -1.220367   -0.088091    0.000000
1      2.175682    0.180320    0.000000
1      1.202434   -1.380365    0.000000
1      0.093759    1.520589    0.000000
1     -2.103216    0.524456    0.000000
1     -1.370262   -1.153947    0.000000

```

```

=====
CAS(2,3)/6-31G* (C2v)
-----
State=2-A2\HF=-116.4835863
Potential energy minimum
single-point energy with the 6-311++G** basis:
HF=-116.5152663
      X           Y           Z
6      0.000000    1.231166   -0.197848
6      0.000000    0.000000    0.447178
6      0.000000   -1.231166   -0.197848
1      0.000000    2.151856    0.353754
1      0.000000    1.299089   -1.270783
1      0.000000    0.000000    1.525159

```

```

1      0.000000   -2.151856    0.353754
1      0.000000   -1.299089   -1.270783
=====
B3LYP/6-31G(2df,p) (C1) (from G4 calculation)
-----
State=2-A\E(UB3LYP)=-117.270872793
Potential energy minimum
G4-energy:-117.161927 (enthalpy:-117.160983)
      X           Y           Z
6      1.227456   -0.195280   -0.000005
6     -0.000002    0.441011   -0.000009
1      2.156261    0.362017   -0.000023
1      1.296468   -1.278356    0.000017
1      0.000004    1.529986   -0.000031
6     -1.227457   -0.195281    0.000013
1     -1.296455   -1.278358    0.000032
1     -2.156262    0.362014    0.000011
=====
B3LYP/cc-pVTZ+d (C1) (from W1BD calculation)
-----
State=2-A\E(RB3LYP)=-117.309273065
potential energy minimum
W1BD-energy:-117.211587 (enthalpy:-117.210643)
      X           Y           Z
6      1.224590   -0.195297   -0.000005
6     -0.000001    0.440549   -0.000009
1      2.149484    0.362340   -0.000023
1      1.292866   -1.275372    0.000016
1      0.000002    1.526337   -0.000030
6     -1.224590   -0.195297    0.000013
1     -1.292861   -1.275373    0.000034
1     -2.149485    0.362338    0.000009
=====
B3LYP/6-311++G** (C1)
-----
State=2-A\E(UB3LYP) = -117.298273923
Potential energy minimum
      X           Y           Z
6      1.228102   -0.196020   -0.000003
6     -0.000006    0.442224   -0.000010
1      2.155196    0.362803   -0.000020
1      1.296821   -1.278536    0.000021
1      0.000011    1.530390   -0.000034
6     -1.228104   -0.196023    0.000010
1     -1.296784   -1.278539    0.000028
1     -2.155198    0.362797    0.000021

```

4. twisted allyl radical

```

=====
UHF/STO-3G (Cs)
-----
State=2-A'\HF=-115.0158088\S2=0.772562
first oder saddle point
      X           Y           Z
6     -1.238111    0.007877    0.000000
6      0.000000    0.440429    0.000000
6      1.210823   -0.446581    0.000000
1     -1.481285   -1.046068    0.000000
1     -2.080709    0.685771    0.000000
1      0.192857    1.510710    0.000000

```

```
1      1.766431   -0.580382    0.921535
1      1.766431   -0.580382   -0.921535
```

=====
ROHF/STO-3G (Cs)

State=2-A'\HF=-115.0124915

first oder saddle point

	X	Y	Z
6	-1.239198	0.009941	0.000000
6	0.000000	0.435283	0.000000
6	1.205916	-0.459629	0.000000
1	-1.488077	-1.042544	0.000000
1	-2.078136	0.692191	0.000000
1	0.199692	1.504023	0.000000
1	1.783108	-0.533620	0.915701
1	1.783108	-0.533620	-0.915701

=====
CAS(2,3)/STO-3G (Cs)

State=2-A'\HF=-115.0547881

first oder saddle point

	X	Y	Z
6	-1.257609	-0.032537	0.000000
6	0.000000	0.443559	0.000000
6	1.226611	-0.423355	0.000000
1	-1.468329	-1.092879	0.000000
1	-2.113872	0.627229	0.000000
1	0.161625	1.517819	0.000000
1	1.803282	-0.489086	0.916142
1	1.803282	-0.489086	-0.916142

=====
UHF/3-21G (Cs)

State=2-A'\HF=-115.7927605\S2=0.86194

first oder saddle point

	X	Y	Z
6	-1.233656	-0.034272	0.000000
6	0.000000	0.452875	0.000000
6	1.223122	-0.382808	0.000000
1	-1.422900	-1.091096	0.000000
1	-2.092366	0.609665	0.000000
1	0.142730	1.522242	0.000000
1	1.717867	-0.627790	0.922143
1	1.717867	-0.627790	-0.922143

=====
ROHF/3-21G (Cs)

State=2-A'\HF=-115.7887007

first oder saddle point

	X	Y	Z
6	-1.232284	-0.019353	0.000000
6	0.000000	0.445312	0.000000
6	1.211968	-0.408975	0.000000
1	-1.438724	-1.072865	0.000000
1	-2.081408	0.637140	0.000000
1	0.162822	1.511379	0.000000
1	1.739604	-0.588778	0.917909
1	1.739604	-0.588778	-0.917909

=====
CAS(2,3)/3-21G (Cs)

State=2-A'\HF=-115.8183881

first oder saddle point

	X	Y	Z
6	-1.242633	-0.044671	0.000000
6	0.000000	0.452294	0.000000
6	1.224073	-0.387070	0.000000
1	-1.425469	-1.102468	0.000000
1	-2.103392	0.596613	0.000000
1	0.141497	1.521073	0.000000
1	1.749362	-0.569265	0.918257
1	1.749362	-0.569265	-0.918257

=====
UHF/6-31G* (Cs)

State=2-A'\HF=-116.4385098\S2=0.83542

first oder saddle point

	X	Y	Z
6	-1.238369	-0.031789	0.000000
6	0.000000	0.443770	0.000000
6	1.223016	-0.387791	0.000000
1	-1.440183	-1.088811	0.000000
1	-2.090575	0.624515	0.000000
1	0.140910	1.516328	0.000000
1	1.740982	-0.598585	0.919608
1	1.740982	-0.598585	-0.919608

=====
ROHF/6-31G* (Cs)

State=2-A'\HF=-116.4338996

first oder saddle point

	X	Y	Z
6	-1.237754	-0.020461	0.000000
6	0.000000	0.436302	0.000000
6	1.213199	-0.411825	0.000000
1	-1.453660	-1.074696	0.000000
1	-2.081672	0.646500	0.000000
1	0.157554	1.506298	0.000000
1	1.762555	-0.551099	0.914451
1	1.762555	-0.551099	-0.914451

=====
CAS(2,3)/6-31G* (Cs)

State=2-A'\HF=-116.4621532

first oder saddle point

single-point energy with the 6-311++G** basis:

HF=-116.493977

	X	Y	Z
6	-1.248495	-0.046119	0.000000
6	0.000000	0.442269	0.000000
6	1.225452	-0.388959	0.000000
1	-1.442061	-1.104306	0.000000
1	-2.104100	0.605368	0.000000

1	0.136752	1.514639	0.000000
1	1.773833	-0.529423	0.914628
1	1.773833	-0.529423	-0.914628

=====
B3LYP/6-31G(2df,p) (C1) (from G4 calculation)

State=2-A\E(UB3LYP)=-117.243240828

First order saddle point

G4-energy:-117.140014 (enthalpy:-117.139070)

	X	Y	Z
6	1.220224	-0.237154	0.000000
6	0.067822	0.430826	-0.000001
1	2.174350	0.279840	0.000000
1	1.251363	-1.322287	0.000000
1	0.109543	1.525160	0.000000
6	-1.271622	-0.167576	0.000000
1	-1.816902	-0.319648	-0.926464
1	-1.816898	-0.319644	0.926466

=====
B3LYP/cc-pVTZ+d (C1) (from W1BD calculation)

State=2-A\E(UB3LYP)=-117.281892941

First order saddle point

W1BD-energy:-117.188108 (enthalpy:-117.187164)

	X	Y	Z
6	1.216932	-0.237989	0.000000
6	0.068091	0.430337	0.000000
1	2.166524	0.280650	0.000001
1	1.245021	-1.320230	-0.000004
1	0.113605	1.521273	0.000003
6	-1.269686	-0.165060	0.000000
1	-1.808592	-0.322703	-0.925189
1	-1.808586	-0.322715	0.925190

=====
B3LYP/6-311++G** (C1)

State=2-A\E(UB3LYP) = -117.271134362

First order saddle point

	X	Y	Z
6	1.220329	-0.238854	0.000045
6	0.067785	0.432355	-0.000114
1	2.172189	0.280765	-0.000026
1	1.247859	-1.323539	0.000289
1	0.112323	1.525695	-0.000183
6	-1.272919	-0.165487	0.000016
1	-1.811766	-0.326108	-0.927696
1	-1.811772	-0.324896	0.927938

5. planar allyl anion

=====
HF/STO-3G (C2v)

State=1-A1\HF=-114.8384175

Potential energy minimum

	X	Y	Z
6	0.000000	1.253672	-0.176125
6	0.000000	0.000000	0.373580
6	0.000000	-1.253672	-0.176125
1	0.000000	2.132612	0.438564
1	0.000000	1.415590	-1.236439

1	0.000000	0.000000	1.467776
1	0.000000	-2.132612	0.438564
1	0.000000	-1.415590	-1.236439

=====
CAS(2,3)/STO-3G (C2v)

State=1-A1\HF=-114.8710059

second order saddle point

	X	Y	Z
6	0.000000	1.260189	-0.178950
6	0.000000	0.000000	0.382954
6	0.000000	-1.260189	-0.178950
1	0.000000	2.145492	0.428943
1	0.000000	1.419686	-1.241118
1	0.000000	0.000000	1.474019
1	0.000000	-2.145492	0.428943
1	0.000000	-1.419686	-1.241118

=====
CAS(2,3)/STO-3G (no symmetry, pyramidalized)

check!

State=1-A1\HF=-114.8710059

second order saddle point

	X	Y	Z
6	0.000000	1.260189	-0.178950
6	0.000000	0.000000	0.382954
6	0.000000	-1.260189	-0.178950
1	0.000000	2.145492	0.428943
1	0.000000	1.419686	-1.241118
1	0.000000	0.000000	1.474019
1	0.000000	-2.145492	0.428943
1	0.000000	-1.419686	-1.241118

=====
HF/3-21G

State=1-A1\HF=-115.7461332

Potential energy minimum

	X	Y	Z
6	0.000000	1.264876	-0.176930
6	0.000000	0.000000	0.376003
6	0.000000	-1.264876	-0.176930
1	0.000000	2.145093	0.444783
1	0.000000	1.420910	-1.243945
1	0.000000	0.000000	1.465461
1	0.000000	-2.145093	0.444783
1	0.000000	-1.420910	-1.243945

=====
CAS(2,3)/3-21G

State=1-A1\HF=-115.7673846

Potential energy minimum

	X	Y	Z
6	0.000000	1.269617	-0.178879
6	0.000000	0.000000	0.381809
6	0.000000	-1.269617	-0.178879
1	0.000000	2.152890	0.439463
1	0.000000	1.423350	-1.247124
1	0.000000	0.000000	1.471017
1	0.000000	-2.152890	0.439463

1 0.000000 -1.423350 -1.247124

=====
HF/6-31G*

State=1-A1\HF=-116.3934911

Potential energy minimum

	X	Y	Z
6	0.000000	1.270573	-0.174928
6	0.000000	0.000000	0.368167
6	0.000000	-1.270573	-0.174928
1	0.000000	2.145046	0.458352
1	0.000000	1.440139	-1.243101
1	0.000000	0.000000	1.459637
1	0.000000	-2.145046	0.458352
1	0.000000	-1.440139	-1.243101

=====
CAS(2,3)/6-31G* (C2v)

State=1-A1\HF=-116.4133991

second order saddle point

single-point energy with the 6-311++G** basis:

HF=-116.2511931

	X	Y	Z
6	0.000000	1.274965	-0.176753
6	0.000000	0.000000	0.373581
6	0.000000	-1.274965	-0.176753
1	0.000000	2.152404	0.452797
1	0.000000	1.443517	-1.245554
1	0.000000	0.000000	1.465061
1	0.000000	-2.152404	0.452797
1	0.000000	-1.443517	-1.245554

=====
CAS(2,3)/6-31G* (C2, pyramidalized)

State=1-A\HF=-116.4140757

potential energy minimum

single-point energy with the 6-311++G** basis:

HF=-116.4713863

	X	Y	Z
6	0.000000	1.275468	-0.176745
6	0.000000	0.000000	0.379202
6	0.000000	-1.275468	-0.176745
1	-0.284940	2.124577	0.432627
1	-0.130644	1.409667	-1.245064
1	0.000000	0.000000	1.470599
1	0.284940	-2.124577	0.432627
1	0.130644	-1.409667	-1.245064

=====
B3LYP/6-31G(2df,p) (C1) (from G4 calculation)

State=1-A\E(RB3LYP)=-117.254667596

Potential energy minimum

G4-energy:-117.180369 (enthalpy:-117.179425)

	X	Y	Z
6	1.277973	-0.174987	0.000013
6	0.000000	0.368816	-0.000002
1	2.160418	0.458929	-0.000026

1	1.449698	-1.251170	0.000024
1	0.000000	1.471423	-0.000025
6	-1.277973	-0.174987	-0.000020
1	-1.449698	-1.251170	0.000038
1	-2.160418	0.458929	0.000041

=====
B3LYP/cc-pVTZ+d (C1) (from W1BD calculation)

State=1-A\E(RB3LYP)=-117.314160692
Potential energy minimum
W1BD-energy:-117.229109 (enthalpy:-117.228164)

	X	Y	Z
6	1.274346	-0.177467	0.000005
6	0.000000	0.375889	-0.000004
1	2.155906	0.452834	-0.000024
1	1.436114	-1.252276	0.000020
1	0.000000	1.473154	-0.000025
6	-1.274346	-0.177467	-0.000007
1	-1.436113	-1.252276	0.000037
1	-2.155905	0.452834	0.000029

=====
B3LYP/6-311++G** (C1)

State=1-A\E(RB3LYP) = -117.314077118
Potential energy minimum

	X	Y	Z
6	1.274498	-0.180292	0.000010
6	-0.000007	0.384777	-0.000019
1	2.162162	0.444039	0.000021
1	1.425840	-1.257820	0.000033
1	0.000023	1.482438	-0.000028
6	-1.274505	-0.180295	-0.000018
1	-1.425776	-1.257831	0.000054
1	-2.162164	0.444032	0.000081

6. twisted allyl anion

=====
HF/STO-3G

State=1-A'\HF=-114.7981644
first oder saddle point

	X	Y	Z
6	-1.262818	0.003752	0.000000
6	0.000000	0.385099	0.000000
6	1.244215	-0.540828	0.000000
1	-1.545580	-1.037699	0.000000
1	-2.096173	0.694544	0.000000
1	0.114594	1.484086	0.000000
1	1.819387	-0.114536	0.852761
1	1.819387	-0.114536	-0.852761

=====
CAS(2,3)/STO-3G

State=1-A1\HF=-114.8447245
first oder saddle point

	X	Y	Z
6	-1.275998	-0.039373	0.000000
6	0.000000	0.398138	0.000000
6	1.262143	-0.503777	0.000000
1	-1.517943	-1.092484	0.000000

1	-2.136294	0.620044	0.000000
1	0.067559	1.499109	0.000000
1	1.834903	-0.078299	0.854144
1	1.834903	-0.078299	-0.854144

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=====
HF/3-21G

State=1-A'\HF=-115.7064361\
first oder saddle point

	X	Y	Z
6	-1.257879	-0.019098	0.000000
6	0.000000	0.405647	0.000000
6	1.223641	-0.504444	0.000000
1	-1.462211	-1.074811	0.000000
1	-2.107322	0.650760	0.000000
1	0.098621	1.503522	0.000000
1	1.838171	-0.186051	0.871976
1	1.838171	-0.186051	-0.871976

=====
CAS(2,3)/3-21G

State=1-A'\HF=-115.7334726
first oder saddle point

	X	Y	Z
6	-1.265588	-0.041744	0.000000
6	0.000000	0.416214	0.000000
6	1.232871	-0.486375	0.000000
1	-1.443409	-1.102414	0.000000
1	-2.130545	0.609032	0.000000
1	0.074861	1.515816	0.000000
1	1.847698	-0.175503	0.873670
1	1.847698	-0.175503	-0.873670

=====
HF/6-31G*

State=1-A'\HF=-116.1389889
first oder saddle point

	X	Y	Z
6	-1.259192	-0.042411	0.000000
6	0.000000	0.389763	0.000000
6	1.231823	-0.478379	0.000000
1	-1.469543	-1.100651	0.000000
1	-2.109585	0.629805	0.000000
1	0.070811	1.492334	0.000000
1	1.836265	-0.117661	0.861783
1	1.836265	-0.117661	-0.861783

=====
CAS(2,3)/6-31G*

State=1-A'\HF=-116.3863719
first oder saddle point
single-point energy with the 6-311++G** basis:
HF=-116.4451123

	X	Y	Z
6	-1.266445	-0.063318	0.000000
6	0.000000	0.399970	0.000000
6	1.240423	-0.461824	0.000000

1	-1.454139	-1.125619	0.000000
1	-2.131580	0.590362	0.000000
1	0.049853	1.503666	0.000000
1	1.845999	-0.108686	0.863217
1	1.845999	-0.108686	-0.863217

=====
B3LYP/6-31G(2df,p) (C1) (from G4 calculation)

State=1-A\E(RB3LYP)=-117.217199434

First order saddle point

G4-energy:-117.147735 (enthalpy:-117.146791)

	X	Y	Z
6	-1.247618	-0.196668	-0.000006
6	-0.036183	0.386720	0.000005
1	-2.180240	0.374568	0.000030
1	-1.325055	-1.283906	-0.000048
1	-0.126550	1.508823	0.000041
6	1.274097	-0.329305	-0.000029
1	1.844977	0.117887	0.856349
1	1.845090	0.118152	-0.856194

=====
B3LYP/cc-pVTZ+d (C1) (from W1BD calculation)

State=1-A\E(RB3LYP)=-117.277370158

First order saddle point

W1BD-energy:-117.197553 (enthalpy:-117.196609)

	X	Y	Z
6	-1.245569	-0.200090	-0.000001
6	-0.039984	0.387367	0.000001
1	-2.170720	0.377564	0.000005
1	-1.317027	-1.284792	-0.000009
1	-0.117657	1.503810	0.000008
6	1.269995	-0.311643	-0.000005
1	1.849369	0.074785	0.864904
1	1.849387	0.074832	-0.864880

=====
B3LYP/6-311++G** (C1)

State=1-A\E(RB3LYP) = -117.278825880

First order saddle point

	X	Y	Z
6	1.247497	-0.206369	0.000056
6	0.043600	0.393019	-0.000094
1	2.174922	0.370834	-0.000118
1	1.315996	-1.292641	0.000353
1	0.117172	1.509254	-0.000337
6	-1.271833	-0.287912	0.000160
1	-1.861554	0.009168	-0.884188
1	-1.862123	0.010958	0.883564

7. planar benzyl cation

=====
CAS(4,6)/3-21G

State=1-A1\HF=-267.4307213

potential energy minimum

	X	Y	Z
6	0.000000	0.000000	0.983925
6	0.000000	0.000000	-1.796970

6	0.000000	1.237575	0.255481
6	0.000000	-1.237575	0.255481
6	0.000000	-1.228053	-1.116602
6	0.000000	1.228053	-1.116602
1	0.000000	2.162470	0.796975
1	0.000000	-2.162470	0.796975
1	0.000000	-2.143505	-1.670108
1	0.000000	2.143505	-1.670108
1	0.000000	0.000000	-2.868963
6	0.000000	0.000000	2.337646
1	0.000000	-0.914020	2.900538
1	0.000000	0.914020	2.900538

=====
B3LYP/6-31G(2df,p) (from G4 calculation)

State=1-A1\HF=-270.6812673
potential energy minimum
G4-energy:-270.460553 (enthalpy:-270.459608)

	X	Y	Z
6	0.000000	0.000000	0.980416
6	0.000000	0.000000	-1.797783
6	0.000000	1.243961	0.253624
6	0.000000	-1.243961	0.253624
6	0.000000	-1.233603	-1.118712
6	0.000000	1.233603	-1.118712
1	0.000000	2.176188	0.808534
1	0.000000	-2.176188	0.808534
1	0.000000	-2.159288	-1.681415
1	0.000000	2.159288	-1.681415
1	0.000000	0.000000	-2.883861
6	0.000000	0.000000	2.347226
1	0.000000	-0.925990	2.915756
1	0.000000	0.925990	2.915756

=====
B3LYP/6-311++G** (Cs)

State=1-A'\E(RB3LYP) = -270.725073707
Potential energy minimum

	X	Y	Z
6	0.000014	0.981579	0.000000
6	0.000030	0.253588	1.244197
6	0.000030	-1.119187	1.233294
6	-0.000030	-1.799109	0.000000
6	0.000030	-1.119187	-1.233294
6	0.000030	0.253588	-1.244197
1	0.000030	0.805159	2.177557
1	0.000068	-1.681045	2.158748
1	-0.000167	-2.884252	0.000000
1	0.000068	-1.681045	-2.158748
1	0.000030	0.805159	-2.177557
6	-0.000074	2.349334	0.000000
1	-0.000103	2.916192	0.925906
1	-0.000103	2.916192	-0.925906

8. twisted benzyl cation

=====
CAS(4,6)/3-21G

State=1-A1\HF=-267.3495271
first order saddle point

	X	Y	Z
6	0.000000	0.944906	0.000000
6	0.000000	-1.814662	0.000000
6	0.000000	0.260806	1.223599
6	0.000000	0.260806	-1.223599
6	0.000000	-1.129096	-1.200365
6	0.000000	-1.129096	1.200365
1	0.000000	0.784723	2.158586
1	0.000000	0.784723	-2.158586
1	0.000000	-1.662149	-2.128775
1	0.000000	-1.662149	2.128775
1	0.000000	-2.885102	0.000000
6	0.000000	2.394926	0.000000
1	-0.923215	2.954331	0.000000
1	0.923215	2.954331	0.000000

=====
B3LYP/6-31G(2df,p) (from G4 calculation)

State=1-A\E(RB3LYP)=-270.605040313
First order saddle point
G4-energy:-270.388313 (enthaply:-270.387369)

	X	Y	Z
6	-0.963397	-0.000011	-0.112811
6	-0.266660	1.226813	-0.057013
6	1.127244	1.200814	0.012977
6	1.826566	0.000009	0.066476
6	1.127257	-1.200806	0.013028
6	-0.266647	-1.226823	-0.056960
1	-0.800579	2.167865	-0.073655
1	1.658559	2.145964	-0.033108
1	2.908588	0.000016	0.115282
1	1.658583	-2.145952	-0.033013
1	-0.800557	-2.167880	-0.073553
6	-2.372589	-0.000001	0.089483
1	-3.098382	-0.000015	-0.731637
1	-2.796849	0.000029	1.098597

=====
B3LYP/6-311++G** (C1)

State=1-A\E(RB3LYP) = -270.649360713
First order saddle point

	X	Y	Z
6	0.964065	0.000012	-0.112856
6	0.266801	-1.226778	-0.058477
6	-1.127867	-1.201337	0.012801
6	-1.826788	-0.000001	0.068216
6	-1.127882	1.201327	0.012547
6	0.266830	1.226795	-0.058064
1	0.797568	-2.169007	-0.079611
1	-1.660129	-2.145165	-0.031906
1	-2.908146	0.000027	0.117633
1	-1.660189	2.145090	-0.033078
1	0.797572	2.169045	-0.078638
6	2.375219	0.000021	0.091541
1	3.098001	0.000307	-0.730555
1	2.793052	-0.000533	1.101916

9. planar benzyl radical

=====
CAS(4,6)/3-21G (C2v)

```

-----
\State=2-B1\HF=-267.6620294
potential energy minimum
      X           Y           Z
6      0.000000    0.000000    0.982380
6      0.000000    0.000000   -1.828319
6      0.000000    1.209630    0.251397
6      0.000000   -1.209630    0.251397
6      0.000000   -1.199235   -1.135709
6      0.000000    1.199235   -1.135709
1      0.000000    2.141565    0.782570
1      0.000000   -2.141565    0.782570
1      0.000000   -2.127149   -1.672960
1      0.000000    2.127149   -1.672960
1      0.000000    0.000000   -2.900414
6      0.000000    0.000000    2.408197
1      0.000000   -0.918823    2.959693
1      0.000000    0.918823    2.959693

```

```

=====
B3LYP/6-31G(2df,p) (from G4 calculation)
-----

```

```

State=2-B1\HF=-270.9341523G
potential energy minimum
G4-energy:-270.728922 (enthaply:-270.727978)
      X           Y           Z
6      0.000000    0.000000    0.993480
6      0.000000    0.000000   -1.835697
6      0.000000    1.215556    0.251266
6      0.000000   -1.215556    0.251266
6      0.000000   -1.209244   -1.131119
6      0.000000    1.209244   -1.131119
1      0.000000    2.156346    0.793175
1      0.000000   -2.156346    0.793175
1      0.000000   -2.149485   -1.673329
1      0.000000    2.149485   -1.673329
1      0.000000    0.000000   -2.920167
6      0.000000    0.000000    2.396267
1      0.000000   -0.927082    2.957213
1      0.000000    0.927082    2.957213

```

```

=====
B3LYP/6-311++G** (Cs)
-----

```

```

State=2-A'\E(UB3LYP) = -270.987311951
Potential energy minimum
      X           Y           Z
6     -0.000194    0.994266    0.000000
6      0.000100    0.251577    1.216887
6      0.000100   -1.132022    1.210342
6      0.000041   -1.837104    0.000000
6      0.000100   -1.132022   -1.210342
6      0.000100    0.251577   -1.216887
1      0.000233    0.790927    2.158163
1      0.000177   -1.674216    2.149609
1     -0.000011   -2.920805    0.000000
1      0.000177   -1.674216   -2.149609
1      0.000233    0.790927   -2.158163
6     -0.000325    2.398913    0.000000
1     -0.000171    2.958140    0.927240
1     -0.000171    2.958140   -0.927240

```

10. twisted benzyl radical

=====
CAS(4,6)/3-21G (Cs, almost C2v)

State=2-A'\HF=-267.6509684
first order saddle point

	X	Y	Z
6	0.000000	0.961426	0.000000
6	-0.000041	-1.836082	0.000000
6	1.202178	0.248499	0.000000
6	-1.202159	0.248524	0.000000
6	-1.196981	-1.143231	0.000000
6	1.196985	-1.143234	0.000000
1	2.132070	0.782593	0.000000
1	-2.132048	0.782622	0.000000
1	-2.126808	-1.677323	0.000000
1	2.126796	-1.677355	0.000000
1	-0.000052	-2.908214	0.000000
6	0.000015	2.449182	0.000000
1	0.000028	2.993587	0.923533
1	0.000028	2.993587	-0.923533

=====
B3LYP/6-31G(2df,p) (from G4 calculation)

State=2-A\E(UB3LYP) = -270.911529581
First order saddle point
G4-energy:-270.711482 (enthalpy:-270.710537)

	X	Y	Z
6	0.969551	0.000000	0.000000
6	0.249170	-1.202832	-0.000020
6	-1.143051	-1.203060	-0.000020
6	-1.844450	0.000000	0.000001
6	-1.143051	1.203060	0.000021
6	0.249170	1.202832	0.000020
1	0.790497	-2.143474	-0.000037
1	-1.679859	-2.146331	-0.000036
1	-2.929381	0.000000	0.000001
1	-1.679859	2.146331	0.000037
1	0.790497	2.143474	0.000036
6	2.444766	0.000000	-0.000001
1	3.007741	0.000015	-0.927699
1	3.007742	-0.000016	0.927697

=====
B3LYP/6-311++G** (C1)

State=2-A\E(RB3LYP) = -270.964950427
First order saddle point

	X	Y	Z
6	0.970274	-0.000001	0.000003
6	0.249757	-1.204126	-0.000009
6	-1.143903	-1.203840	-0.000008
6	-1.845923	0.000001	0.000004
6	-1.143901	1.203841	0.000007
6	0.249760	1.204125	0.000002
1	0.789272	-2.144937	-0.000021
1	-1.680559	-2.146314	-0.000015
1	-2.930094	0.000002	0.000007
1	-1.680556	2.146316	0.000014
1	0.789276	2.144935	0.000003
6	2.447287	-0.000001	0.000003
1	3.006274	0.000160	-0.929152
1	3.006275	-0.000158	0.929158

11. planar benzyl anion

=====
CAS(4,6)/3-21G (C2v)

State=1-A1\HF=-267.6175902

potential energy minimum

	X	Y	Z
6	0.000000	0.000000	1.038988
6	0.000000	0.000000	-1.863137
6	0.000000	1.212981	0.240024
6	0.000000	-1.212981	0.240024
6	0.000000	-1.190357	-1.135397
6	0.000000	1.190357	-1.135397
1	0.000000	2.158138	0.756204
1	0.000000	-2.158138	0.756204
1	0.000000	-2.129690	-1.666100
1	0.000000	2.129690	-1.666100
1	0.000000	0.000000	-2.937312
6	0.000000	0.000000	2.415356
1	0.000000	-0.918659	2.977167
1	0.000000	0.918659	2.977167

=====
UB3LYP/6-31G(2df,p) (Cs) (from G4 calculation)

State=1-A'\E(RB3LYP) = -270.941745773

potential energy minimum

G4-energy:-270.763479 (enthalpy:-270.762535)

	X	Y	Z
6	0.000027	1.043226	0.000000
6	0.000020	0.242331	1.209670
6	0.000020	-1.137360	1.195446
6	-0.000038	-1.877630	0.000000
6	0.000020	-1.137360	-1.195446
6	0.000020	0.242331	-1.209670
1	-0.000005	0.766425	2.165293
1	0.000011	-1.667326	2.150236
1	0.000216	-2.963230	0.000000
1	0.000011	-1.667326	-2.150236
1	-0.000005	0.766425	-2.165293
6	-0.000077	2.422733	0.000000
1	-0.000087	2.987704	0.927716
1	-0.000087	2.987704	-0.927716

=====
B3LYP/6-311++G** (Cs)

State=1-A'\E(RB3LYP) = -271.017953503

Potential energy minimum

	X	Y	Z
6	0.000062	1.037380	0.000000
6	0.000021	0.243445	1.211190
6	0.000021	-1.138740	1.199188
6	-0.000147	-1.877672	0.000000
6	0.000021	-1.138740	-1.199188
6	0.000021	0.243445	-1.211190
1	0.000027	0.767424	2.164999
1	-0.000030	-1.668948	2.151395
1	0.000490	-2.962413	0.000000
1	-0.000030	-1.668948	-2.151395

1	0.000027	0.767424	-2.164999
6	-0.000067	2.428048	0.000000
1	-0.000037	2.991231	0.927787
1	-0.000037	2.991231	-0.927787

12. twisted benzyl anion

=====
CAS(4,6)/3-21G (Cs, almost C2v)

State=1-A'\HF=-267.5746967

first order saddle point

	X	Y	Z
6	0.000000	0.991796	0.000000
6	-1.193242	0.252406	0.000000
6	-1.223451	-1.127751	0.000000
6	-0.037846	-1.861430	0.000000
6	1.172729	-1.171949	0.000000
6	1.184295	0.222471	0.000000
1	-2.099503	0.825009	0.000000
1	-2.167065	-1.645242	0.000000
1	-0.057036	-2.936184	0.000000
1	2.099470	-1.719891	0.000000
1	2.125830	0.741206	0.000000
6	-0.062970	2.529353	0.000000
1	0.530606	2.862862	0.875393
1	0.530606	2.862862	-0.875393

=====
B3LYP/6-31G(2df,p) (from G4 calculation)

State=1-A\E(RB3LYP) = -270.895466362

first order saddle point

G4-energy:-270.726427 (enthaply:-270.725483)

	X	Y	Z
6	-1.011736	-0.045063	0.000052
6	-0.207229	-1.207442	0.000028
6	1.187371	-1.175788	-0.000044
6	1.866310	0.042347	-0.000096
6	1.116273	1.220351	-0.000077
6	-0.276220	1.168252	-0.000007
1	-0.744243	-2.153194	0.000074
1	1.751756	-2.107950	-0.000057
1	2.953451	0.075844	-0.000149
1	1.626260	2.184216	-0.000115
1	-0.842293	2.098693	0.000007
6	-2.514174	-0.172599	0.000143
1	-2.854204	0.461075	0.857393
1	-2.854300	0.460961	-0.857151

=====
B3LYP/6-311++G** (C1)

State=1-A\E(RB3LYP) = -270.977388113

First order saddle point

	X	Y	Z
6	1.006956	-0.044352	0.000536
6	0.208790	-1.210484	0.000270
6	-1.187754	-1.177138	-0.000100
6	-1.867851	0.041582	-0.000222
6	-1.119663	1.221293	0.000039

6	0.275526	1.171760	0.000281
1	0.739997	-2.157108	0.000221
1	-1.749040	-2.109066	-0.000352
1	-2.953921	0.073285	-0.000501
1	-1.627929	2.184075	-0.000163
1	0.841822	2.099161	0.000067
6	2.505897	-0.144993	-0.000461
1	2.908135	0.382227	-0.883407
1	2.909527	0.381424	0.882082

13. Methane

=====
 B3LYP/6-31G(2df,p) (Td) (from G4 calculation)

State=1-A1\E(RB3LYP) = -40.5236859938

Potential energy minimum

G4-energy:-40.462426 (enthalpy:-40.461481)

	X	Y	Z
6	0.000000	0.000000	0.000000
1	0.630364	0.630364	0.630364
1	-0.630364	-0.630364	0.630364
1	-0.630364	0.630364	-0.630364
1	0.630364	-0.630364	-0.630364

14. Methyl cation

=====
 B3LYP/6-31G(2df,p) (D3h) (from G4 calculation)

State=1-A1'\E(RB3LYP) = -39.4848566083

Potential energy minimum

G4-energy:-39.434823 (enthalpy:-39.433879)

	X	Y	Z
6	0.000000	0.000000	0.000000
1	0.000000	1.095321	0.000000
1	-0.948576	-0.547661	0.000000
1	0.948576	-0.547661	0.000000

15. Methyl radical

=====
 B3LYP/6-31G(2df,p) (D3h) (from G4 calculation)

State=2-A2"\E(UB3LYP) = -39.8433559259

Potential energy minimum

G4-energy:-39.796857 (enthalpy:-39.795913)

	X	Y	Z
6	0.000000	0.000000	0.000000
1	0.000000	1.081657	0.000000
1	-0.936742	-0.540828	0.000000
1	0.936742	-0.540828	0.000000

16. Methyl anion

=====
 B3LYP/6-31G(2df,p) (D3h) (from G4 calculation)

State=1-A1\E(RB3LYP) = -39.8000335451

Potential energy minimum

G4-energy:-39.796576 (enthaply:-39.795632)

	X	Y	Z
6	0.000000	0.000000	0.180122
1	0.000000	0.993712	-0.360244
1	-0.860580	-0.496856	-0.360244
1	0.860580	-0.496856	-0.360244

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