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EFFECTS OF CF_2 GROUP PYRAMIDALIZATION IN THE 1,1,3,3-TETRAFLUOROPROPENYL ANION

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Ab initio calculations with the 6–31G* basis set were carried out on planar and pyramidalized geometries of the 1,1,3,3-tetrafluoropropenyl anion and on two geometries with one CF_2 group rotated out of conjugation. Structures with at least one pyramidalized CF_2 group are substantially lower in energy than the corresponding unpyramidalized structures for both rotated and unrotated geometries. At the MP2/6–31G* level of theory, three structures of approximately equal energy all lie 17–18 kcal mol^{-1} below the planar C_{2v} structure. These include a C_s geometry with one CF_2 group rotated out of conjugation, an unrotated C_1 structure with unequal CC bond lengths and an unrotated, pyramidalized C_2 structure with equal CC bond lengths.

INTRODUCTION

The effects of fluorines on allylic radicals have been investigated both experimentally[1] and computationally.[2] Replacement of the four terminal hydrogen atoms in the allyl radical by fluorines has been found to lower the allyl rotational barrier[3] by about 9 kcal mol^{-1}.[1] Our *ab initio* calculations have confirmed the conjecture that CF_2 group pyramidalization is the major factor responsible for this large decrease in the barrier to rotation in fluorinated allyl radicals.[2]

CF_2 group pyramidalization would be expected to be even more important in fluorinated allylic anions. Indeed, in an interesting computational study of allylic anions with terminal CF_2 groups, Dixon *et al.*[4] found that a C_s geometry for pentafluoroallyl anion, in which the anionic CF_2 group is pyramidalized and rotated out of conjugation, lies 25–28 kcal mol^{-1} below the conjugated C_{2v} structure. However, they did not report the energies of conjugated geometries in which one or both of the CF_2 groups were pyramidalized.

As an extension of our study of pyramidalization in the 1,1,3,3-tetrafluoropropenyl radical,[2] we have performed *ab initio* calculations on the corresponding anion. Our aim was to determine whether conjugated geometries with pyramidalized CF_2 groups would be competitive in energy with a geometry in which the anionic CF_2 group is pyramidalized and rotated out of conjugation. Calculations were performed at the six geometries depicted in Figure 1.

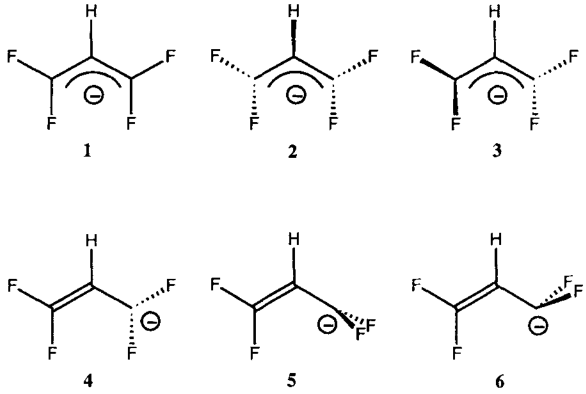

Figure 1. Schematic depiction of molecular geometries for the 1,1,3,3-tetrafluoropropenyl anion

Three of these geometries are conjugated and have both CC bond distances equal. These include the planar C_{2v} structure **1** and the pyramidalized C_s(**2**) and C_2(**3**) structures. The remaining three geometries each have two unequal CC bond lengths. These structures are the conjugated C_1 geometry (**4**) and two rotated C_s geometries, with the twisted CF_2 group planar in **5** and pyramidalized in **6**. In this paper, we discuss the results of our calculations of the relative energies of these six geometries.

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COMPUTATIONAL METHODOLOGY

Geometries were fully optimized within each symmetry constraint by RHF calculations performed with the 6–31G* basis set.[5] Diffuse functions were not included in the basis set, as Smart *et al.*[4] found them to have little effect on the relative energies of planar and rotated geometries of allyl,[6] pentafluoroallyl and 1,1-difluorallyl anions. The RHF energies are given in Table 1 and the optimized geometries in Table 2. Vibrational analyses were carried out with the 6–31G* RHF wavefunction for the C_{2v} (**1**), C_2 (**3**) and C_1 (**4**) and rotated C_s (**6**) geometries, in order to determine whether each of these stationary points was a minimum or an energy maximum with respect to one or more normal coordinates. The effect of electron correlation on the relative energies of the optimized geometries was determined by MP2/6–31G* calculations.[7] All of the calculations were performed with the Gaussian 86 package of programs.[8]

Table 1. Calculated relative 6–31G* energies and numbers of imaginary frequencies for geometries **1–6** of the 1,1,3,3-tetrafluoropropenyl anion

Geometry	E (kcal mol^{-1}) RHF	MP2	Imaginary frequencies
1	24·0	17·3	2
2	14·8	—	1[a]
3	10·5	0·1	1
4	0·2	−1·1	0
5	52·6	—	—[b]
6	0·0[c]	0·0[d]	0

[a] Predicted, not calculated; see text.
[b] Not a stationary point, so no frequency analysis performed.
[c] $E = -511{\cdot}8247$ hartree.
[d] $E = -512.8798$ hartree.

RESULTS AND DISCUSSION

The relative RHF and MP2 energies calculated for the optimized geometries **1–6** are presented in Table 1. Delocalization of the four π-electrons is at a maximum in the planar C_{2v} geometry **1**. Loss of conjugation by rotation of one CF_2 group without any pyramidalization in **5** raises the RHF energy by 28·6 kcal mol^{-1}. However, full optimization of the rotated geometry in C_s symmetry gives **6**, in which the pyramidalization angle at rotated CF_2 group is 73.9° This angle, which is defined as the angle between the CF_2 plane and the extension of the CC bond, is considerably larger than the pyramidalization angle of 54.7° for a tetrahedral geometry. The 28.6 kcal mol^{-1} increase in energy resulting from the loss of conjugation in **5** is more than compensated by the 52.6 kcal mol^{-1} decrease in energy which accompanies pyramidalization of the carbanionic CF_2 group in the rotated structure **6**. At the RHF level, **6** is calculated to lie 24.0 kcal mol^{-1} below **1**, in close agreement with the results of Dixon *et al.*[4] for the pentafluorallyl anion.

CF_2 group pyramidalization was also found to be energetically favorable at conjugated geometries.

Table 2. Optimized geometries for structures **1–6**

Structure		1	2	3	4	5	6
Bond length (Å)	C—H	1·078	1·078	1·076	1·077	1·124	1·082
	C-1—C-2	1·353	1·378	1·379	1·307	1·318	1·303
	C-2—C-3	1·353	1·378	1·379	1·504	1·420	1·521
	C-1—F-1	1·367	1·378	1·381	1·340	1·332	1·333
	C-1—F-2	1·358	1·367	1·363	1·322	1·312	1·317
	C-3—F-3	1·367	1·378	1·381	1·435	1·395	1·438
	C-3—F-4	1·358	1·367	1·363	1·418	1·385	1·438
Bond angle (°)	H—C-2—C-1	112·5	112·8	114·2	114·3	108·2	115·5
	H—C-2—C-3	112·5	112·8	114·2	115·1	127·0	120·7
	C—C—C	134·9	131·6	131·7	130·1	124·8	123·8
	C-2—C-1—F-1	123·4	116·5	116·9	124·3	124·6	124·8
	C-2—C-1—F-2	127·1	120·0	119·3	128·3	128·6	128·0
	C-2—C-3—F-3	123·4	116·5	116·9	102·4	125·0	110·4
	C-2—C-3—F-4	127·1	120·0	119·3	105·2	125·0	100·4
	F-1—C-1—F-2	109·5	106·3	105·8	107·4	106·8	107·2
	F-3—C-3—F-4	109·5	106·3	105·8	101·1	110·0	99·5
Dihedral angle (°)	H—C-2—C-1—C-3	180·0	161·1	180·0	172·6	180·0	180·0
	H—C-2—C-1—F-1	0·0	28·7	34·2	0·9	0·0	0·0
	H—C-2—C-1—F-2	180·0	159·2	163·7	178·2	180·0	180·0
	H—C-2—C-3—F-3	0·0	−28·7	34·2	50·3	90·0	50·9
	H—C-2—C-3—F-4	180·0	−159·2	163·7	155·7	−90·0	−50·9

Vibrational analysis revealed two imaginary frequencies for the C_{2v} structure **1**, corresponding to modes of b_1 and a_2 symmetry. These modes correspond, respectively, to *syn*- and *anti*-pyramidalization of the CF_2 groups, in both cases without rotation. Of the two modes, the one leading to the anti-pyramidalized C_2 structure **3** is calculated to produce the greater energy lowering. Structure **3** is calculated to lie 13·5 kcal mol^{-1} below **1** and 4·3 kcal mol^{-1} below the *syn*-pyramidalized structure **2**.

Pyramidalization of the CF_2 groups in **2** and **3** is pronounced. The pyramidalization angle at each CF_2 group is 37·9° in **2** and 38·6° in **3**. CF_2 group pramidalization results in the lengthening of the CC bonds by 0·025 Å in both **2** and **3**, compared with **1**. The energetic cost of decreased π-bonding in **2** and **3** is apparently outweighed by the stabilization that results from pyramidalization of the negatively charged CF_2 groups.

Vibrational analysis showed the optimized C_2 structure **3** to have one imaginary frequency. Examination of the normal coordinates of this mode revealed that a major component is asymmetric stretching of the CC bonds. This result is interesting because, in the C_{2v} structure **1**, the b_2 mode for asymmetric C–C stretching was calculated to have a frequency of 1941 cm^{-1}. Even in the C_2 structure **3**, pure asymmetric C–C stretching has a positive force constant.

Symmetry breaking[9] in **3** can be understood by considering how the a_2 mode for *anti*-pyramidalization of the terminal CF_2 groups in **1** might be coupled with the b_1 mode for *syn*-pyramidalization. As noted above, both modes have negative force constants and, in the harmonic approximation, they are independent of each other. Consequently, any combination of these modes must, within this approximation, also lower the energy below that of the C_{2v} geometry.

Group theory shows that a vibration of b_2 symmetry can couple vibrations of b_1 and a_2 symmetry. The energy associated with the coupling term has the form $\Delta E = k\ \Delta x(a_2)\ \Delta x(b_1)\ \Delta x(b_2)$, where each Δx is the linear displacement from C_{2v} symmetry along one of the three normal coordinates. Because this cubic term is linear in each displacement, it is zero unless all three Δx terms are non-zero. Whether this term raises or lowers the energy depends on the relative signs of all three distortions.

This analysis predicts that because a b_2 vibration has a positive quadrtic force constant, b_2 distortion of the C—C bond lengths from equality can be energetically favorable only when the modelcule is simultaneously distorted along both a_2 and b_1 modes of CF_2 pyramidalization and when the b_2 mode has the correct phase, relative to the phases of a_2 and b_1. Physically, when distortion along both a_2 and b_1 modes occurs simultaneously, pyramidalization is additive at one terminal CF_2 group and tends to cancel at the other. The mode of C—C bond length distortion that is energetically favorable is that which lengthens the C—C bond to the more highly pyramidalized CF_2 group and shortens the bond to the more nearly planar one.

In fact, distortion of the C_2 geometry (**3**) along the vibrational mode with the imaginary frequency leads to a C_1 energy minimum (**4**), lying 10·3 kcal mol^{-1} below **3**, and having the geometrical features expected on the basis of the foregoing analysis. The C-1—C-2 bond length in **4** is 1·307 Å, and the geometry around both doubly bonded carbons is nearly planar. The C-2—C-3 distance is 1·504 Å, and the negative charge is localized primarly on C-3, which has a pyramidalization angle of 67·8°.

The C_1 geometry of structure **4** can also be reached by asymmetric distortion of the C_s geometry (**2**). Since **2** lies higher in energy than the C_2 geometry (**3**), a vibrational analysis was not performed on **3**; however, like **3**, **2** should have an imaginary frequency for the vibration that takes it to **4**.

Structure **4** is calculated to lie just 0·2 kcal mol^{-1} above **6**, which has the singly bonded CF_2 group twisted out of conjugation, and which is the most stable of the six geometries at the RHF level. Comparison of these two structures reveals that in **4** the C-2—C-3 bond is 0·017 Å shorter, C_3 is slightly less pyramidalized (67·8° vs 73·9°) and there is less negative charge at C_3 (−0·64 vs −0·70) than in **6**. These differences are consistent with some delocalization of the negative charge at C-3 in the conjugated structure **4**. However, delocalization in **4** is weak because of the long C-2–C-3 distance and the highly pyramidalized geometry at C-3. The stabilizing effect of conjugation of the lone pair with the double bond in **4** is presumaly balanced in **6** by overlap of the π-bond with the combination of CF bonds at C-3 with the same symmetry.

When the hydrogen at C-2 in **6** is replaced with fluorine, additional stabilization of this geometry is provided by overlap of the lone pair on C-3 with the unfilled C-2—F antibonding orbital. This extra stabilization by anionic hyperconjugation is presumably responsible for the finding that in the pentafluoropropenyl anion a conjugated structure, analogous to **4**, is not an energy minimum and rotates without a barrier to a non-conjugated structure, analogous to **6**.[10]

The inclusion of electron correlation, which characteristically lowers the energy of more delocalized structures relative to localized ones,[9] also does so in 1,1,3,3-tetrafluoropropenyl anion. At the MP2/6–31G* level, the decrease is 6·7 kcal mol^{-1} for the C_{2v} structure (**1**) and 10·4 kcal mol^{-1} for the C_2 structure (**3**), relative to the energy of the unconjugated anion (**6**). Although **1** still lies more than 17 kcal mol^{-1} above **6** at the MP2 level, the energies of **3** and **6** now differ by only 0·1 kcal mol^{-1}. The energy of the conjugated, but weakly delocalized, C_1 structure (**4**) decreases by only 1·3 kcal mol^{-1} relative to **6**, but this small change is enough to make **4** the more stable of the two structures by 1·1 kcal mol^{-1}.

At the MP2 level, the potential energy surface for rotation about the CC single bond in **4** and for equalization of the two CC bond lengths is calculated to be fairly flat. Consequently, geometry reoptimization at the MP2/6–31G* level could change the relative energies of **3**, **4** and **6**, as could inclusion of diffuse functions in the basis set and higher levels of electron correlation. Nevertheless, our MP2/6–31G* calculations at the SCF-optimized geometries indicate that the geometry of lowest energy is the conjugated but localized structure **4**. The C_s structure (**6**) appears to be an intermediate for CF_2 group rotation, and the C_2 structure (**3**) is a low-lying transition state connecting the equivalent C_1 minima (**4**).

Although higher levels of calculation would be required to predict unequivocally the equilibrium gas-phase geometry of the 1,1,3,3-tetrafluoropropenyl anion, the major finding of this study is that the carbanion is rather floppy. Thus, in solution exchange of the fluorines among the four non-equivlaent NMR environments in **4** is predicted to be rapid, even at very low temperatures.

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