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NON-PLANAR STRUCTURES OF THE PENTAFLUOROALLYL AND 1,1-DIFLUOROALLYL ANIONS

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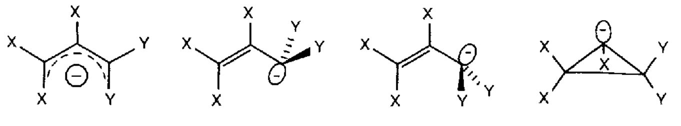
ABSTRACT

The structures of the allyl anion (**1**) and two fluoro-substituted derivatives, perfluoro (**2**) and 1,1-difluoro (**3**) have been calculated by *ab inito* molecular orbital theory. Geometries were gradient optimized, and force fields and an MP-2 correlation correction were determined at stationary points. The calculations were done with a double zeta basis set augmented by d functions on carbon (DZ + D_C). Final self-consistent field (SCF) and MP-2 energy calculations were done with the DZ + D_C basis set augmented by diffuse functions. The ground state of **1** is the planar allyl anion (C_{2v}). The rotation barrier in **1** is 21·1 kcal/mol at the MP-2 level. The cyclopropyl carbanion is 27·0 kcal/mol higher in energy at the MP-2 level. The perfluoroallyl anion is not planar, and the rotated structure is 25·7 kcal/mol more stable than the C_{2v} structure at the MP-2 level. The lowest energy structure on the potential energy surface for **2** is the perfluorocyclopropyl carbanion which is 27·8 kcal/mol more stable than the C_{2v} structure at the MP-2 level. The 1,1-difluoroallyl anion is also not planar. Here the most stable structure on the potential energy surface is the rotated allyl anion which is 8·3 kcal/mol more stable than the all-planar allyl anion structure.

The planar, delocalized allyl radical and anion with their associated out-of-plane p orbitals are well accepted structures that play a central role in molecular orbital theory as models for orbital interactions and electronic effects. Both the radical and anion possess substantial delocalization energies and are known experimentally to have high barriers to internal rotation about the allyl bond, 15·7 ± 1 kcal/mol for the allyl radical[1] and 18·0 ± 0·3 kcal/mol for allylcesium in solution.[2] Our finding some time ago that replacement of all the hydrogens by fluorines lowers the rotational barrier in the allyl radical by over 9 kcal/mol[3] and our current



A B C D

1 X=Y=H
2 X=Y=F
3 X=H, Y=F

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interest in polyfluorinated anions[4] prompted us to investigate the effects of fluorination on the allyl anion. We report here an *ab initio* molecular orbital study of the title anions which show that they do not exist as classical, planar structures but instead have minimum energy structures which closely resemble the transition state for rotation in the parent allyl anion!

The geometries of the allyl anions in conformations **A**–**C** and the isomeric cyclopropyl anions **D** were gradient optimized[5] using the programs HONDO[6] on an IBM/3081 and GRADSCF on a CRAY-1A. (GRADSCF is an ab initio gradient program system designed and written by A. Komornicki at Polyatomics Research). The optimizations were performed with a double-ζ basis set augmented by polarization functions on all carbon atoms ($\mathrm{DZ} + \mathrm{D_C}$).[7] The force fields were determined analytically[8] at the stationary points as were correlation corrections at the MP-2 level[9] using the program GRADSCF. Subsequent SCF and MP-2 energy calculations were done at the $\mathrm{DZ} + \mathrm{D_C}$ geometries with the $\mathrm{DZ} + \mathrm{D_C}$ basis set augmented by diffuse functions ($\mathrm{DZ} + \mathrm{D_C}$ + Diff). For the $\mathrm{DZ} + \mathrm{D_C}$ + Diff basis set, a set of diffuse p functions[7] was added to the C and F basis sets and a diffuse s orbital ($\alpha(1s) = 0{\cdot}049$) was added to the H basis set. The results are given in Table 1 together with the number of imaginary frequencies for each optimized conformation which define whether the structure is a minimum (all positive directions of curvature), a transition state (one negative direction of curvature), or a point with a given symmetry on the potential energy hypersurface (more than one negative direction of curvature). The occupied orbital eigenvalues are negative for all allyl and cyclopropyl structures.

Table 1. Relative energies for allyl and cyclopropyl anions[a]

	ΔE (SCF)		ΔE (MP-2)		iv[b]
Anion	$\mathrm{DZ} + \mathrm{D_C}$[c]	$\mathrm{DZ} + \mathrm{D_C}$ + Diff[d]	$\mathrm{DZ} + \mathrm{D_C}$[c]	$\mathrm{DZ} + \mathrm{D_C}$ + Diff[d]	
1A	0·0[e]	0·0[f]	0·0	0·0	0
1B	21·3	20·6	23·0	21·1	1
1C	22·8	22·8	24·3	23·5	1
1D	30·5	31·5	26·7	27·0	0
2A	26·8	25·7	28·8	27·8	3
2B	−0·8	−2·2	4·0	2·1	0
2C	2·1	1·0	6·5	5·0	1
2D	0·0[g]	0·0[h]	0·0	0·0	0
3A	10·0	11·1	5·5	8·3	2
3B	0·0[i]	0·0[j]	0·0	0·0	0
3C	6·2	6·5	5·5	6·3	1
3D	10·5	13·3	3·7	8·5	0

[a] Energies in kcal/mol given relative to the most stable isomer at the MP-2 level.

[b] Number of imaginery frequencies (number of negative directions of curvature) determined with the $\mathrm{DZ} + \mathrm{D_C}$ basis set.

[c] Double-ζ basis set, carbon atoms polarized.

[d] $\mathrm{DZ} + \mathrm{D_C}$ basis set augmented by diffuse functions.

[e] **1A**. $E(\mathrm{SCF}) = -116{\cdot}424714$ au. $E(\mathrm{MP\text{-}2}) = -116{\cdot}807108$ au.

[f] **1A**. $E(\mathrm{SCF}) = -116{\cdot}436554$ au. $E(\mathrm{MP\text{-}2}) = -116{\cdot}828967$ au.

[g] **2D**. $E(\mathrm{SCF}) = -610{\cdot}803876$ au. $E(\mathrm{MP\text{-}2}) = -611{\cdot}712752$ au.

[h] **2D**. $E(\mathrm{SCF}) = -610{\cdot}813796$ au. $E(\mathrm{MP\text{-}2}) = -611{\cdot}738790$ au.

[i] **3B**. $E(\mathrm{SCF}) = -314{\cdot}185270$ au. $E(\mathrm{MP\text{-}2}) = -314{\cdot}771392$ au.

[j] **3B**. $E(\mathrm{SCF}) = -314{\cdot}198893$ au. $E(\mathrm{MP\text{-}2}) = -314{\cdot}800769$ au.

As expected, the parent allyl anion has the planar C_{2v} structure **1A**. Its rotational barrier via transition state **1B** is 20·6 kcal/mol at the SCF level and 21·1 kcal/mol at the MP-2 level, which compare to a barrier of 23·6 kcal/mol through **1B** calculated by Schleyer and co-workers at the MP-2/4-31+G level.[10] The isomeric cyclopropyl anion **1D** is also an energy minimum structure, but lies 27·0 kcal/mol above **1A** at the MP-2 level. This is substantially less than the 41·0 kcal/mol difference in energy between **1D** and **1A** found previously at the MP-2/4-31+G level. The discrepancy at the 4-31+G level can be largely attributed to the absence of d functions which stabilize strained rings.[11]

Fluorination dramatically affects the allyl anion conformation and the relative energy of the cyclopropyl anion. *The perfluoroallyl anion is not planar.* The rotated structure **2B** is the energy minimum allyl conformer and the perfluorocyclopropyl anion **2D** is only 2·2 kcal/mol higher in energy at the SCF level. When correlation is included, **2D** is actually more stable than **2B** by 2·1 kcal/mol. The classical anion structure with C_{2v} symmetry is 25·7 kcal/mol above **2B**, but it has three negative directions of curvature and is simply a high energy point on the potential energy hypersurface.

The gem-difluoro structures **3A–3D** are closer together in energy, but the rotated structure **3B** is still the lowest energy allyl conformer. The 2,2-difluorocyclopropyl anion **3D** is higher in energy than **3B** at the MP-2 level, which is opposite to the case for the perfluorinated isomers. Although the planar C_s structure **3A** is moderately close in energy to **3B**, it is characterized by two negative directions of curvature and is not a minimum on the energy surface.

These results clearly show that the planar form of the allyl anion is markedly destabilized upon substitution of hydrogen by fluorine at the terminal carbons. We believe that the proclivity of α-fluorinated carbanions to be pyramidal is the principal reason for this destabilization. Notably, the vertex inversion barrier for CH_3^- is less than 2 kcal/mol,[12] whereas the inversion barriers for CH_2F^-, CHF_2^-, and CF_3^- are calculated to be 14·0, 45·6, and 106·0 kcal/mol, respectively, at the MP-2/DZ + D_C + Diff level. These values compare to SCF values of 17·5 and 17·2 kcal/mol for CH_2F^- with a polarized double-ζ basis set augmented by diffuse functions,[13] and 119·1 kcal/mol for CF_3^- with a large Slater basis set.[14] For CH_2F^-, a value of 13·8 kcal/mol is reported at the MP-2/6-31+G* level.[13b] From a simple model of the allyl anion with excess charge of −0·5e on the terminal methylenes, we can roughly estimate the energy of pyramidalization at each CF_2 group to be one half of the inversion barrier of CHF_2^-, 22·8 kcal/mol. From the energy difference between **1A** and **1B** of 21·1 kcal/mol for the parent allyl anion and the 22·8 kcal/mol favoring pyramidalization, we estimate that the planar 1,1-difluoroallyl anion (**3A**) should be about 2 kcal/mol above the rotated pyramidal form **3B**, which compares to the MP-2 value of 8·3 kcal/mol. Similarly for the perfluoroallyl anion where pyramidalization is favored by about 46 kcal/mol (2 CF_2 sites each with a charge of −0·5e) compared with the 21·1 kcal/mol barrier for rotation, **2A** is estimated to lie 25 kcal/mol above **2B**, which is essentially the same as the calculated value of 25·7 at the MP-2 level. Albeit admittedly oversimpified, this analysis suggests that pyramidalization of the negatively charged CF_2 groups is indeed the predominant effect on conformation of the fluorinated allyl anions.

Our results directly bear on the chemistry of the 1,1-difluoroallyl anion in solution. Seyferth and coworkers have generated $[CF_2CHCH_2]^- Li^+$ *in situ*, trapped it with a variety of electrophiles, and found that the electrophiles always add regiospecifically to the CF_2 terminus.[15] This regiospecificity may be a consequence of the rotated structure of the anion **3B**. Clearly negative charge is highly localized on the CF_2 group in **3B** which makes it the preferred site of electrophilic attack, and thus the observed regiospecificity can be readily accounted for without invoking specific Li counterion interactions.[15] Of course, this explanation presupposes 1,1-difluoroallyllithium is a separated ion pair. Detailed calculations on 1,1-difluoroallyllithium itself are required to confirm that **3B** is a suitable electronic model for this organolithium species.

We plan to further investigate the potential energy surfaces that connect the fluorinated allyl anion conformers and cyclopropyl anion isomers, and to experimentally test the prediction that the rearrangement of the perfluoroallyl to the perfluorocyclopropyl anion is favorable thermodynamically.

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APPENDIX

The following are the molecular coordinates for **1–3** (**A–D**) in atomic units.

1A

Molecular coordinates

Atom	*X*	*Y*	*Z*
Carbon	0·000000	0·000000	2·980086
Carbon	−2·412101	0·000000	4·026816
Carbon	2·412101	0·000000	4·026816
Hydrogen	−2·715811	0·000000	6·048623
Hydrogen	2·715811	0·000000	6·048623
Hydrogen	−4·065039	0·000000	2·829367
Hydrogen	4·065039	0·000000	2·829367
Hydrogen	0·000000	0·000000	0·920944

1B

Molecular coordinates

Atom	*X*	*Y*	*Z*
Carbon	−0·071204	−0·552009	0·000000
Carbon	2·759030	−0·132855	0·000000
Carbon	3·953175	2·101032	0·000000
Hydrogen	4·067092	−1·749315	0·000000
Hydrogen	2·889339	3·841572	0·000000
Hydrogen	5·998048	2·244456	0·000000
Hydrogen	−0·450476	−1·794016	−1·641931
Hydrogen	−0·450476	−1·794016	1·641931

1C

Molecular coordinates

Atom	*X*	*Y*	*Z*
Carbon	−0·100562	−0·644114	0·000000
Carbon	2·719373	−0·061353	0·000000
Carbon	3·977659	2·144334	0·000000
Hydrogen	3·983956	−1·693652	0·000000
Hydrogen	3·006964	3·945163	0·000000
Hydrogen	6·028618	2·212871	0·000000
Hydrogen	−0·916841	0·337844	−1·645237
Hydrogen	−0·916841	0·337844	1·645237

1D

Atom	Molecular coordinates *X*	*Y*	*Z*
Carbon	1·790165	0·000000	−0·136861
Carbon	−0·734437	1·429772	−0·002338
Carbon	−0·734437	−1·429772	−0·002338
Hydrogen	−1·418158	−2·327174	1·720591
Hydrogen	−1·418158	2·327174	1·720591
Hydrogen	−1·423546	−2·404085	−1·677782
Hydrogen	−1·423546	2·404085	−1·677782
Hydrogen	2·623730	0·000000	1·766720

2A

Atom	Molecular coordinates *X*	*Y*	*Z*
Fluorine	0·000000	0·000000	0·407358
Carbon	0·000000	0·000000	2·965532
Carbon	−2·356585	0·000000	3·993557
Carbon	2·356585	0·000000	3·993557
Fluorine	−2·837821	0·000000	6·517125
Fluorine	2·837821	0·000000	6·517125
Fluorine	−4·556724	0·000000	2·658154
Fluorine	4·556724	0·000000	2·658154

2B

Atom	Molecular coordinates *X*	*Y*	*Z*
Fluorine	−0·369110	−2·350305	−2·079238
Fluorine	−0·369110	−2·350305	2·079238
Carbon	−0·409933	−0·650859	0·000000
Carbon	2·767592	−0·228271	0·000000
Carbon	3·841960	2·005174	0·000000
Fluorine	4·403829	−2·202436	0·000000
Fluorine	2·693774	4·215237	0·000000
Fluorine	6·327207	2·396436	0·000000

2C

Molecular coordinates

Atom	X	Y	Z
Fluorine	−1·044742	0·710996	−2·075802
Fluorine	−1·044742	0·710996	2·075802
Carbon	−0·095152	−0·734973	0·000000
Carbon	2·719316	−0·117180	0·000000
Carbon	3·890016	2·060184	0·000000
Fluorine	4·261165	−2·161012	0·000000
Fluorine	2·788682	4·293717	0·000000
Fluorine	6·385825	2·385372	0·000000

2D

Molecular coordinates

Atom	X	Y	Z
Carbon	1·636593	−0·116383	0·000000
Carbon	−0·727212	−0·026443	−1·394420
Carbon	−0·727212	−0·026443	1·394420
Fluorine	−1·741219	2·079203	−2·487009
Fluorine	−1·741219	2·079203	2·487009
Fluorine	−1·478926	−1·963936	−2·923712
Fluorine	−1·478926	−1·963936	2·923712
Fluorine	3·219138	1·999291	0·000000

3A

Molecular coordinates

Atom	X	Y	Z
Hydrogen	0·091912	0·924171	0·000000
Carbon	−0·011782	2·967842	0·000000
Carbon	−2·446553	4·042042	0·000000
Carbon	2·310658	3·988484	0·000000
Hydrogen	−2·728807	6·060044	0·000000
Hydrogen	−4·082496	2·832797	0·000000
Fluorine	2·886952	6·495923	0·000000
Fluorine	4·538297	2·663370	0·000000

3B

	Molecular coordinates		
Atom	*X*	*Y*	*Z*
Fluorine	−0·265738	−2·384882	−2·091368
Fluorine	−0·265738	−2·384882	2·091368
Carbon	−0·025258	−0·612761	0·000000
Carbon	2·815438	−0·199839	0·000000
Carbon	3·893338	2·067182	0·000000
Hydrogen	4·008150	−1·868057	0·000000
Hydrogen	2·747314	3·750424	0·000000
Hydrogen	5·922114	2·307794	0·000000

3C

	Molecular coordinates		
Atom	*X*	*Y*	*Z*
Fluorine	−0·964973	0·820856	−2·086330
Fluorine	−0·964973	0·820856	2·086330
Carbon	−0·056154	−0·703509	0·000000
Carbon	2·798318	−0·138835	0·000000
Carbon	3·926810	2·106762	0·000000
Hydrogen	3·990745	−1·802493	0·000000
Hydrogen	2·841343	3·829566	0·000000
Hydrogen	5·960817	2·301669	0·000000

3D

	Molecular coordinates		
Atom	*X*	*Y*	*Z*
Carbon	0·108225	0·017261	0·221376
Carbon	−1·432354	0·004650	2·517491
Carbon	1·576606	0·103668	2·500341
Hydrogen	−2·463630	−1·728928	2·884441
Hydrogen	2·347737	−1·754762	2·933890
Hydrogen	−2·457152	1·695595	3·055507
Fluorine	−0·052692	−2·079775	−1·347856
Fluorine	−0·021605	2·016313	−1·454691